

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**MACROMOLECULAR ARCHITECTURES BASED ON
POLYPHENYLATION PROCESS**

Ph.D. Thesis by

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Programme: Polymer Science and Technology

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To my mother and my father ...

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LIST of ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
ROP	: Ring-opening Polymerization
PSt	: Polystyrene
PPP	: Poly(p-phenylene)
LED	: Light-Emitting Diodes
¹H-NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
IR	: Infrared Spectrophotometer
GPC	: Gel Permeation Chromatography
AIBN	: α,α' -Azobisisobutyronitrile
AFM	: Atomic Force Microscopy
PCL	: Poly(ϵ -Caprolactone)
LEC	: Light-Emitting Electrochemical Cells
DSC	: Differential Scanning Calorimetry
CL	: Epsilon Caprolactone
PMMA	: Poly(methyl methacrylate)
PP	: Polyphenylene
Sn(Oct)₂	: Stannous Octoate
UV	: Ultra Violet
MWD	: Molecular Weight Distribution
CRP	: Controlled Radical Polymerization
RP	: Radical Polymerization
PDI	: Polydispersity Index
SPC	: Suzuki Polycondensation
SCC	: Suzuki Cross-Coupling
Bipy	: 2,2'-Bipyridine
dTBipy, dHBipy	
dNBipy	: Substituted Bipyridines
TMEDA	: <i>N,N,N',N'</i> -Tetramethylethylenediamine
PMDETA	: <i>N,N,N',N'',N'''</i> -Pentamethyldiethylenetriamine
HMTETA	: <i>N,N,N',N'',N''',N'''</i> -Hexamethyltriethylenetetraamine
Me₆-TREN	: Tris[2-(dimethylamino)ethyl]amine
DMF	: Dimethyl Formamide
THF	: Tetrahydrofuran
TGA	: Thermogravimetric Analyzer
MMA	: Methyl Methacrylate
DXO	: 1,5-Dioxepan-2-one
DMAc	: Dimethyl Acetamide
RAFT	: Reversible Addition-Fragmentation Chain Transfer Polymerization
NMP	: Nitroxide Mediated Polymerization
SFRP	: Stable Free Radical Polymerization

PBA	: Poly(butyl acrylate)
PMA	: Poly(methyl acrylate)
PtBA	: Poly(<i>tert</i> -butylacrylate)
PPh₃	: Triphenylphosphine
M₀	: Initial molar concentration of the monomer
I₀	: Initial molar concentration of the initiator
M_{n,th}	: Theoretical molecular weight
M_I	: Molecular weights of the initiator
PTHF	: Polytetrahydrofuran
AN	: Acrylonitrile
St	: Styrene
LRP	: Living Radical Polymerization
TEA	: Triethylamine
NBS	: <i>N</i> -bromosuccinimid

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LIST of SYMBOLS

λ	: Wavelength
$R\cdot$	: Radical
I	: Initiator
M	: Monomer
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution
P_n^*	: Propagating species
M_t^n	: Transition metal
P_n^-	: Polymer having a double bond at the chain end due to termination by disproportionation
P_{n+m}	: Polymer terminated by chain combination
X	: Halide group
k_a	: Rate constant of activation
k_{da}	: Rate constant of deactivation
k_p	: Rate constant of propagation
k_t	: Rate constant of termination

MACROMOLECULAR ARCHITECTURES BASED ON POLYPHENYLATION PROCESS

SUMMARY

Poly(p-phenylene) (PPP) and its derivatives are a promising class of high-performance polymers because of their excellent thermal and mechanical properties. Polyphenylene (PP) is used as a coating material in the packaging industry to protect integrated circuits from breakage, humidity, and corrosion. Other interesting and important properties that PPPs exhibit include liquid crystallinity and photo- and electroluminescence.

As PPPs are insoluble in many organic solvents, which limit their processability, attachment of conformationally mobile alkyl side chains to the backbone has been important because it has allowed the controlled synthesis of soluble and processable polymers with high molecular weight. In view of the expected large persistence length of the main chain and of the flexibility of the side chains, such molecules have been termed “hairy-rod” polymers. On combining a stiff, insoluble, rod-like polymer such as PPP with a soft coil, for example polystyrene (PSt), it is possible to form a new polymer with novel and interesting properties. Taking in account the considerable interest not only in the synthesis of new types of plastic materials, but also in the modification of the commodity polymers to improve their properties to meet the requirements for high-tech applications, PSt or poly(methyl methacrylate) (PMMA) were used, in which nanostructured photoactive conjugated oligo(phenylene vinylene)s segments are attached as side chains to the backbone.

Living polymerizations are chain growth reactions that the final average molecular weight of the polymer can be adjusted by varying the initial monomer/initiator ratio, with a narrow molecular weight distribution. Atom transfer radical polymerization (ATRP), appears to be a powerful tool for the polymer chemists, providing new possibilities in structural and architectural design.

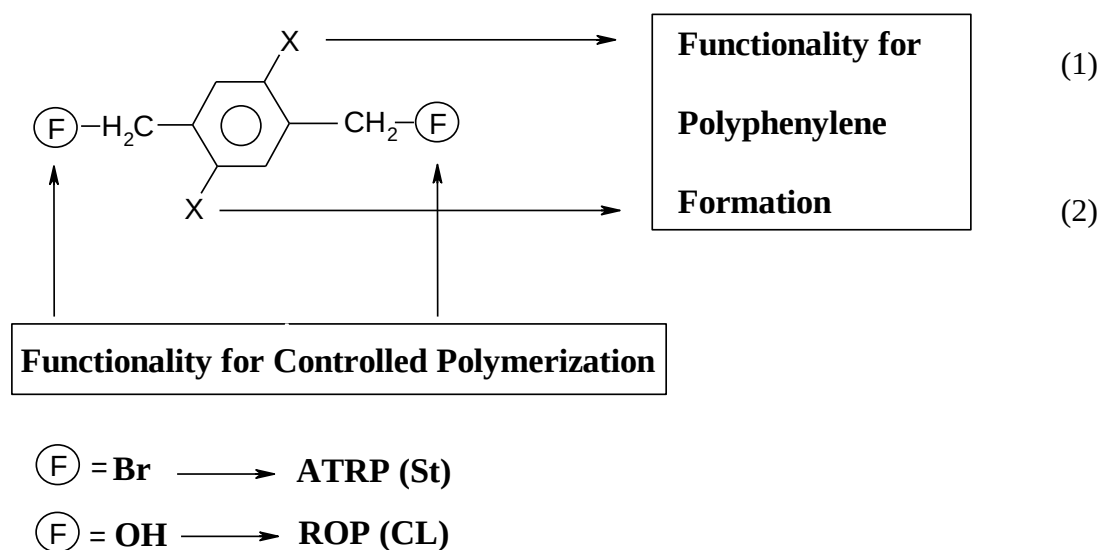
Current methodologies for the direct synthesis of derivatized PPs are primarily based upon nickel- and palladium- mediated cross-coupling reactions due largely to their preservation of regiochemistry and nearly quantitative yields.

The present work described the synthesis and characterization of PPs with well-defined polymeric side-chains by cross-coupling methods.

For this purpose, new mono and bifunctional Atom Transfer Radical Polymerization (ATRP) and Ring-Opening Polymerization (ROP) initiators were synthesized. 2,5-Dibromo-1,4-(dihydroxymethyl)benzene was prepared and used as initiator in ROP of ϵ -caprolactone (CL) in the presence of stannous octoate ($\text{Sn}(\text{Oct})_2$) catalyst. On

the other hand, 1,4-Dibromo-2-(bromomethyl)benzene and 1,3-Dibromo-5-(bromomethyl)benzene were prepared and used as initiators in ATRP of styrene (St) in conjunction with CuBr /2,2'-bipyridine as catalyst. As these polymers were intended to be used in further polymerization reactions, efforts were directed toward obtaining a low molecular weight combined with a low polydispersity and a high yield.

The resulting poly(ϵ -caprolactone) (PCL) and PSt based macromonomers, were used in combination with 2,5-Dihexylbenzene-1,4-diboronic acid for a Suzuki coupling in the presence of Pd(PPh₃)₄ as catalyst or using the system NiCl₂/bpy/PPh₃/Zn for a Yamamoto type polymerization. The general formula of the initiators used in the synthetic strategy for the preparation of PPs is shown in Scheme 1.

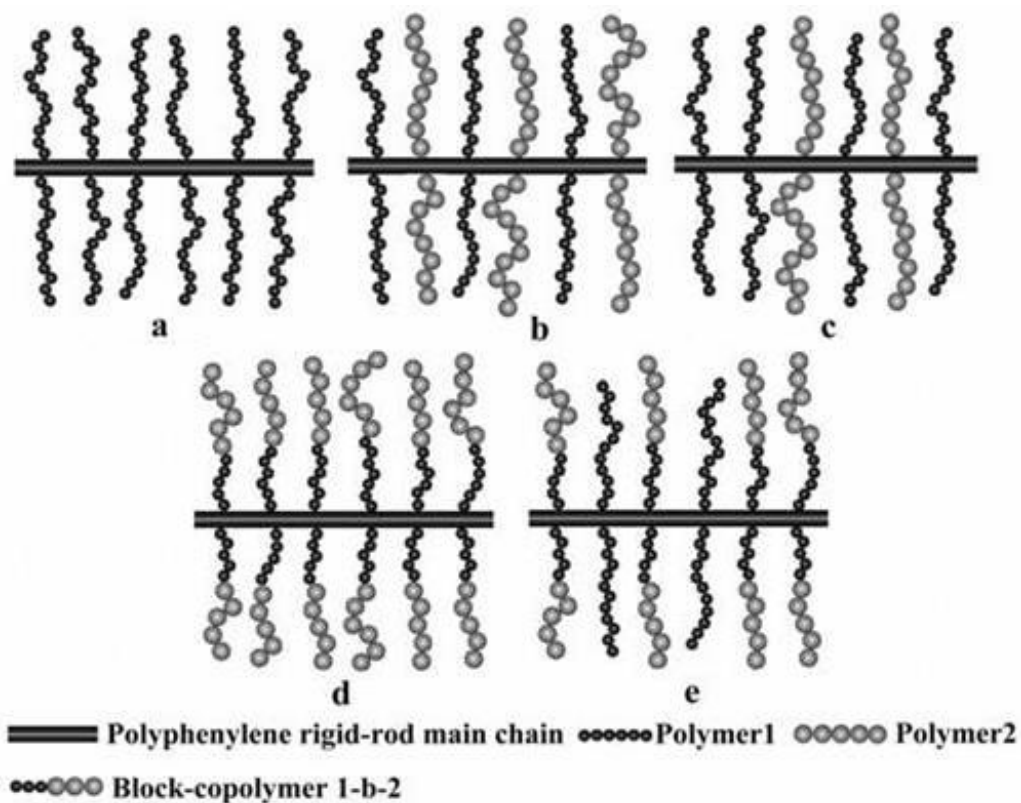


Scheme 1. Schematic representation of the initiators used for the preparation of PPs.

Pol(p-phenylene)-g-Poly(ϵ -caprolactone) copolymers were prepared by using PCL macromonomer. PPs with PSt chains as substitution groups were also obtained. The same macromonomers were used in Yamamoto type copolycondensation reactions, resulting PPs with PSt/PCL side chains. The obtained PPs, have good solubility properties in common organic solvents at room temperature similar with those of the starting macromonomers.

Furthermore, PCL macromonomer was reacted with 4-bromomethyl benzoyl chloride to give a bifunctional macroinitiator for ATRP. The polymerization of St in the presence of benzyl bromide functionalized PCL furnished a well defined block-copolymer having a low polydispersity. The resulting polymer, still preserving the central aromatic dibromo groups, can be used in Suzuki or Yamamoto polycondensations for the synthesis of PPPs bearing block-copolymers as side chains. The bromo functional block macromonomer was tested in a Suzuki type cross-coupling reaction in combination with 2,5-Dihexylbenzene-1,4-diboronic acid. This way a polymer with alternating hexyl and PCL-*b*-PSt side chains was obtained. The new polymers were characterized by ¹H (¹³C)-NMR, UV and by GPC measurements.

By these methods, complex macromolecular architectures with well-defined structures were obtained and their idealized structures of PPPs are given in Scheme 2.



Scheme 2. The idealized structures of PPPs

POLİFENİLLEME İŞLEMİNE DAYALI MAKROMOLEKÜLER MİMARİ

ÖZET

Polifenilenler (PF) ve türevleri, mükemmel termal ve mekanik özelliklerinden dolayı yüksek teknoloji polimerlerin önemli bir sınıfını oluştururlar. PF ler elektrik devrelerini kırılma, nem ve korozyondan korumak için kaplama malzemesi olarak kullanılırlar. Diğer önemli özelliklerinin arasında likit kristallilik, foto ve elektroluminesans gelmektedir.

PF lerin birçok organik çözücude çözünmemesi işlenebilirliklerini kısıtlayıcı rol oynar. Bu yüzden, ana zincire hareketli alkil yan zincirlerinin eklenmesi, çözünür ve işlenebilir yüksek molekül ağırlıklı polimerlerin kontrollü sentezine izin vermesi yönünden önem kazanmıştır. Ana zincirin uzunluğu ve yan zincirlerin esnekliğinden dolayı bu tür polimerler “hairy-rod” olarak adlandırılırlar. Sert, çözünmez, çubuk şeklindeki PF lere yumuşak bir Polistiren (PSt) grubunun eklenmesiyle tamamen yeni özelliklere sahip bir polimerin sentezi mümkün olabilir.

Yaşayan polimerizasyonlar geri dönüşümsüz zincir transferi veya zincir sonlanması olmaksızın ilerleyen zincir büyüme reaksiyonlarıdır. Polimerin sonuç molekül ağırlığı, dar bir molekül ağırlığı dağılımı sağlanarak, başlangıç monomer/başlatıcı oranı değiştirilerek ayarlanabilir. ATRP birçok monomerde etkilidir ve orijinal mimarilerin tasarlanmasında olduğu kadar mevcut monomerler ile yeni ürünlerin geliştirilmesinde de polimer kimyacıları için güçlü bir araçtır.

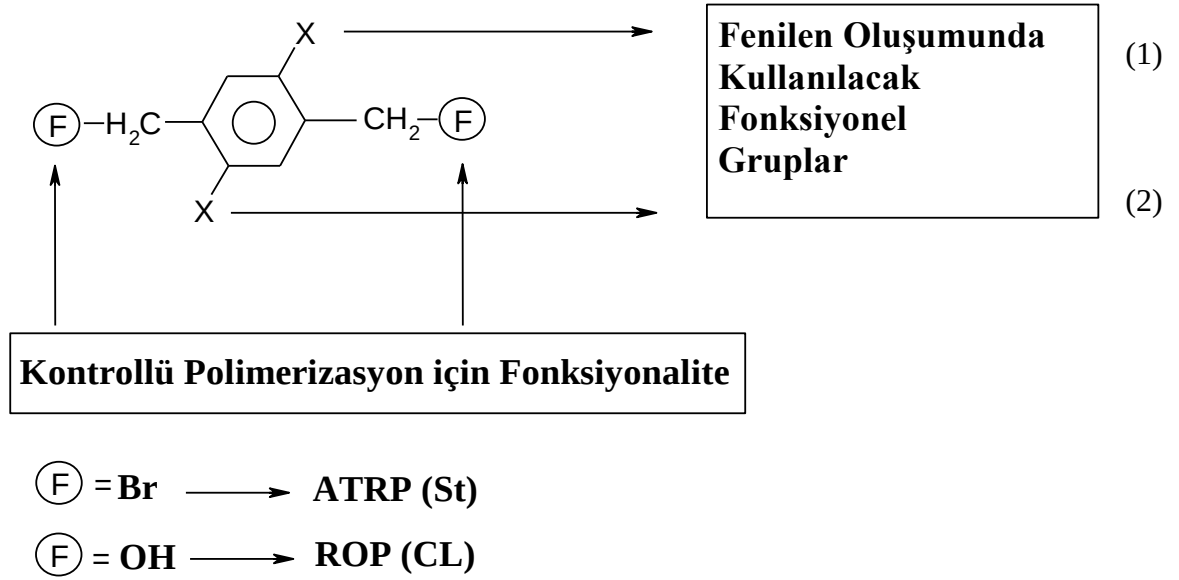
Son yıllarda PF lerin sentezi Ni ve Pd katalizli çapraz-kenetlenme reaksiyonları ile yapılmaktadır.

Bu çalışmada, çapraz-kenetlenme reaksiyonları aracılığıyla, iyi tanımlanmış yan zincirler içeren polifenilenlerin sentezi ve karakterizasyonu ele alınmıştır.

Bu amaçla, yeni tek ve çift fonksiyonlu Atom Transfer Radikal Polimerizasyonu (ATRP) ve Halka-Açılma Polimerizasyonu (Ring-Opening Polymerization ROP) başlatıcıları hazırlanmıştır. 2,5-Dibromo-1,4-(dihidroksimetil)benzen sentezlenmiş ve kaprolaktonun (ϵ -CL) ROP’ unda stannous oktoat ($\text{Sn}(\text{Oct})_2$) varlığında başlatıcı olarak kullanılmıştır. Diğer yandan, 1,4-Dibromo-2-(bromometil)benzene ve 1,3-Dibromo-5-(bromometil)benzen sentezlenmiş ve $\text{CuBr} / 2,2'$ -bipridin katalizörü ile Stirenin (St) ATRP’unda başlatıcı olarak kullanılmışlardır. Bu polimerler, ileriki polimerizasyonlarda da kullanılacaklarından dolayı, düşük molekül ağırlıklı ve düşük polidispersiteli olmalarına özen gösterilmiştir.

Elde edilen Polikaprolakton (PCL) ve PSt bazlı makromonomerler, $\text{Pd}(\text{PPh}_3)_4$ katalizörü varlığında, 2,5-Dihekzilbenzen-1,4-diboronik asit kombinasyonu ile

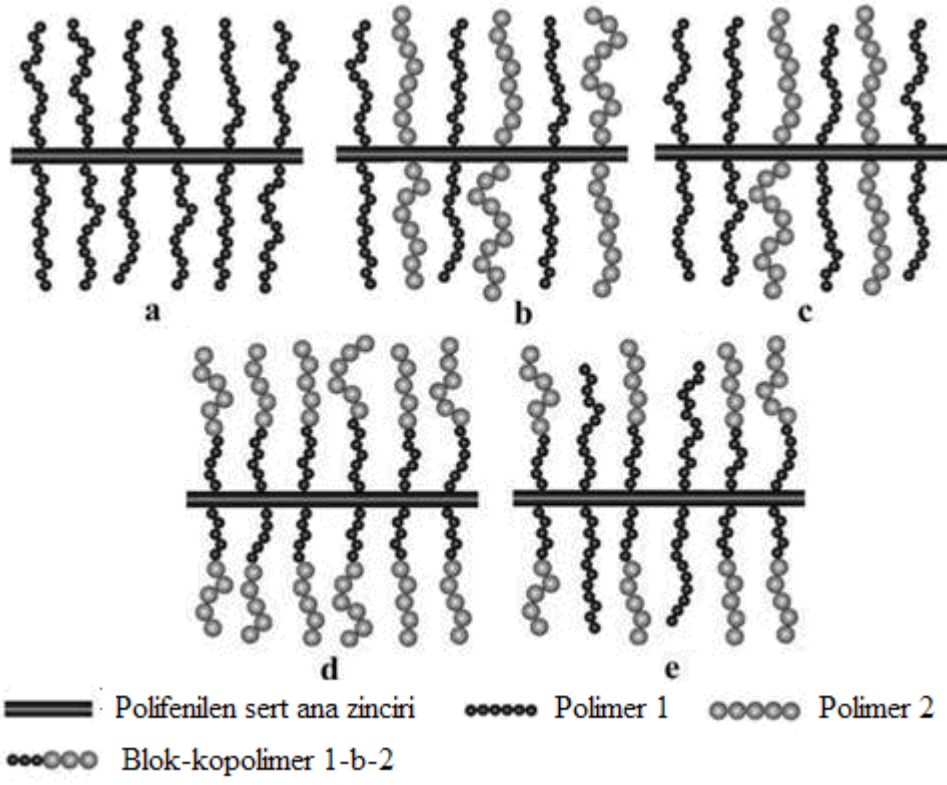
Suzuki Kenetlenmesi, $\text{NiCl}_2/\text{bpy}/\text{PPh}_3/\text{Zn}$ sistemi ile de Yamamoto tipi polimerizasyonda kullanılmıştır. PF lerin hazırlanmasında kullanılan sentetik strateji Şema 1. de gösterilmiştir.



Şema 1. Polifenilenlerin hazırlanmasının şematik gösterimi.

Poli(p-fenilen)-g-Poly(ϵ -kaprolakton) kopolimerleri PCL makromonomeri kullanılarak hazırlanmıştır. PSt makromonomerleri kullanılarakda, yan zincirde PSt içeren PF ler sentezlenmiştir. Aynı makromonomerler Yamamoto tipi kopolikondenzasyon reaksiyonlarında PCL ile PSt/PCL yan zincirleri içeren PF ler vermiştir. Oluşan PF ler, başlangıçtaki makromonomerlerde olduğu gibi, oda sıcaklığında birçok organik çözücüde iyi çözünürlük özelliklerine sahiptirler.

Ayrıca, PCL makromonomerinin 4-bromometil benzoil klorür ile reaksiyonundan ATRP için çift fonksiyonlu bir makrobaşılatıcı elde edilmiştir. St sentezlenen benzil bromür fonksiyonlu PCL makrobaşılatıcısıyla polimerizasyonu düşük polidispersiteli bir blok-kopolimer vermiştir. Bu blok-kopolimeri Suzuki ve Yamamoto polikondenzasyon reaksiyonlarında kullanarak, yan zincirde blok-kopolimer içeren Poli(p-fenilen)ler (PPP) ler sentezlemek mümkündür. Brom fonksiyonlu makromonomer, 2,5-dihexilbenzen-1,4-diboronik asit ile Suzuki çapraz-kenetlenme reaksiyonunda denenmiş ve alternatif hekzil ve PCL-b-PSt yan zincirlerine sahip PF sentezi gerçekleştirilmiştir. Elde edilen tüm polimerler ^1H (^{13}C)-NMR, UV ve GPC ile karakterize edilmiştir. PF lerin idealize edilmiş yapıları şema 2 de verilmiştir.



Şema 2. Polifenilenlerin ideal yapıları

1. INTRODUCTION

Over the past decade the main scientific and applied interest of modern materials science has been associated with the creation of so-called "smart" materials capable of being highly sensitive to environmental influences and responding easily to external stimuli (electrical or magnetic field, light, temperature, pressure, solvent, etc.) [1]. Conducting polymers could be considered as valuable candidates for this aforementioned class of materials. They can be incorporated into electronic devices as diodes and light-emitting diodes (LED) or as light-emitting electrochemical cells (LEC) [2-4].

Because of the considerable interest not only in the synthesis of new types of plastic materials, but also in the modification of the commodity polymers to improve their properties to meet the requirements for high-tech applications, polystyrene (PSt) or poly(methyl methacrylate) (PMMA) have been used; nanostructured, photoactive, conjugated oligo(phenylene vinylene) segments are attached as side chains to the backbone [5,6]. Since the discovery that polyphenylene (PP) conducts electricity when doped with oxidizing or reducing agents [7], a great deal of research has gone into the study of this material and its derivatives [8-10].

PP is a typical conjugated polymer with excellent mechanical properties and thermal and thermo oxidative stability. PP is used as a coating material in the packaging industry to protect integrated circuits from breakage, humidity, and corrosion. Other interesting and important properties that PPs exhibit include liquid crystallinity [11] and photoluminescence and electroluminescence [12]. If one considers the interdisciplinary connection between synthesis and material science, an impetus for research is only obtained when an additional condition is fulfilled: it is necessary to generate a defined, macroscopic architecture [13-15]. The key structural factor in describing the supramolecular ordering of PP is their anisotropic shape, which follows from a rodlike architecture that differentiates them from flexible polymers

[16]. Unfortunately, PPs are insoluble in many organic solvents, which limit their processability. Therefore, the attachment of conformationally mobile alkyl side chains to the backbone has been important because it has allowed the controlled synthesis of soluble and processable PPs with high molecular weight. In view of the expected large persistence length of the main chain and of the flexibility of the side chains, such molecules have been termed “hairy-rod” polymers [17]. Through the combination of a stiff, insoluble, rod-like polymer such as PP with a soft coil, for example PSt, it is possible to form a new polymer with novel and interesting properties [18]. Current methodologies for the direct synthesis of derivatized PP are primarily based upon nickel- and palladium- mediated cross-coupling reactions, largely because of their preservation of regiochemistry and nearly quantitative yields [10-12,19].

Living polymerizations are chain growth reactions that proceed in the absence of irreversible chain transfer and chain termination. The final average molecular weight of the polymer can be adjusted by varying the initial monomer/initiator ratio, while maintaining a narrow molecular weight distribution ($M_w/M_n < 1.5$) [20]. Therefore, polymers can be end-functionalized and block copolymerized with other monomers. This has opened new pathways to create many new materials with vastly differing properties by varying the topology of the polymer (comb, star, dendritic, etc.), the composition/architecture of the polymer (random, periodic, graft, etc.), or the functional groups at various sites of the polymer (end, center, side) [21]. Atom transfer radical polymerization (ATRP), introduced by Matyjaszewski [22,23] and coworkers, has been proven to be effective for a wide range of monomers and appears to be a powerful tool for the polymer chemists, providing new possibilities in structural and architectural design and allowing the development of new products with monomers currently available.

Because of various applications, homopolymers and copolymers of polylactones, especially poly(ϵ -caprolactone) (PCL), are attracting great interest [24-27].

The purpose of this work is to report new PCL and PSt based macromonomers, for the synthesis of PPs with polymeric side chains. PPs with both PSt and PCL side chains were also obtained by combination of PSt and PCL macromonomers in Yamamoto copolycondensation reactions. Also, a macromonomer consisting of

blocks of PCL and PSt, was synthesized, suitable for the preparation of PPs with polymeric substituents by cross-coupling processes.

2. THEORETICAL PART

2.1 Polyphenylenes

Poly(p-phenylene) (PPP), one of the most structurally simple of all the linear, rigid-rod polymers, is arguably one of the potentially most useful engineering materials. Its primary properties include high mechanical strength, excellent thermal and thermal oxidative stability, insolubility in all solvents, intractability, and the ability to conduct electricity upon oxidative or reductive doping. Despite its deceptively simple structure and its unique combination of attractive materials properties, PPP has traditionally been a very difficult polymer to synthesize and fabricate. The struggle to find efficient methods for producing PPP with both a regioregular linear structure and high molecular weight, together with the inherent lack of processability of the material, have retarded the development of PPP as a viable, useful material. Only within the past five to ten years has the problematic synthesis of high molecular weight, structurally regular PPP been solved through a number of ingenious strategies. In addition, a number of methods have been recently found to overcome the processing difficulties commonly associated with this polymer. Furthermore, non-traditional roles have also been found for PPPs of all qualities in applications far removed from the traditional roles of the polymer as a high-performance structural material and organic conductor [9].

Mechanical properties of fabricated PPP were compared to those of commercial polyimide and carbon graphite, and were found to fall between the properties of the two [28]. PPP retains toughness over a wide range, but is inherently less tough than polyimide. In high-temperature air-aging studies, property retention was similar to that of polyimide, but the values were lower at the start. It seems that metal-containing impurities, probably mostly copper, accelerate the oxidative degradation of PPP. High-temperature hydrolytic stability of the aromatic polymer was excellent, as would be expected.

A curious, unusual phenomenon was observed in the ablation-compaction of PPP. When a compacted bar drilled with holes was heated at 590°C under hydrogen pressure, the recovered sample resembled the original very closely except that it was substantially smaller in all dimensions, including the holes. The overall reduction could be as much as 80%. This can be regarded as the chemical counterpart of the aboriginal "shrunk heads". Apparently, as pore volume increases during ablation, surface area increases, in conflict with thermodynamics which requires minimization of surface area. Contraction occurs in order to minimize the energy. No other polymer tested gave a similar result, suggesting that PPP may be unique in this property.

PPP is a thermally and thermooxidatively stable material. No significant decomposition occurs below 400°C in air and only 7% of the mass is lost when the polymer is heated in N₂ to 900°C at a rate of 150°C/h. Thermal loss of H and CH₄ from PPP begins about 400°C, whereas analogous decomposition of benzene occurs at approximately 600°C. The decreased thermal stability of PPP relative to benzene was attributed to structural irregularity and presence, in the polymer, of residual impurities such as C1 and O. PPP has been reported to have a greater resistance to thermooxidative degradation than benzene and lower p-phenylene oligomers. The temperature at which thermal oxidation commenced was determined by defect structures in the polymer. The enhanced stability was attributed to coplanarity of rings, strong intermolecular interactions and high conjugation energy. Thermal and oxidative degradation of PPP is a complex process which consists of bond cleavage and formation of a crosslinked carbon char. Upon further heating to 2800°C, the char readily graphitizes. PPP is also resistant to radiation. The strength of a compressed pellet of the material was essentially un-changed following exposure to 8.95×10^8 rads from a Co⁶⁰ source.

Although PPPs were first introduced as conducting materials, in recent years the other new applications have gained more importance. However, in order to give information of their initial usage, we would like to present a brief survey on their conductivity.

2.1.1. Polyphenylenes as Conducting Polymers

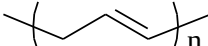
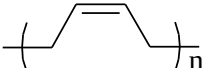
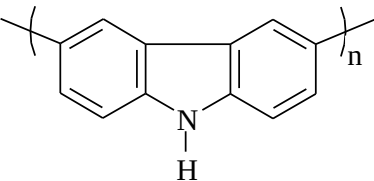
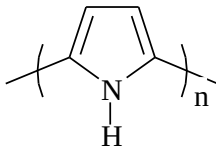
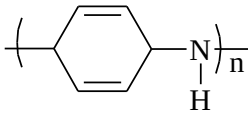
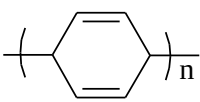
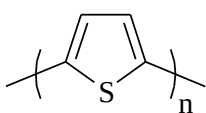
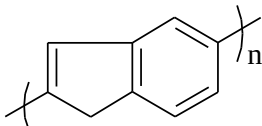
The emergence of the synthetic polymer industry from the middle of the nineteenth century through the rapid growth in the 1940s and 1950s has produced a range of polymers which provide acceptable alternatives to most traditional materials. The attraction of polymers lies in their combination of toughness, plasticity, strength-to-weight ratio, low cost, and ease of fabrication. The range of applications of these modern synthetic polymers, however, is dwarfed by that of biological systems. Here polymeric systems are used not only for their passive mechanical properties, but also in a variety of subtle active roles such as separation, energy generation, information storage, and vision.

One of the major applications where, so far, polymers have failed to be successful is in the replacement of metals. Indeed, the primary use of polymers in the electrical and electronic industries is as insulators. One of the most exciting and attractive polymer is polyacetylene.

Polyacetylene was first produced insoluble and infusible. Its attraction lies in the fact that it can be made to conduct using the coordination catalyst system which is commonly used to polymerize ethylene and propylene in 1955 by Natta et al.[29]. Unlike the soluble, white products of these reactions, polyacetylene is a brown-black, intractable powder. Various groups of workers investigated this material through the 1960s with interesting results [30-33]. It was found that polyacetylene behaved as a semiconductor, but that treatment with reagents such as boron trifluoride and ammonia produced dramatic changes in conductivity.

In the early 1970s Shirakawa and co-workers improved the synthetic route and characterized the product [34-38]. Their synthesis produced a fibrillar mat with fibrils about $200 \text{ \AA}$ in diameter and two-third void space. These “films” were easier to handle than the powders and, combined with the subsequent development work at the University of Pennsylvania, clearly established polyacetylene as the first semiconducting and metallic organic polymer. Subsequent work has yielded other systems such as PPP, polypyrrole and polythiophene. (Table 2.1)

Table 2.1. Structures and band gaps of some important conducting polymers.

<u>Polymer</u>	<u>Structure</u>	<u>Energy gap (ev)</u>
Trans-polyacetylene		1.4
Cis-polyacetylene		2.0
Polycarbazole		2.2
Polypyrrole		2.5
Polyaniline		1.6
Poly(p-phenylene)		3.0
Polythiophene		2.0
Polyindole		3.2

2.1.1.1 Conduction

Band Model

There are several models for electrical conduction. The most widely used is the one-electron band model. This is based on extending the simple model of a bond between two atoms over a whole crystalline solid.

When two identical atoms each having a half-filled orbital are brought together closely enough for their orbitals to overlap, the two orbitals interact to produce two new orbitals, one of lower energy and one of higher energy. The magnitude of this energy difference is determined by the extent of orbital overlap. The two electrons go into the lower-energy orbital. The lower energy orbital is a bonding orbital and the higher-energy orbital is an antibonding orbital. (Fig. 2.1)

If the leap to a crystalline solid is taken and the same argument applied, then the band picture is obtained. The orbital overlap of N ($\sim 10^{23}$) atoms produces $N/2$ higher-energy orbitals and $N/2$ lower-energy orbitals. In a semiconductor or an insulator there is a “gap” between the highest of the low-energy orbitals and the lowest of the high-energy orbitals. This is caused by the interaction of the electrons with the crystalline lattice and increases with decreasing atomic separation. The difference between energy levels within these two sets of orbitals is so small that the “bands” may be regarded as continuous and the electron can take any energy within. Since there are N electrons and each of the $N/2$ orbitals within the lower-energy band is filled. This band is known as the “antibonding” or “conduction” band. (Fig.2.1)

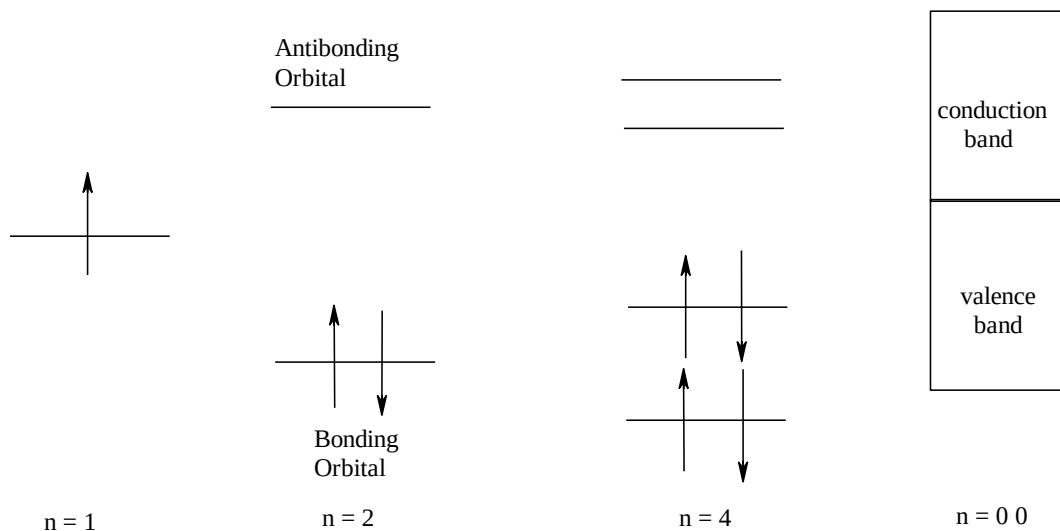


Figure 2.1 Band model for electrical conduction

The nature of the electrical properties of a solid is determined by the extent of occupation of the energy bands and the magnitude of the gap between them. Within each band the electrons are said to be delocalized. This means that they are not bound to any one atom but, rather, spread over several. For any net movement of electrons (a current) there must be orbitals available for the electrons to move to. A

completely full band, such as the lower one, has no such vacancies, and an empty band, such as the higher one, has nothing to move.

In a metal there is no gap, or the number of electrons is such that the highest filled orbital is not at the top of a band. This means that orbitals are freely available for conduction. (Fig.2.2)

In a semiconductor the magnitude of the gap is such that electrons may be thermally excited across it, putting electrons into the empty upper band, where they can conduct, and leaving “holes” in the lower band, which can also conduct. (Fig.2.2) An insulator has a large band gap, and hence thermal excitation of carriers is not possible. (Fig.2.2)

The magnitude of the conductivity is determined by the number of charge carriers available for conduction and by the rate at which they move. Since moving charge carriers are prone to scattering by the atoms of the lattice, the mobility of a charge carrier is a function of the number of obstacles it encounters and its speed between them.

In order to consider the effect of temperature on the electrical conductivity of the three main classes of materials, it is therefore necessary to consider its effect on both charge carrier concentration and mobility.

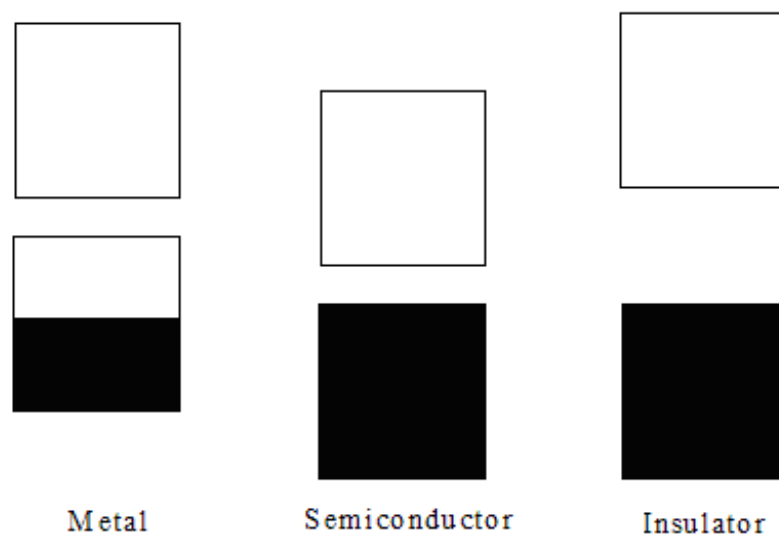


Figure 2.2 Energy level diagrams for three types of solids in terms of conductivity

In a metal all the electrons are available for conduction, so the conductivity is determined by the mobility. As the temperature of a crystal lattice is increased, the atoms vibrate and interact with the electrons to scatter them. Thus in a metal the conductivity decreases with increasing temperature. (Fig.2.3)

In a semi conductor the same is true, but also the charge carrier concentration increases with increasing temperature. Since the charge carrier concentration is much more temperature dependent than the mobility, this is the dominant factor and conductivity increases with increasing temperature. (Fig.2.3)

In an insulator the band gap is so large that it is very difficult to thermally excite electrons across it to provide charge carriers, and thus at reasonable temperatures the conductivity remains low (Fig.2.3) [39].

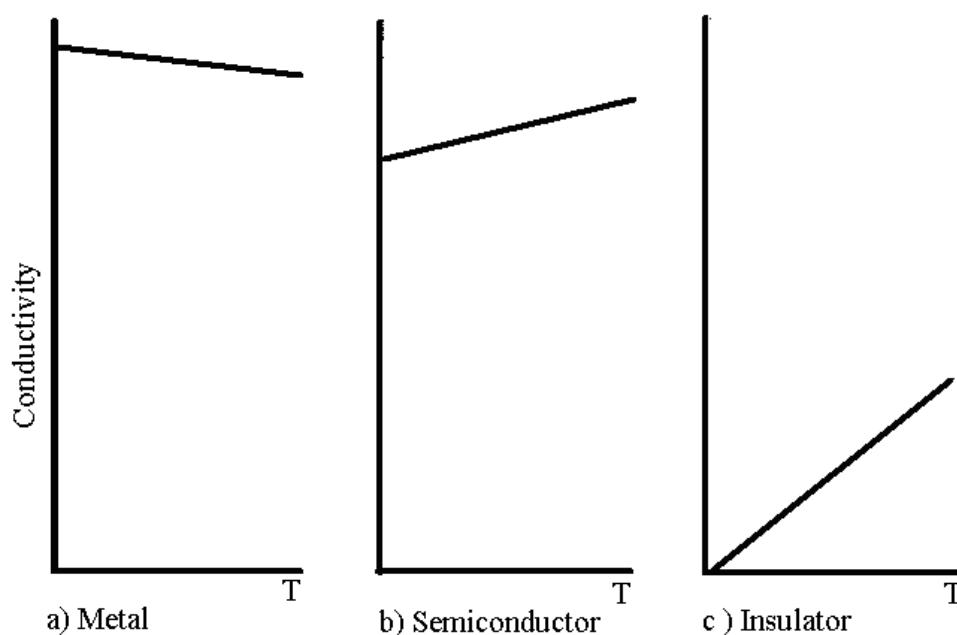


Figure 2.3 Effect of temperature on conductivity : (a) metal, (b) semiconductor, (c) insulator

2.1.1.2. Conduction Mechanism of Poly(p-phenylene)

Like polyacetylene, PPP was first synthesized some time before the current interest in conducting polymers [40]. Indeed, it was originally produced as a temperature-resistant polymer and investigated as such through the 1960s [41]. It was first shown in 1979 by Baughmann et al. [7,42] to interact with species such as arsenic pentafluoride and sodium naphthalide to give highly conducting complexes.

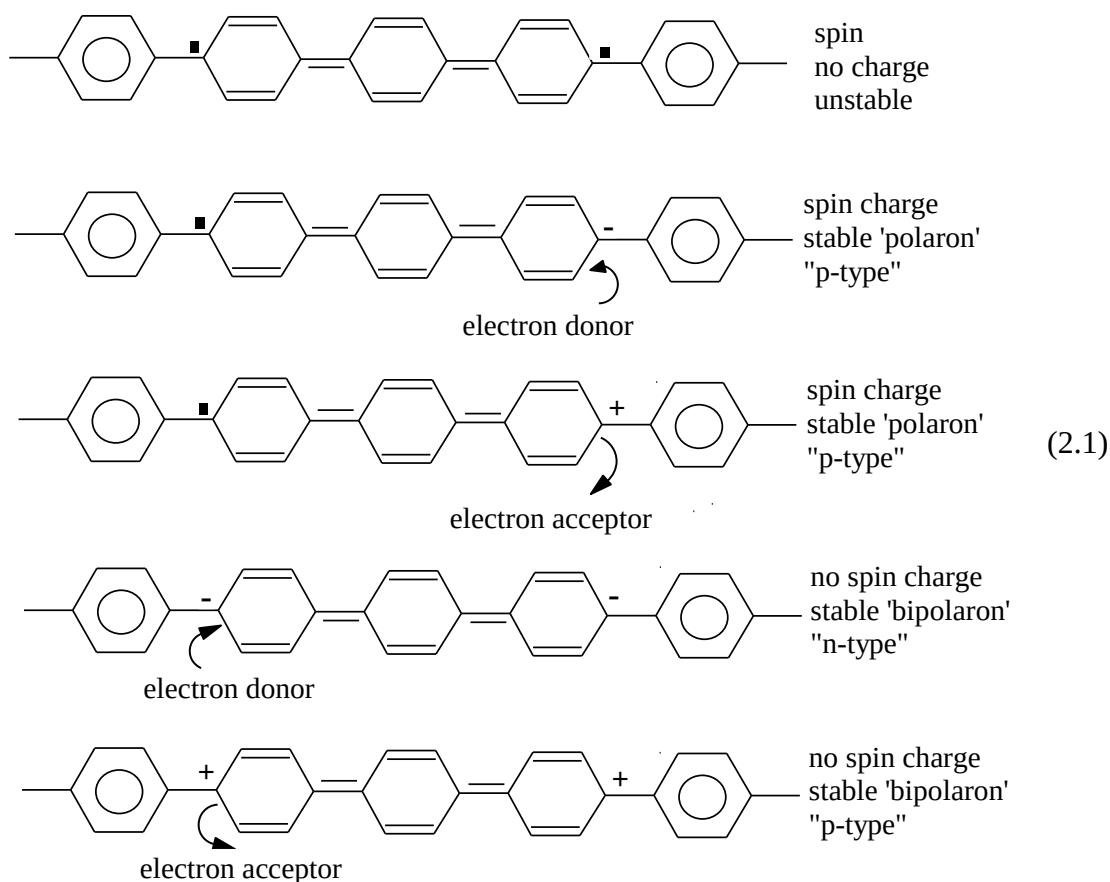
Pristine PPP as produced by most of the available synthetic routes is a light-tan powder. Studies have shown it to be predominantly para linked, but its degree of polymerization is low, possibly less than 20 [43]. It has a band gap of around 3 eV [44]. This suggests that the delocalization of the π -electron system is limited. Diffraction studies have shown that the bond between the phenyl units has very low π -bond order, confirming this hypothesis.

The diffraction data also show a very similar crystalline structure to polyacetylene for the undoped polymer [42], a major difference being that because the polymer is more stable, it can be annealed to increase its crystallinity [45].

Another similarity with polyacetylene is that even the pristine PPP shows a spin concentration of around 10^{18} spins per gram [46]. The structure of PPP means that it can not support a soliton, since interchanging the double and single bonds does not produce a structure of equivalent energy. The quinonoid structure must therefore be limited by another defect. Since if both defects are neutral there is no barrier to recombination, one or both of the defects must be charged. These defect structures are known as a “polaron” and “bipolaron” respectively [47] which is shown in 2.1.

PPP has a higher ionization potential than polyacetylene. This means that it is unaffected by atmospheric oxygen at ambient temperatures, but that it requires stronger p-type dopants than polyacetylene. Thus PPP is unaffected by iodine but dopes to metallic levels of conductivity on exposure to arsenic pentafluoride.

The interactions of the dopants seem identical to those found in polyacetylene. The dopants abstract or add an electron to the π -electron system. At first these add to the polarons already present to form bipolarons, but these are quickly saturated and new polarons are formed by direct interaction of the dopant and pristine phenylene chain. Recent studies [44] have shown that on p-type doping, the principal absorption peak at about 2.4eV is found.



2.1.2. New Applications for Poly(p-phenylene)s

PPP has been investigated in two roles: as a durable, high-strength polymer, and as an organic conducting polymer that could potentially replace metals in certain applications. In particular, doped PPP was initially proposed for use as a component in a light-weight electrical-storage battery. However, the inherent difficulty in fabricating PPP has limited its development as a useful structural engineering material, despite its excellent strength and inertness, although these concerns are currently being addressed. Only very recently have viable precursor routes to PPP been developed. Although the basic chemistry has been established in these precursor strategies, actual control of polymer morphology via processing is only now being investigated [48]. Obviously, more processing studies will have to be undertaken before the true potential of PPP made from precursor routes can be exploited. Likewise, interest in doped PPP as a substitute for metals has diminished over recent years because of the inherent environmental instability of this material, its relatively low conductivity, and its expense in comparison with conventional

metallic conductors such as copper and aluminium. However, research into the use of PPP (made by the chemical and electrochemical oxidative polymerization of benzene) as an electrode material in storage cells continues today [49,50]. Interestingly, research in this area has recently turned away from the use of PPP itself as the active electrode, and has begun to examine the glassy carbon chars generated by the reductive pyrolysis of PPP for such an application. Sato et al. have recently demonstrated that amorphous carbons made from the pyrolysis of Kovacic-type PPP can intercalate Li atoms. These materials have sufficiently high charge-discharge current densities that they may potentially be useful for electrodes in high-energy secondary Li batteries [51]. At the present time, only fundamental studies on this Li storage phenomenon have been undertaken. A working battery utilizing the PPP chars has yet to be made.

Current research into the potential applications of PPP is proceeding along entirely new directions by taking advantage of some of the unique optical and chemical properties of the polymer. For example, Leising and co-workers discovered that pristine PPP could serve as the active layer in polymer-based, light-emitting diodes with blue electroluminescence [52]. This discovery has since prompted examination of the electro- and photoluminescent properties of PPPs made by different methods, as well as of substituted PPPs and PPP-analogous ladder polymers, as a means of tuning the emission [53]. PPP films have also been investigated as chemical sensing elements. For example, Robinson et al. found that PPP-modified electrodes decreased the overpotential of oxidation for various biologically important molecules, such as NADH (nicotinamide adenine dinucleotide, reduced form) and ascorbic acid, in water and methanol. They proposed that the characteristic potential changes observed with these modified electrodes for various compounds might be useful in detecting these compounds in the presence of other molecules [54]. On a different note, PPP precursor technology has also been recently investigated for potential use in microlithography. Kim and Ober demonstrated that photogenerated acids can be used to catalyze the conversion of PPP precursor films into PPP [55]. Aligned PPP made by the same precursor method has also been investigated for use as pre-tilt layers for liquid crystal display devices [56]. PPP has also been found to have interesting photocatalytic properties. Yanagida and co-workers recently demonstrated that PPP made by the Yamamoto method is able to photoreduce water,

carbonyl compounds and olefins under visible light irradiation in the presence of sacrificial electron donors such as amines [57]. Interestingly, they found that PPP made by the Kovacic chemical oxidation method was inactive in this regard. These two methods of synthesis yield drastically different materials in terms of polymer structure and morphology. Undoubtedly these two parameters play important roles in defining the subtle variations in the macroscopic properties of PPP.

Three patents disclose the application of PPP as a solid lubricant [58, 59]. Other patents deal with the use of PPP as a lubricant additive [60] which bestows the following favorable properties: thermal stability, rust inhibition, low coefficient of friction and wear resistance. PPP can be molded under pressure; [61] subsequent sintering at 500-600⁰C produces a toughened material with good thermal and thermooxidative stability.

Various composite materials have employed PPP as a component. Among the other components have been ZrB, SiC, mica [62] and carbon or graphite fibers. The composites possess good mechanical strength and exhibit high thermal and oxidative resistance. Hydroxylated PPP has been used in the preparation of a composite with polymethylene-polyphenylene isocyanate and fiberglass cloth.

Pyrolysis of PPP or partially chlorinated PPP produces a microporous carbon with moderately crystalline domains. Carbonization of polymers obtained via Kovacic polymerization of pyrene or 1,3,5-triphenylbenzene yielded carbonaceous material with a high degree of graphitization. Mesophase pitch suitable for formation of highly oriented carbon fiber was obtained from heat treatment of naphthalene or phenanthrene polymers prepared under Kovacic conditions.

Miscellaneous uses claimed for PPP include a filler in rubber stock to increase the heat and thermal aging resistance of the vulcanizate; a thin film optical shutter; and a model for petroleum asphaltenes, in their complexing behaviour with titanium tetrachloride.

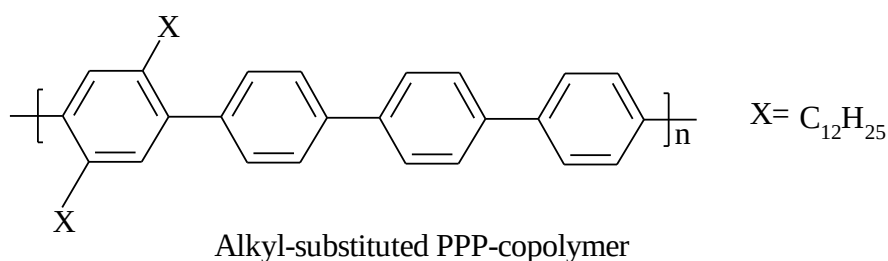
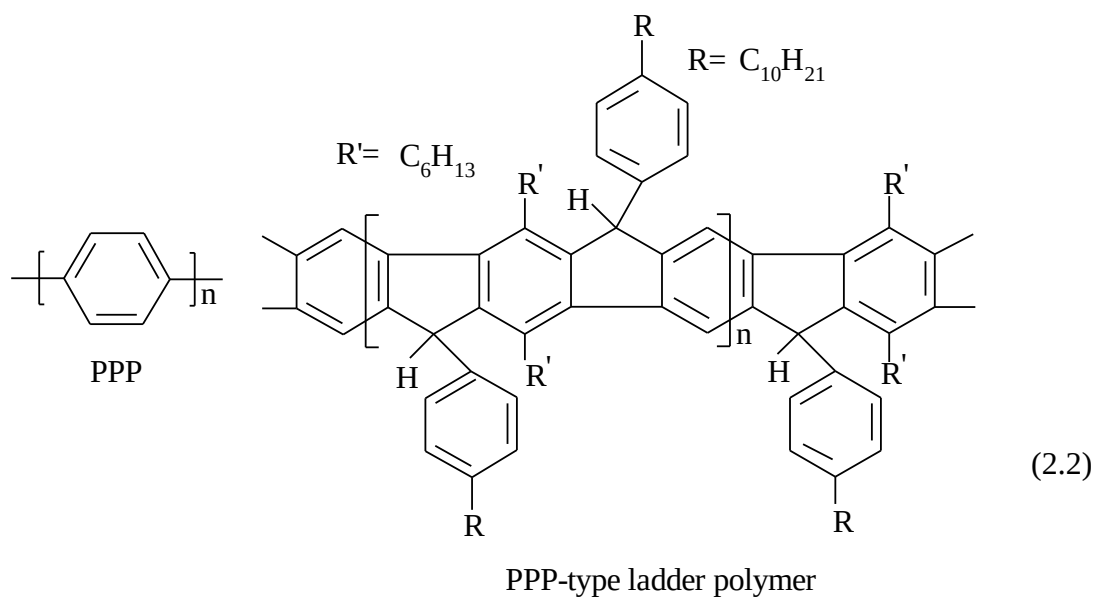
2.1.2.1. Poly(p-phenylene)s as LEDs

Optical indicators and displays play a role of increasing importance for various technical applications and consumer electronics. High-definition television (HDTV),

new computer and software generations need large screens with excellent pixel resolution. The video telephone might be the communication of the future. All these technologies are based on high quality, cheap, bright, flat, colour screens with high resolution and low power consumption.

Electroluminescence (EL) devices based on poly-conjugated materials are currently investigated worldwide as a possible display technology for the future.

It has been demonstrated that carrier injection of both kind, into a thin low molecular weight dye-layer produces a bright electroluminescence emission [63], which can be strongly enhanced with a special multilayer structure [64]. The breakthrough for conjugated polymers was the discovery of the Cambridge group, that PPP can act as the luminescent layer in a polymeric EL device showing green-yellow emission [65], which can be improved with a low work function metal (Ca) for the electron injecting contact [66]. Soluble conjugated polymers like poly(alkylthiophene) and poly(alkylfluorene) produced red and blue colors in EL devices [67,68]. PPP thin films produce visible blue light in a metal-polymer-metal [69] and a metal-polymer-insulator-metal EL device [70]. The emission color can be modified by the type of the PPP polymer [13].



A sterically planar structure of PPP, a PPP type ladder polymer, which is soluble, can be synthesized via a bridging of functionalized PPP-precursors [71]. A soluble form of PPP can be realized by a 2,5-alkyl substitution [72]. These three types of PPP are presented in 2.2. All these forms of PPP have very good film forming properties and have been successfully utilized as active layers in EL devices. A typical polymer EL device is based upon an ITO (Indium-Tin-Oxide) coated glass substrate, which is covered with the active polymer layer and a top metal contact (Fig.2.4).

The reliability and the lifetime of the device is increased if it is fabricated under inert conditions. For the top electrode any low work function metal is suitable (Ca, Mg, Mg: Ag, In, Al).

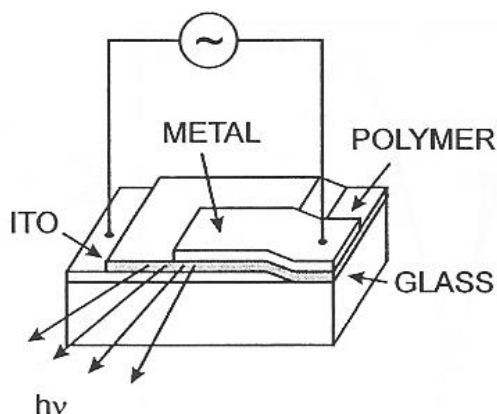


Figure 2.4 Schematic view of a polymer light-emitting device.

The blue emission spectrum of an EL device with PPP as the active material and aluminium for the top contact is shown in Fig.2.5 together with the photoluminescence and the optical absorption. The photoluminescence spectrum mirrors nicely the EL emission spectrum around the emission maximum. The optical absorption is smooth and structureless and the bandgap is around 2.7eV.

In Fig.2.6 the yellow emission of the EL device with the PPP-type ladder polymer as the active layer. The emission maximum is shifted to about 600nm compared to about 470nm for the PPP-EL device. The agreement of the EL emission spectrum with the photoluminescence emission is much better in the ladder polymer device. According to the fully planar structure of the ladder polymer and the defined conjugated length of the material the optical absorption spectrum shows a very steep and defined band edge of the interband transition and a nicely resolved vibronic structure. The band gap of the PPP-type ladder polymer is somewhat lower compared to PPP [13].

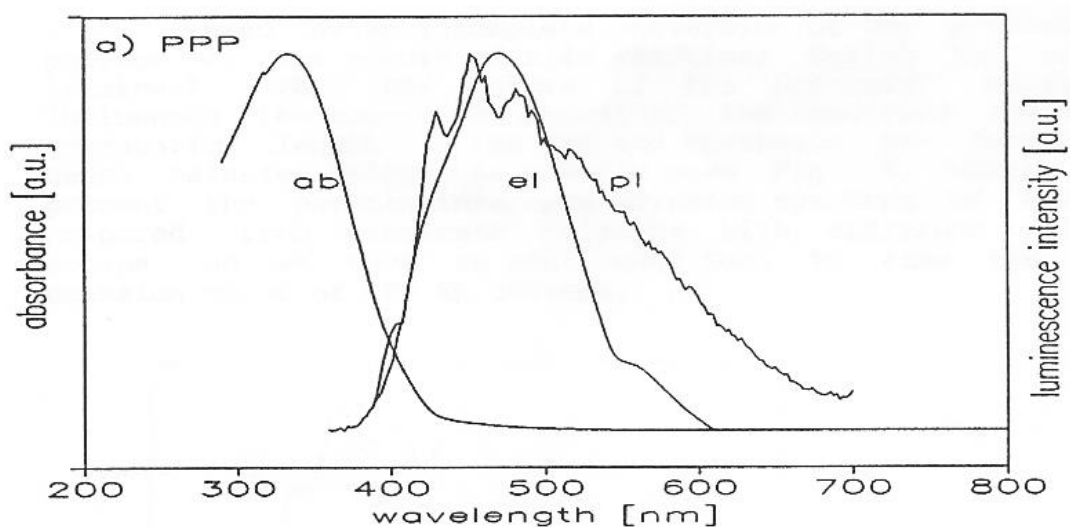


Figure 2.5 Spectra of the optical absorption (ab), photoluminescence with $\lambda_{\text{excitation}}=351\text{nm}$ (pl) and electroluminescence (el) of poly(p-phenylene).

The average conjugation length of PPP prepared by the precursor route is about 10-12 phenyl rings with a broad distribution [13], which results in the long band edge seen in the optical absorption (Fig.2.5). However, the molecular weight of the precursor polymer is quite high. The low values for the conjugation lengths are either due to chemical defect during the polymerization (ortho-links) [73], caused by an incomplete conversion of the precursor polymer or the result of side reactions during the heat treatment.

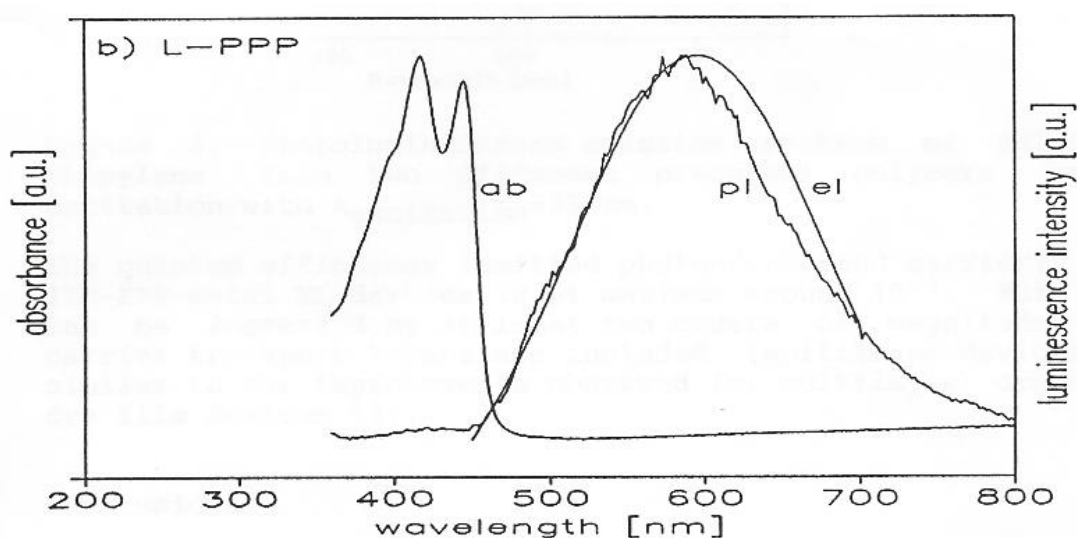


Figure 2.6 Spectra of the optical absorption (ab), photoluminescence with $\lambda_{\text{excitation}}=458\text{nm}$ (pl) and electroluminescence (el) of PPP-type ladder polymer.

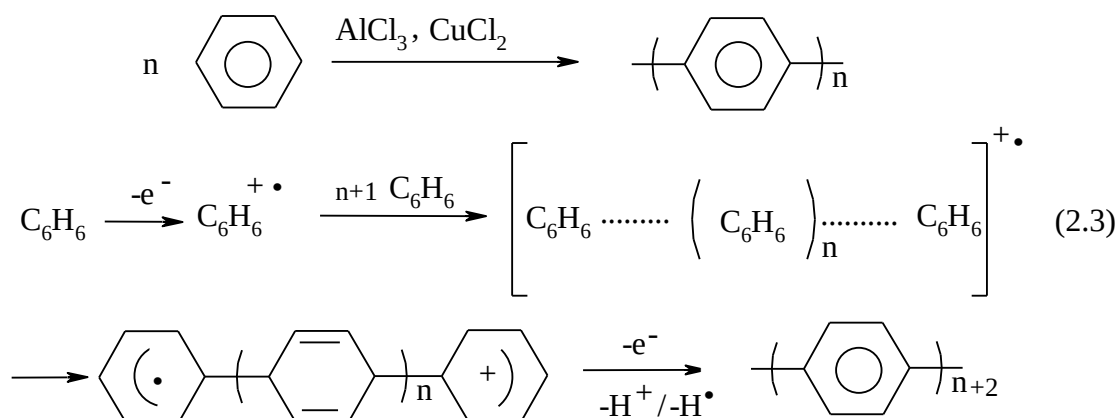
2.1.2.2 Poly(p-phenylene)s as Fibers and Fibrils

Oriented fibers from PPP powder can be fabricated by solid state extrusion [74]. The die was filled with the polymer powder, heated up and pressurized. This extrusion process gave PPP fibers that were easy to handle and had a length of several meters. Polymer chain orientation in the fibers was confirmed by X-ray scattering measurements. The fibers were afterwards doped with AsF₅ in the gas phase at different pressures. The doping process was followed optically by using a conventional light source and two lenses. When the picture of the fibers was magnified on a screen, swelling of the fibers could be seen. It was also found that doping of the fibers was rather inhomogeneous. The electrical conductivity was found to be highest in the direction of the chains. PPP fibrils have also been produced electrochemically by using benzene as the precursor [75]. The fibers started to grow parallel to each other but upon prolonged polymerization they started to grow together and formed a film with a high tensile strength along the fibers.

2.2. Synthesis of Polyphenylenes

2.2.1. Oxidative Coupling

There are several routes for the synthesis of polyphenylenes(PP) [76]. The most commonly employed method for the preparation of PP involves the oxidative coupling of substituted and unsubstituted benzenes via treatment with a Lewis acid catalyst/oxidant system. In 1963 Kovacic and Kyriakis synthesized PPP by stirring benzene, anhydrous AlCl₃ and anhydrous CuCl₂ for 2 hr at temperatures between 25⁰C and 35⁰C. The reaction is believed to involve an initial one- electron oxidation of benzene to its radical cation, followed by reaction of the radical cation with several benzene molecules (2.3) to give an oligomeric radical cation. A second one-electron oxidation, followed by loss of two protons aromatizes the terminal rings, and oxidative rearomatization of the dihydro structures by CuCl₂ yields the polymer [77].



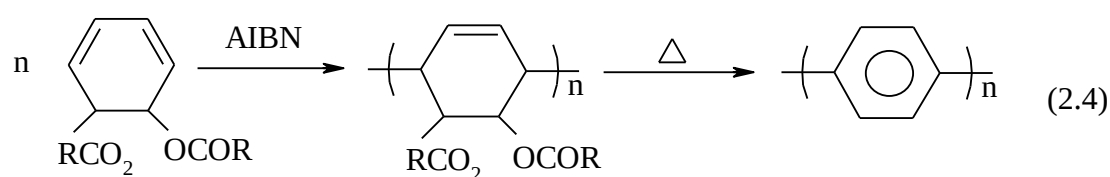
A number of other catalyst/oxidant systems have been employed for the conversion of benzenes to polyphenylenes. These include Cu^{+2} and Ru^{+3} ion-exchanged montmorillonite clays [78] and $\text{AsF}_3/\text{AsF}_5$ [79]. The structural features and physical properties of the polymer prepared via oxidative polymerization depend to a large extent on the nature of the reagents. Thus, it has been claimed that polyphenylenes with *ortho* linkages can be obtained from the oxidative polymerization of monosubstituted benzenes (e.g. toluene, chlorobenzene) under conditions analogous to those employed for the preparation of PPP. PPs linked at the *meta* position are in general synthesized by treatment of m-terphenyl or mixtures of the m-terphenyl and biphenyl with anhydrous $\text{AlCl}_3/\text{CuCl}_2$ at elevated temperatures (85°C and 180°C). Polymers substituted in the *para* position are in general more difficult to process than the *ortho* and *meta* substituted analogues. Oxidations in liquid SO_2 at -75°C or concentrated sulfuric acid in the presence of AlCl_3 are claimed to result in the efficient formation of homogenous PPP which is almost completely amorphous [80]. Highly crystalline films of this polymer can be deposited from benzene in concentrated sulfuric acid emulsion [81].

An alternative means for the synthesis of PP involves the anodic electrochemical oxidation of benzene or biphenyl in liquid sulfur dioxide on an appropriate electrode. The reaction yields passivating films if quaternary ammonium perchlorate is used as the electrolyte or conductive dendritic deposits quaternary ammonium tetrafluoroborate is employed. In both cases the polymer formed is reported to be linked at the *para* position but contains variable amounts of oxygen as phenolic groups. The electrochemical polymerization of benzene in nitromethane with aluminium chloride and water or an amine as additive results in the deposition of black polyphenylene on a platinum electrode. Free-standing polyphenylene films

containing *ortho*, *para* and *meta* links are obtained if the electrochemical oxidation of benzene is carried out in a two phase HF/benzene system. The anodic oxidation of benzene in nitrobenzene solution with CuCl_2 and LiAsF_6 results in the formation of flexible, electrically conducting films of PPP as does the anodic oxidation of benzene in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ [82]. The yields of the polymers prepared by this method are restricted by the area of the anode irrespective of whether the reaction is carried out in nitrobenzene or in the bulk [83].

2.2.2. Dehydrogenation of Polycyclohexylenes

The polymerization of 1,3-cyclohexadiene in the presence of various Ziegler type initiator systems or *n*-butyllithium yields poly(1,3-cyclohexadiene). Dehydrohalogenation of this precursor polymer with chloranil or via halogenation/pyrolysis gives polyphenylene. Cationic polymerization of the same monomer produces a mixture of 1,4- and 1,2-bonded structures which on halogenation/pyrolysis form a polyphenylene with *ortho* and *para* linkages. Diester derivatives of 5,6-dihydroxy-1,3-cyclohexadiene have also been polymerized under radical conditions using benzoyl peroxide or 2,2'-azobisisobutyronitrile (AIBN) after which the resulting polycyclohexylenes were converted to polyphenylenes by pyrolysis [84] like in reaction 2.4, the favoured precursor being the methyl carbonate derivatives.

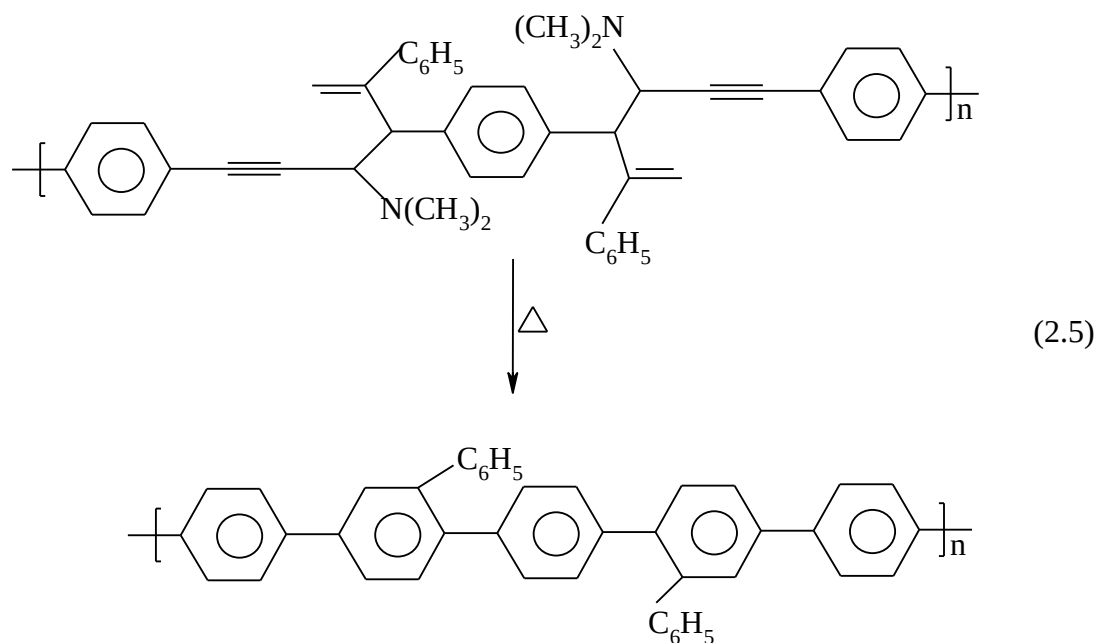


The molecular weight of the thus formed polyphenylenes are greatly influenced by the relative stereochemistry and size of the diester substituted polymers.

2.2.3. Cycloaddition Reactions

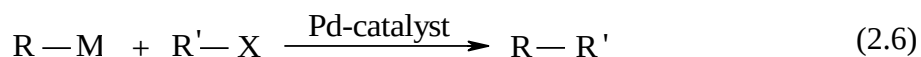
1,4-cycloadditions of biscyclopentadienones with bisacetylenes can yield high molecular weight polymers which contain approximately equal proportions of *meta* and *para* substituted phenylene units. Low molecular weight polyphenylenes containing ethynyl branches have been prepared [85] by polycyclotrimerization of

diacetylene in the presence of $\text{Al}(\text{i-Bu})_3$ and TiCl_4 whereas polyphenylene copolymers with phenyl, vinyl and alkyl branches can be obtained by the reaction of diacetylene with an appropriately substituted acetylene. The thermal eliminative ring closure of 1,4-diphenyl-3-(N,N-dimethyl-amino)-hex-5-en-1-yne has been shown [86] to give terphenyl and by an analogous method the poly(N,N-dimethylaminohex-5-en-1-yne) derivative shown in reaction 2.5 affords phenyl substituted PPPs on pyrolysis [87].



2.2.4. Organometallic Coupling

The cross-coupling reaction now accessible via a variety of organometallic reagents may provide a fundamentally common synthetic methodology (2.6).



Kumada and Tamao [88] and Corriu [89] reported independently, in 1972, that the reaction of organomagnesium reagents with alkenyl or aryl halides could be markedly catalyzed by $\text{Ni}(\text{II})$ complex. Kochi [90] found the efficiency of $\text{Fe}(\text{III})$ catalyst for the cross-coupling of Grignard reagents with 1-halo-1-alkenes and $\text{Li}_2\text{-CuCl}_2$ catalyst for haloalkanes. The palladium-catalyzed reaction of Grignard reagents was first reported by Murahashi [91], the synthetic utility of which was then amply demonstrated by Negishi [92] on the reactions of organoaluminum, zinc, and

zirconium reagents. Afterwards, many other organometallic reagents such as organolithiums, organostannans, 1-alkenylcopper(I), have proven to be highly useful as nucleophiles for the cross-coupling reaction [93].

2.2.4.1. Ni-Catalyzed Grignard Coupling (Yamamoto Coupling)

Diorganonickel(II) complexes NiR_2L_n (neutral ligand, e.g., $\text{L}=\text{PPh}_3$) undergo a reductive coupling reaction to give R-R [94-97] (2.7) and this coupling reaction has been utilized to carry out nickel-catalyzed C-C coupling between Grignard reagent and organic halide (2.8) [98] and dehalogenation coupling of organic halides with zinc (2.9) [99,100].

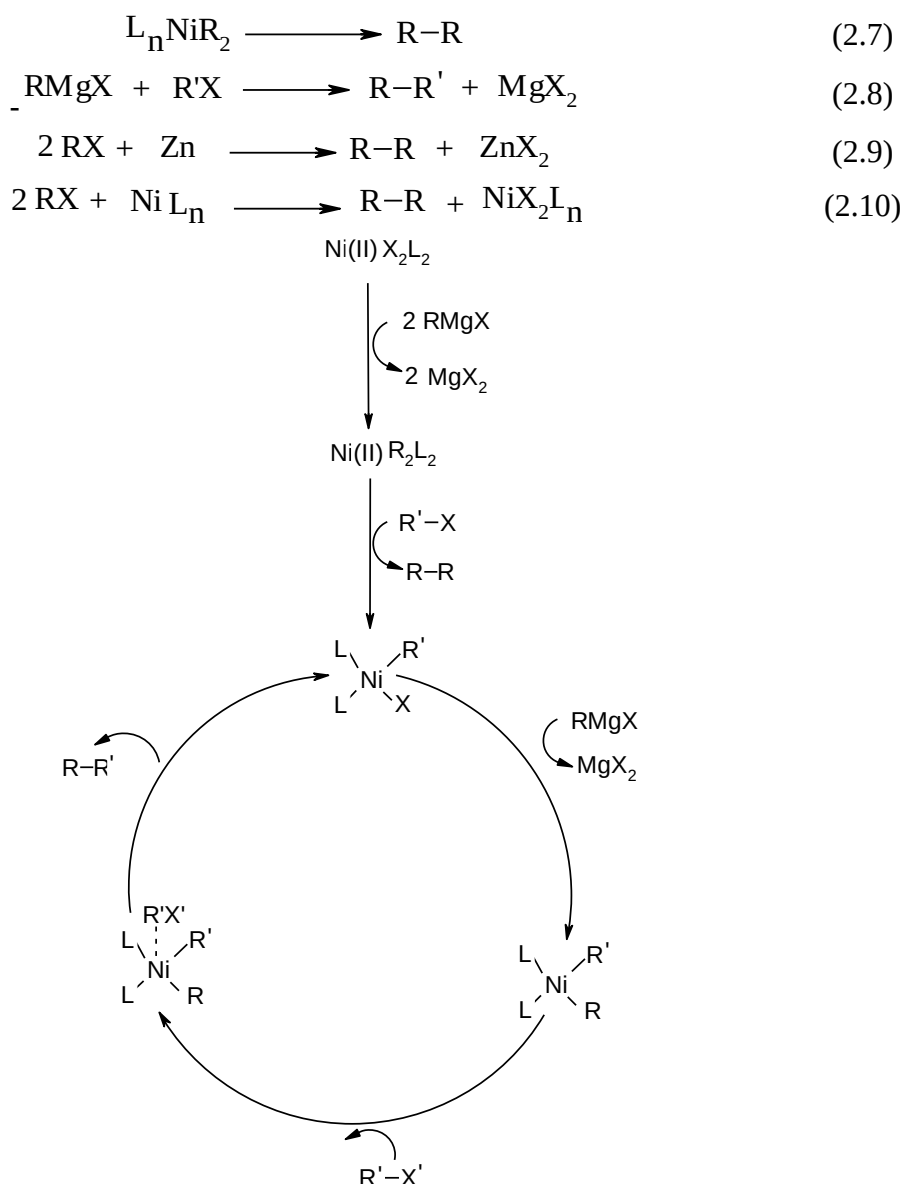
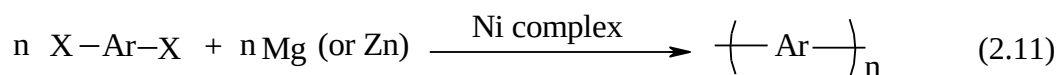


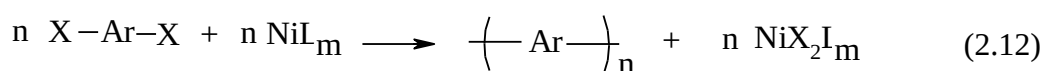
Figure 2.7 Ni- Catalyzed Grignard Coupling

In addition to the coupling reactions expressed by (2.8) and (2.9), Ulmann type coupling of organic halides using zerovalent nickel complex (Fig. 2.7) itself as a dehalogenation reagent has been developed.

Among these organonickel-based coupling reactions, reactions (2.8) and (2.9) have been developed for molecular design of electrically conducting π -conjugated poly(arylene)s (2.11) $-(Ar)-$, e.g., linear PPP [101].

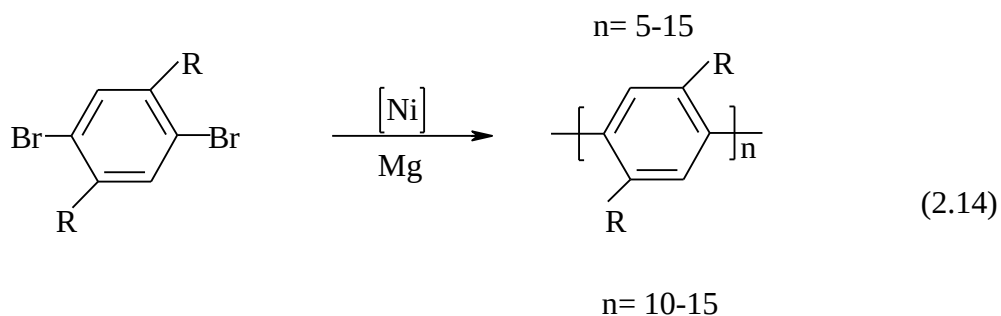
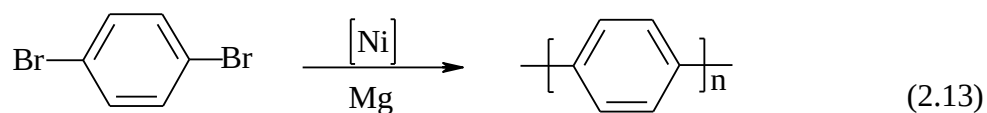


However, much less attention has been paid [102,103] to application of coupling reaction (2.10) to the synthesis of the conjugated polymer. Since coupling reaction (2.10) proceeds under mild conditions, can be applied to a wide range of aromatic compounds (e.g., those with carbonyl and cyano groups) under various reaction conditions (e.g., in various solvents) and is the most direct and simple reaction among the Ni-based coupling reactions, reaction 2.10 is expected to provide versatile means for molecular design and synthesis of electrically conducting π -conjugated polymers from haloaromatic compounds X-Ar-X (2.12).



Unlike the established aromatic polyesters or polyamides, where the aromatic units are connected via carboxylic esters or amides and require CO-bond and CN-bond formations to synthesize, the synthesis of poly(arylene)s involves the formation of CC bonds, which is more difficult to achieve [8]. On the basis of a retrosynthetic analysis of PPP, it was decided to connect the aromatic units directly to one another. Other possibilities for generating aromatic units sometime during the sequence [73] were considered disadvantageous. Consequently, instead of chain growth, a step-growth procedure had to be developed for which it was known that extremely high conversions per individual bond-formation step were a strict necessity if high molar mass polymer was to be obtained. The CC-bond-formation reaction, therefore, had to be chosen with the greatest care. The second aspect was solubility. From short, linearly (1,4-) connected oligophenylenes, it is known that the solubility already drops to negligibly small values after a few connected benzene rings. The solubility

of all-para-linked nonaphenylene, for example, which is just a very short model for PPP, is less than 10^{-8} g/L in toluene at room temperature [104]. Yamamoto's route was considered most interesting because it was the only one that guaranteed the straight, 1,4-connection of benzene rings. It is known that the solubility of rigid molecules increases drastically upon substitution with flexible side chains [105-108]. They render the dissolution of the molecules more attractive, mostly for entropic reasons. These considerations led us to believe that a simple decoration of 1,4-dibromobenzene, the Yamamoto monomer, with flexible alkyl chains may open a generally applicable route into PPPs. Matthias synthesized 1,4-dibromo-2,5-dihexyl benzene (**I**), [109] which turned out to be an extremely valuable compound for other purposes as well, [110,111] and applied the Yamamoto conditions (2.13) and (2.14). The result, however, was quite disappointing [112]. Regardless of how he did the reaction and which catalyst precursors he used, exclusively oligomeric products were obtained. The only improvement was the excellent solubility of the oligomers, which enabled him to accurately determine their molar masses and chemical structures. It is determined that the steric hindrance imposed by the alkyl groups might have been responsible for termination at this early stage of growth, a view that was supported some time later by the successful Yamamoto-type synthesis of a sterically unhindered polyarylene [113].



2.2.4.2. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds (Suzuki Coupling)

The palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides or triflates provides a powerful and general methodology for the

formation of carbon–carbon bonds. Recently, this reaction has been called the Suzuki coupling, Suzuki reaction, or Suzuki–Miyaura coupling. The availability of the reagents and the mild reaction conditions all contribute to the versatility of this reaction. The coupling reaction offers several additional advantages, such as being largely unaffected by the presence of water, tolerating a broad range of functional groups, and proceeding generally regio- and stereoselectively. Moreover, the inorganic by-product of the reaction is non-toxic and easily removed from the reaction mixture thereby making the Suzuki coupling suitable not only for laboratories but also for industrial processes [114].

Organoboron compounds are highly electrophilic, but the organic groups on boron are weakly nucleophilic, thus limiting the use of organoboron reagents for the ionic reactions. The coordination of a negatively charged base to the boron atom has been recognized to be an efficient method of increasing its nucleophilicity to transfer the organic group on boron to the adjacent positive center (1,2-migration reaction). However, intermolecular transfer reactions such as the Grignard-like reaction are relatively rare. Fortunately, organoboron compounds, even organoboronic acids and esters, have sufficiently enough reactivity for the transmetalation to other metals. In 1978, Negishi reported that iodobenzene selectively couples with the 1-alkynyl group on lithium 1-hexynyl(tributyl)borate through a palladium-catalyzed addition-elimination sequence (Heck-type process); however, the cross-coupling reaction of organoboron compounds, which involves the transmetalation to palladium(II) halides as a key step, was found to proceed smoothly when these were activated with suitable bases and have proven to be a quite general technique for a wide range of selective carbon-carbon bond formation [115]. Many organometallic reagents undergo similar cross-coupling reactions, but much attention has recently been focused on the use of organoboronic acids in laboratories and industries since they are convenient reagents, which are generally thermally stable and inert to water and oxygen, thus allow their handling without special precautions.

a) Mechanism of Suzuki Coupling Reactions

A general catalytic cycle for the cross-coupling reaction of organometallics, which involves oxidative addition-transmetalation-reductive elimination sequences, is depicted in Figure 2.8. Although each step involves further knotty processes

including ligand exchanges, there is no doubt about the presence of those intermediates (**1** and **2** in Figure 2.8) which have been characterized by isolation or spectroscopic analyses. It is significant that the great majority of cross-coupling reactions catalyzed by Ni(0), Pd(0), and Fe(I) are rationalized in terms of this common catalytic cycle.

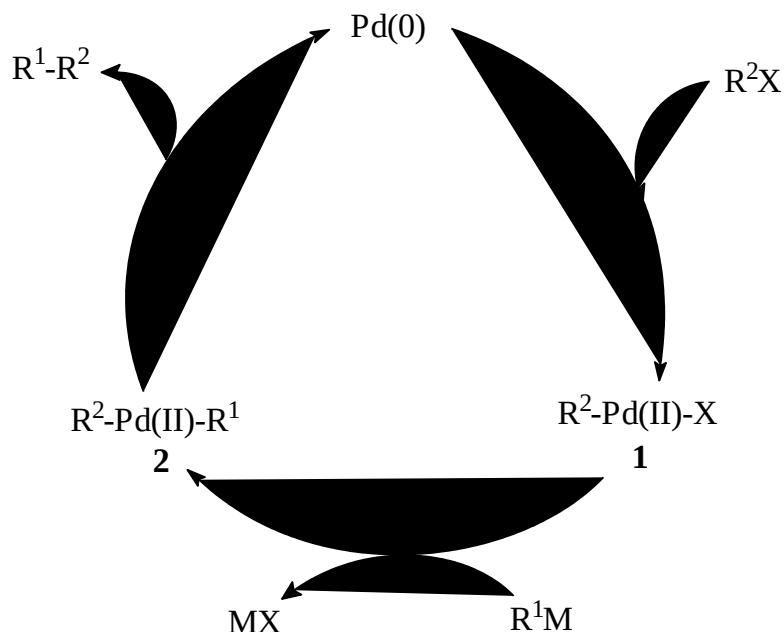


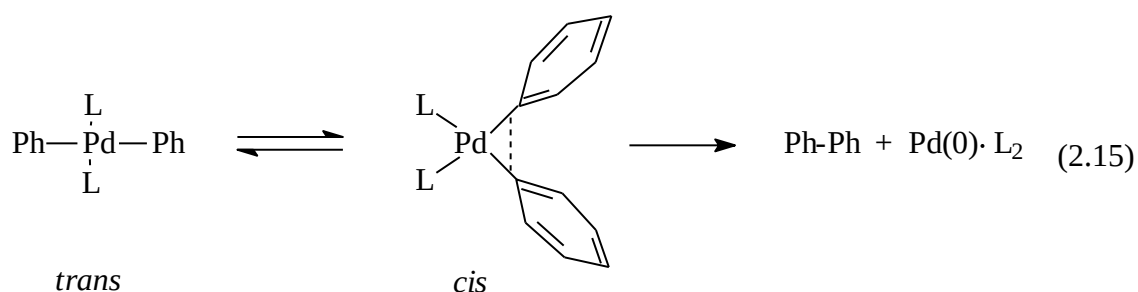
Figure 2.8 A general catalytic cycle for cross-coupling

Oxidative addition of 1-alkenyl, 1-alkynyl, allyl, benzyl, and aryl halides to a palladium(0) complex affords a stable trans- σ -palladium(II) complex (**1**). The reaction proceeds with complete retention of configuration for alkenyl halides and with inversion for allylic and benzylic halides. Alkyl halides having β -hydrogen are rarely useful because the oxidative addition step is very slow and may compete with β -hydride elimination from the σ -organopalladium-(II) species. However, it has been recently shown that iodoalkanes undergo the cross-coupling reaction with organoboron compounds [116].

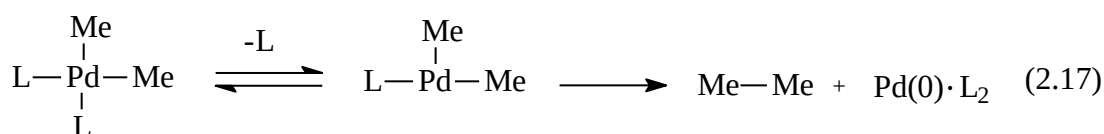
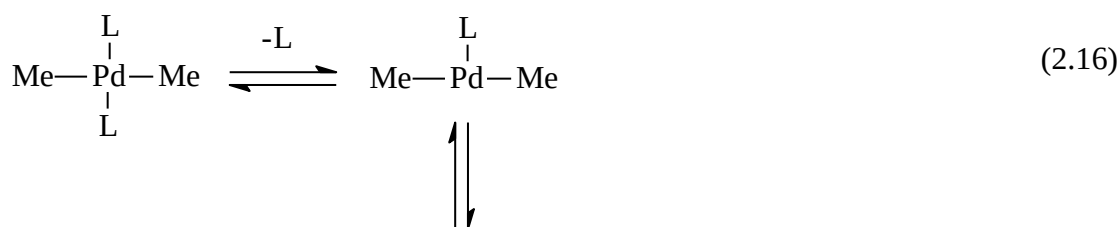
Oxidative addition is often the rate-determining step in a catalytic cycle. The relative reactivity decreases in the order of $\text{I} > \text{OTf} > \text{Br} \gg \text{Cl}$. Aryl and 1-alkenyl halides activated by the proximity of electron-withdrawing groups are more reactive to the oxidative addition than those with donating groups, thus allowing the use of chlorides such as 3-chloroenone for the cross-coupling reaction. A very wide range of palladium(0) catalysts or precursors can be used for cross-coupling reaction.

$\text{Pd}(\text{PPh}_3)_4$ is the most commonly used, but $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{Pd}(\text{OAc})_2$ plus PPh_3 or other phosphine ligands are also efficient since they are stable to air and readily reduced to the active $\text{Pd}(0)$ complexes with organometallics or phosphines used for the cross-coupling.

Reductive elimination of organic partners from **2** reproduces the palladium(0) complex. The reaction takes place directly from *cis*-**2**, and the *trans*-**2** reacts after its isomerization to the corresponding *cis*-complex (reactions 2.15, 2.16 and 2.17). The order of reactivity is diaryl- > (alkyl)aryl- > dipropyl- > diethyl- > dimethylpalladium(II), suggesting participation by the π -orbital of aryl group during the bond formation (reaction 2.15).



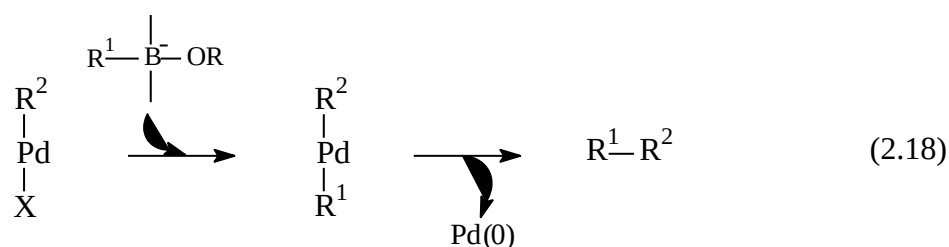
The thermolysis of *cis*-(dialkyl)palladium(II)· L_2 , which is an intermediate on the alkyl-alkyl coupling, is inhibited by excess phosphine (**L**), hence it is considered to be initiated by the rate-determining dissociation of phosphine ligand (**L**) producing a three-coordinated *cis*-(dialkyl)palladium(II)·**L** complex (dissociative mechanism, reactions 2.16 and 2.17). Thus, the effect of phosphine ligands is comparable to the order of ease of their dissociation: $\text{dppe} \ll \text{PEt}_3 < \text{PEt}_2\text{Ph} < \text{PMePh}_2 < \text{PEtPh}_2 < \text{PPh}_3$.



On the other hand, *cis*-alkenyl- and *cis*-arylpalladium(II) complexes, which are intermediates in most of cross-coupling reactions discussed here, directly eliminate organic partners from the four-coordinated complex (nondissociative-nonassociative mechanism, reaction 2.15).

Although the mechanism of oxidative addition and reductive elimination sequences are reasonably well understood and are presumably fundamentally common processes for all cross-coupling reactions of organometallics, less is known about the transmetalation step because the mechanism is highly dependent on organometallics or reaction conditions used for the couplings.

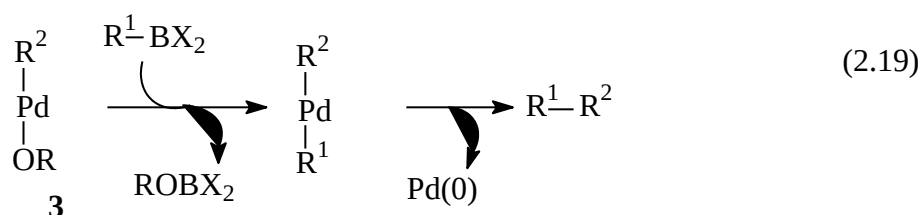
The cross-coupling reaction of organoboron compounds with organic halides or triflates selectively reacts in the presence of a negatively charged base, such as sodium or potassium carbonate, phosphate, hydroxide, and alkoxides. The bases can be used as aqueous solution, or as suspension in dioxane or DMF. In contrast, the cross-coupling reaction with certain electrophiles, such as allylic acetates, 1,3-butadiene monoxide, and propargyl carbonates, occurs under neutral conditions without any assistance of base. The transmetalation of organoboron compounds with palladium halides under basic or neutral conditions can be considered to involve the following three processes illustrated by the reactions 2.18-2.20.



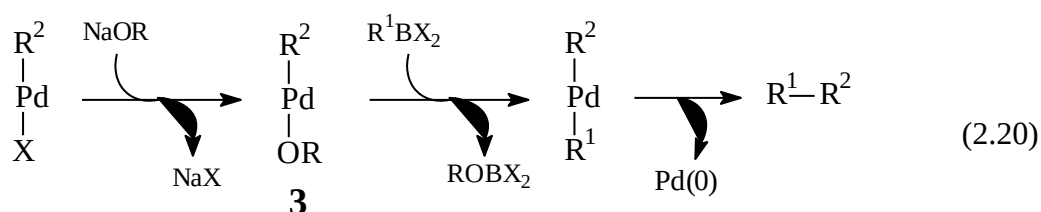
It is apparent that the transmetalation between organopalladium(II) halides and organoboron compounds does not occur readily due to the low nucleophilicity of organic group on boron atom. However, the nucleophilicity of organic group on boron atom can be enhanced by quaternization of the boron with negatively charged bases giving the corresponding “ate” complexes. The quaternization of trialkylboranes accelerates the transmetalation to the palladium(II) halides. Although there is no direct evidence that the boronate anions, such as $\text{RB}(\text{OH})_3^-$, are capable of effecting the transmetalation, it is quite reasonable to assume the similar effect of base for the transmetalation of organoboronic acids. The cross-coupling reaction of

arylboronic acids with aryl halides at pH = 7-8.5 is retarded relative to the reaction at pH = 9.5-11. The pK_A of phenylboronic acid is 8.8, thus suggesting the formation of the hydroxyboronate anion $[RB(OH)_3]^-$ at pH > pK_A and its transmetalation to the palladium(II) halides.

An alternative transmetalation process is that organoboron compounds readily transfer their organic groups to (alkoxo)-palladium(II) complexes under neutral conditions (reaction 2.19).



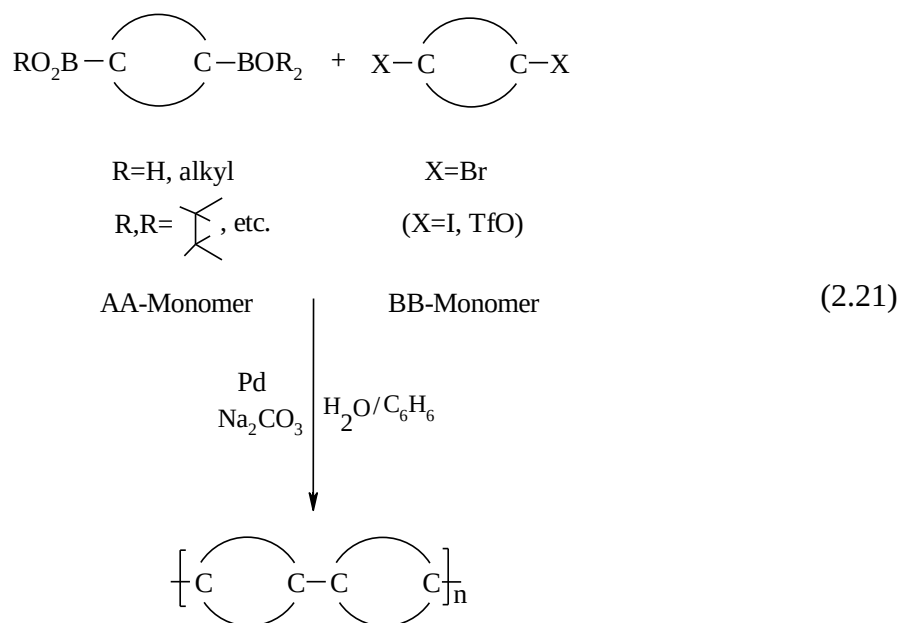
Finally, it is of interest to note the possibility of involvement of the (alkoxo) palladium intermediate **3** in the palladium/base-induced cross-coupling reaction (2.20). It is known that the halogen ligand on organopalladium(II) halide is readily displaced by alkoxy, hydroxy, or acetoxy anion to provide the reactive Pd-OR complexes (**3**), which have been postulated as reaction intermediates or isolated from the reaction of organopalladium(II) halides with sodium hydroxide or methoxide.



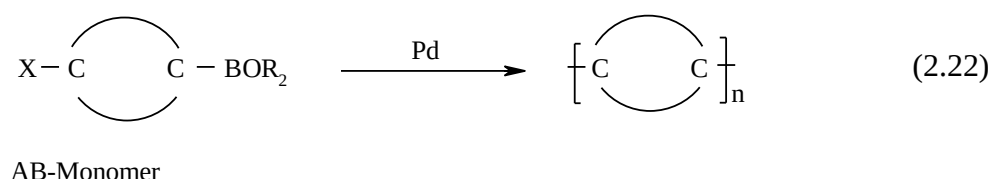
It is not yet obvious in many reactions which process shown in reaction 2.18 or 2.20 is predominant; however, the formation of alkoxo-, hydroxo-, or acetatopalladium(II) intermediate should be considered to be one of the crucial transmetalation processes in the base/palladium-induced cross-coupling reactions.

b) Suzuki Polycondensation

AA / BB-approach



AB-approach



Suzuki cross-coupling successfully transferred to Suzuki Polycondensation (SPC) reaction to polymer synthesis and give soluble and processable polyarylenes. SPC is a step-growth polymerization of bifunctional aromatic monomers to poly(arylene)s and related polymers (2.21) and (2.22) [10,117-118].

The required functional groups, boronic acid or esters on the one side and bromide, iodide, and so forth on the other, may be present in different monomers (AA/BB approach) or combined in the same monomer (AB approach). Both approaches have been successfully applied. AB-type monomers intrinsically have the stoichiometric balance between the two different functional groups that, according to Carother's equation, [119] is a strict necessity in step-growth polymerizations when high molar mass polymer is concerned. There is a simple synthetic reason the AA/BB approach is nevertheless favored. Normally, it is easier to synthesize aromatic monomers with two identical substituents in opposite positions (for benzene, 1,4) than those with

different ones. An additional factor is that once an aromatic dibromide is obtained, its conversion into the corresponding diboronic acid or ester can often be achieved in one simple step and on a large scale. The price to be paid for this, however, is the necessity of applying the AA and BB monomers in strictly equal molar amounts. Purities, methods of how to completely transfer mono-mers into the polymerization vessel, and losses of some of the functional groups during polymerization become important and, all of a sudden, even critical aspects when the molar mass difference between two monomers is very large [120]. The matter of purity is of real importance for SPC and should, therefore, be briefly addressed. Free boronic acid or one of the many cyclic boronic esters are used as boron-based functional groups. During polymerization, these esters may hydrolyze to the acids that then enter the normal cross-coupling or follow an independent mechanism [121]. Boronic acids always contain some water. Otherwise, they are partially or completely condensed to cyclic boroxines. This water content has to be precisely determined for the reasons mentioned previously [122]. Boronic esters, which do not have the problem with additional water, tend to partially hydrolyze on the column upon attempted purification. This renders weighing and, thus, stoichiometry control also somewhat problematical. The boronic monomer counterparts in SPC are aromatic bromides, iodides, or triflates. The bromo group is by far the most often encountered coupling partner in SPC. Iodides [123] and triflates [124] were only seldom used, although iodo compounds may gain increasing attraction because they were recently found to furnish higher molar mass products than their bromo analogues (discussed later). Chloro aromatics, although successfully used in organic chemistry Suzuki Cross-Coupling (SCC), [125] have not been transferred to polymer chemistry yet.

The circles in (2.21) and (2.22) represent aromatic units, which are substituted benzenes in practically all cases but also include naphthalines, thiophenes, pyridines, and pyrroles (with an acceptor on nitrogen). When substituted with boronic acids, electron-rich aromatics tend to undergo deboronification reactions, [126] which lead to stoichiometric misbalance with its detrimental impact on the achievable molar mass. This is why, for example, thiophenes in SPC are always used as dibromides and not as diboronic acids. These aromatic units are connected to one another to linear poly(arylene)s (for benzenes, PPPs) in more than 95% of all publicized cases. In a few examples, regularly kinked poly(arylene)s or related conjugated polymers

containing additional olefinic or acetylenic units or other functional groups as part of the main chain are generated. Linear poly(arylene)s, whose chemical constitution in principle allows the attainment of a totally straight conformation, are considered rigid-rod type polymers. Although they certainly have bent backbones and attain coiled conformations in solution, they have less conformational degrees of freedom, which are available at low energetic cost than, for example, saturated polymers such as polystyrene (PSt). As a result, these poly(arylene)s show poor solubility because they have little driving force to dissolve *molecularly dispers*.

This is why in most cases when SPC comes into play, it is applied to monomers that carry flexible chains of some sort. These chains help keep the growing (and final) polymer in solution and accessible to further growth until growth reaches its system's intrinsic limits.

These limits comprise termination through reduction of the bromo group or phosphorous incorporation through ligand scrambling channels (discussed later) or the removal of catalytically active Pd complexes through the precipitation of Pd(0) intermediates such as Pd black.

The substituents on the poly(arylene)s are not only important for solubility (and processability) reasons.

They can also be used to incorporate function, a feature that has been increasingly and astoundingly successfully used in recent years. As far as the electronic properties of the backbones are concerned, substituents may, however, be disadvantageous, too. They normally lead to an increase of the dihedral angle of consecutive aromatic units, which reduces electronic conjugation and thus further increases the polymers' already quite large highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) gap.

As for SCC, SPC involves only the carbon atoms that carry the functional groups. Polymerizations proceed regiospecifically. This is important because some of the properties of poly(arylene)s depend on their backbone's ability to attain straight conformations without kinks. Also, the functional group compatibility of SPC is the same as for SCC. Aldehydes, nitro and cyano groups, sulfonic esters, ethers, various protected alcohols and amines, amides, and so forth can be present. Even free

hydroxy and free amines have been reported, although they do not seem to work too well. The reaction conditions are like the ones Suzuki reported in his famous, original article of 1981. [127,93,114] Other solvent systems were also applied whenever required by the solubility of the polymer. For example, SPC has even been done in water with both water-soluble monomers and catalyst precursors [72]. The mechanism of SPC is supposed to involve the same steps of oxidative addition, transmetallation, and reductive elimination as for SCC. The standard catalyst precursor is $\text{Pd}(\text{PPh}_3)_4$. Although SPC has not yet been developed into a reaction that is catalytic in an industrial sense, 0.5 mol % Pd complex is sufficient in many cases. Pd complexes with other phosphine ligands have also been employed. For example, *ortho*- and *para*-tolyl ligands proved successful [44,46]. Although the choice of the best catalyst precursor is still a matter of intuition, it is accepted knowledge that the complex used should be as pure as possible. Thus, the commercially available $\text{Pd}(\text{PPh}_3)_4$ should not be used as obtained but rather should be recrystallized and used directly thereafter (under nitrogen). Best results are normally obtained when the Pd complexes are self-prepared and used freshly.

2.3 Controlled Polymerization

Living polymerization was first defined by Szwarc [128] as a chain growth process without chain breaking reactions (transfer and termination). While such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [129-131]. It has been suggested to use a term “controlled polymerization” if these additional criteria are met. A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality. Transfer and termination, which often occur in real systems, are allowed in a controlled polymerization if their contribution

is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

2.3.1 Controlled Radical Polymerization (CRP)

Radical polymerization (RP) is a very convenient commercial process for the preparation of high molecular weight polymers since it can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions, requiring an oxygen free medium, but tolerant to water, and can be conducted over a large temperature range (-80 to 250°C) [132]. Furthermore, many monomers can easily be copolymerized through a radical route, and this leads to an infinite number of copolymers with properties dependent on the proportion of the incorporated comonomers. One of the main disadvantages of RP is the poor control over the microstructure of the synthesized macromolecules. This includes the relatively high polydispersity index (PDI), 1.5 or 2.0, and also the practical impossibility to synthesize block copolymers, and other advanced structures.

Advanced structures can be synthesized via living polymerization techniques. The term living polymerization was initially used to describe a chain polymerization in which chain breaking reactions were absent. In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer and termination. Notable example of these techniques is anionic polymerization [133], which is known to allow the synthesis of low PDI materials as well as block copolymers. The main disadvantages of anionic polymerization are the limited choice of monomers, and the extremely demanding reaction conditions.

On the other hand, living polymerizations will lead to well defined polymers only if the following additional prerequisites are fulfilled:

- initiation is fast in comparison with propagation
- exchange between species of different reactivities is fast in comparison with propagation
- the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

To fairly be termed as "living" a polymerization must meet all of the following criteria.

1. polymerization proceeds until all the monomer has been consumed - further addition of monomer results in continued polymerization
2. the number average molecular weight, M_n (or X_n , the number average degree of polymerization), is a linear function of conversion
3. the number of polymer molecules (and active centers) is a constant, which is sensibly independent of conversion
4. the average molecular weight of the polymer can be controlled by the stoichiometry of the reaction
5. narrow-molecular-weight distribution polymers are produced
6. block copolymers can be prepared by sequential monomer addition
7. chain-end functionalized polymers can be prepared in quantitative yield
8. linearity of a kinetic plot of rate of propagation as a function of time
9. linear dependence of the degree of polymerization as a function of time.

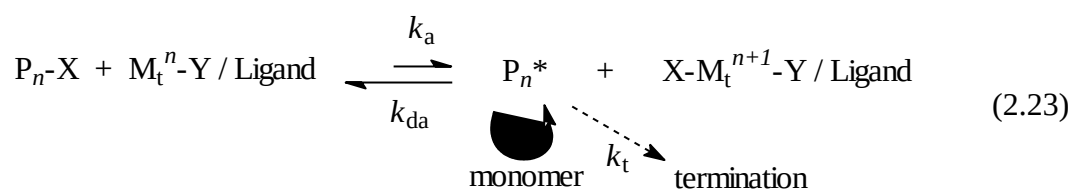
Controlled–“living” radical polymerizations allow for the synthesis of new well-defined and functional materials from a larger range of monomers under simpler reaction conditions than are appropriate for ionic processes [20]. A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality. Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

The past few years have witnessed the rapid growth in the development and understanding of new “controlled/living” radical polymerization (CRP) methods.[20,134] The achievement of controlled radical polymerizations is one of the most important goals in precision polymerization for polymer chemists. In recent years much effort has been put on the development of pseudo-living free radical polymerization methods. The methods at the forefront fall into one of three categories: ATRP [135], Nitroxide Mediated Polymerization (NMP) or Stable Free Radical Polymerization (SFRP) [136] and Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) [137].

All of the CRP methods, include activation and deactivation steps (with rate constants k_{act} and k_{deact}). Generated free radicals propagate and terminate (with rate constants k_p and k_t), as in a conventional free-radical polymerization. Thus, although termination occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems.

2.3.1.1 Atom Transfer Radical Polymerization (ATRP)

The name atom transfer radical polymerization comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [22]. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [138,139].

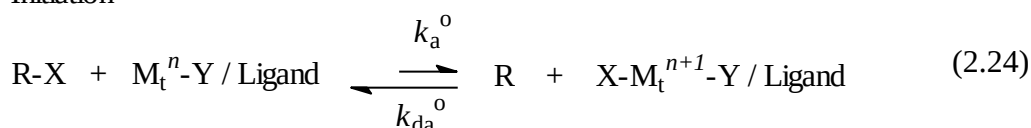


A general mechanism for ATRP is represented by reaction 2.23. The radicals, i.e., the propagating species P_n^* , are generated through a reversible redox process catalyzed by a transition metal complex (activator, $\text{M}_t^n\text{-Y / ligand}$, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, $\text{P}_n\text{-X}$. Radicals react reversibly with the oxidized metal complexes, $\text{X-M}_t^{n+1} / \text{ligand}$, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a , and deactivation k_{da} , respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p . Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and

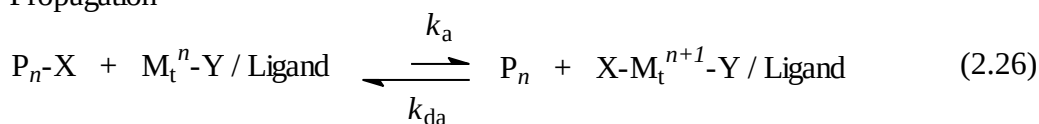
disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below [140]. (2.24-2.28)

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [141]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

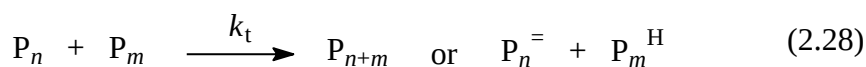
Initiation



Propagation



Termination



As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. Basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents are discussed as follows:

(a) Monomers

Various monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)-acrylamides, dienes, acrylonitrile and other monomers which contain substituents that can stabilize the propagating radicals. Ring-opening polymerization is also possible [135]. The currently used catalyst systems are not sufficient to polymerize less reactive monomers that produce non-stabilized, reactive radicals such as ethylene, α -olefins, vinyl chloride and vinyl acetate, though copolymerization is sometimes successful [20].

The most commonly used monomers in ATRP are Styrenes and MMA.

Styrene: Styrene ATRP is usually conducted at 110 °C for bromide-mediated polymerization and 130 °C for the chloride-mediated polymerization [142]. Generally, bulk system is preferred. Solvents may be used for styrene ATRP and nonpolar solvents are recommended.

Well-defined PSt can be prepared with the molecular weight range of 1000 to 90000. In the region from 1000 to 30000, polydispersities (M_w/M_n) are less than 1.10 and above 30000 polydispersities increase to within the range of 1.10 to 1.50 due to some side reactions, predominantly HX elimination. These side reactions can be reduced at lower polymerization temperatures [20].

(ii) Methyl Methacrylate: The standard conditions for MMA ATRP are similar to those of styrene ATRP except that less copper(I) catalyst is needed and the polymerizations are conducted in 50% solution in diphenyl ether or dimethoxy benzene at 90 °C. The use of copper bromide instead of copper chloride leads to more rapidly decreasing polydispersities. This is due to the better efficiency of bromine in the deactivation step. The polymerization is also less controlled when bpy is used instead of dNbpy due to the correspondingly smaller concentration of deactivator.

Well-defined PMMA has been prepared within the molecular weight range of 1000 to 180000. In the region from 1000 to 90000 the polydispersities are less than 1.10 and above 90000 the polydispersities fall within the range of 1.10 to 1.50 [20].

(b) Initiators

The main role of the initiator is to determine the number of growing polymer chains. The initiation in ATRP may occur in one of two different ways. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of styrene in ruthenium and ruthenium-based ATRP [143,144]. Many different types of halogenated compounds have the potential to initiate ATRP. Typical examples would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization [145], or 1-phenylethyl chloride for the initiation of a styrene polymerization [22]. In addition, there are initiators like 2,2,2-trichloro-ethanol [146] that appear to be very efficient, and that result in hydroxy-functional polymer chains. Percec and co-workers reported the use of sulfonyl chlorides as universal initiators in ATRP [147]. Also the use of di-, tri-, or multifunctional initiators is possible, which will result in polymers growing in two, three, or more directions. Besides, some pseudohalogens, specifically thiocyanates and thiocarbamates, have been used successfully in the polymerization of acrylates [148].

The alternative way to initiate ATRP is via a conventional free-radical initiator, which is used in conjunction with a transition-metal complex in its higher oxidation state. Typically one would use AIBN in conjunction with a Cu(II) complex. Upon formation of the primary radicals and/or their adducts with a monomer unit, the Cu(II) complex very efficiently transfers a halogen to this newly formed chain. In doing so the copper complex is reduced, and the active chain is deactivated. This alternative way of initiation was termed “reverse ATRP” [149].

(c) Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

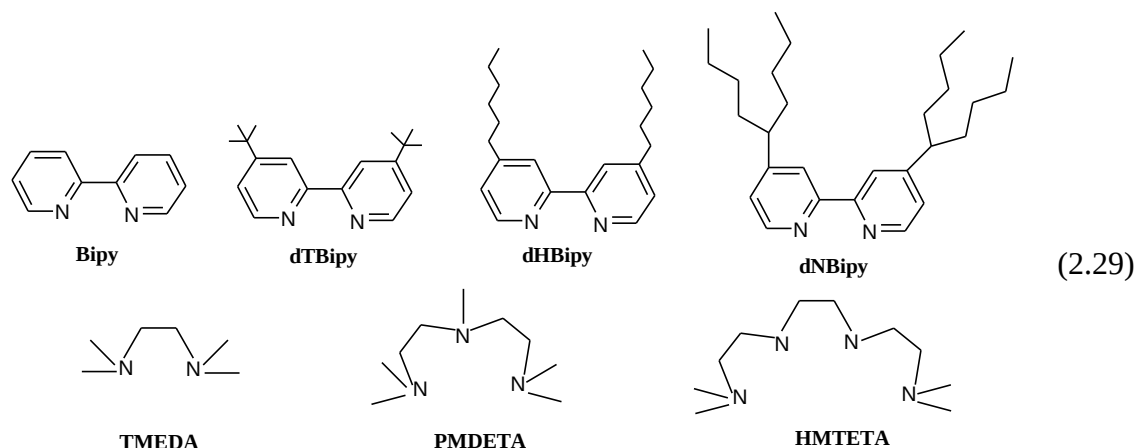
1. The metal center must have at least two readily accessible oxidation states separated by one electron.
2. The metal center should have reasonable affinity toward a halogen.
3. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo)halogen.
4. The ligand should complex the metal relatively strongly.
5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [150].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [151], Ni [152], Ru [153], etc have been used to some extent. Recent work from Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [154].

(d) Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N',N'',N''' pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me₆-TREN). Examples of ligands used in copper-mediated ATRP are illustrated below (2.29) [22,155].



(e) Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [156] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, [157] should be minimized.

f) Deactivators

The deactivator plays a vital role in ATRP in reducing the polymerization rate and the polydispersity of the final polymer. In the limit that the rate of deactivation is too slow or does not occur, and then ATRP simply becomes a redox initiated

polymerization. For copper-catalyzed ATRP, the deactivator is the corresponding copper (II) halide complex (e.g. 2dNbpy/CuX₂) [138].

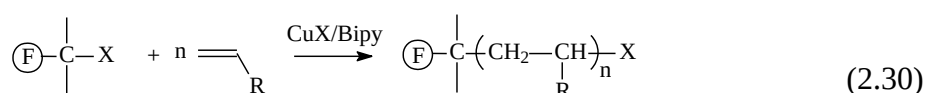
In most systems the concentration of deactivator continuously, but slowly, increases due to slow termination by radical coupling [138].

As a conclusion, ATRP is robust polymerization system that can polymerize a wide variety of monomers including styrenes, methacrylates, acrylates and acrylonitrile. The reaction conditions are not stringent because only the absence of oxygen is required to conduct the polymerizations. The polymer end groups can be transformed to other functional groups, such as amines and a range of polymers with different architectures and compositions can be prepared by relatively simple means. The combination of synthetic versatility and simplicity makes ATRP a powerful technique for use in designing and preparing new and unusual materials [138].

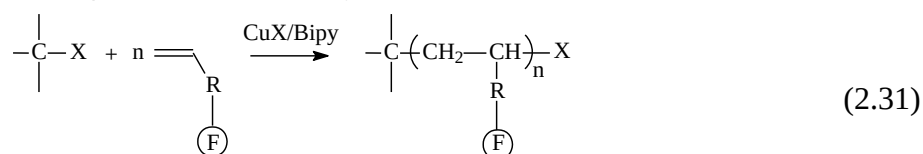
2.3.1.2 Polymer Functionalization by ATRP

Polymer functionalization by ATRP can be achieved by using functional initiators and monomers and the chemical transformation of the halogen end groups [158]. These routes are summarized in reactions 2.30-2.32.

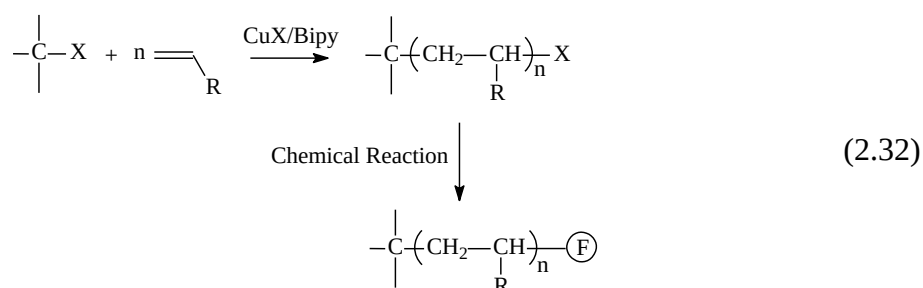
Through Initiator Functionality



Through Monomer Functionality

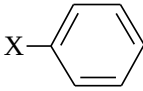
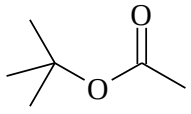
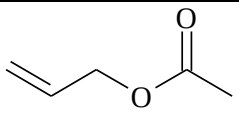
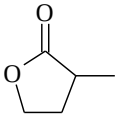


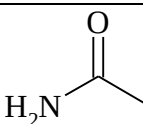
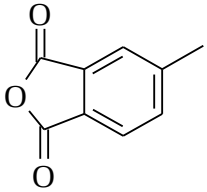
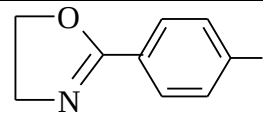
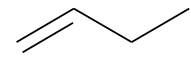
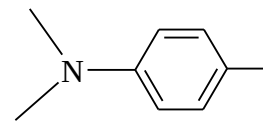
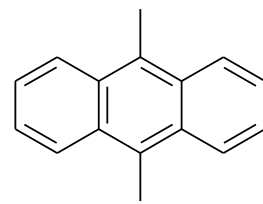
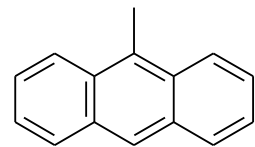
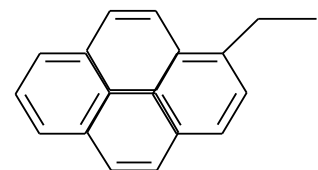
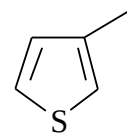
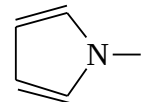
Through Chemical Reaction of Halide End Groups



Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers. For this purpose initiators should be equipped not only with the desired functional groups and also with a radical stabilizing group on the α -carbon atom such as aryl, carbonyl, nitrile, multiple halogens to ensue successful ATRP. Notably, direct bonding of halogen to aryl or carbonyl group does not facilitate radical generation. In this connection, it should also be pointed out that any functionalities in the initiator should not interfere with ATRP, i.e., should be inert to catalyst. The telechelic polymers prepared by using functional initiator approach in ATRP are presented in Table 2.2, along with the functional groups. Carboxylic acid functionalization by ATRP is rather difficult since the acid functionality poison the catalyst. However, ATRP of MMA by using 2-bromoisobutyric acid was reported to proceed. Various protected initiators were also reported for carboxylic acid functionalization. Hydrolysis of the protecting groups yields polymers with the desired carboxylic acid functionalities.

Table 2.2 Monofunctional Telechelic Polymers Prepared by Using Functional Initiators in ATRP

Functional Group	Polymer ^a	Reference
 X = H, CH ₃ , Br, CN, NH ₂ , CHO, NO ₂ , OCH ₃	PSt, PMA	159-163
CN	PSt, PMA	164-166
	PSt, PMA, PtBA	
	PSt, PMA	161
OH	PSt, PMA, PBA, PMMA	163, 167-174
	PSt, PMA	176
	PSt, PMA	161

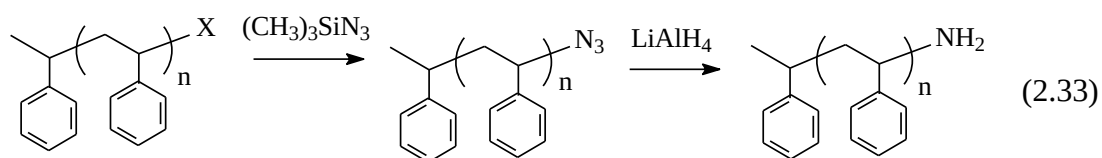
Functional Group	Polymer ^a	Reference
	PSt	161
COOH	PMMA	177
	PSt	178
	PSt	178
	PMA	179-181
	PSt	182
	PSt	183
	PMMA	184
	PSt	185, 186
	PMMA	187
	PSt, PMMA	188

^a:PMMA: poly(methyl methacrylate), PSt: polystyrene, PBA: poly(butyl acrylate), PtBA: poly(*tert*-butylacrylate), PMA: poly(methyl acrylate).

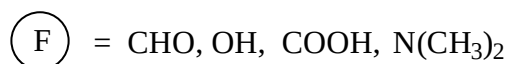
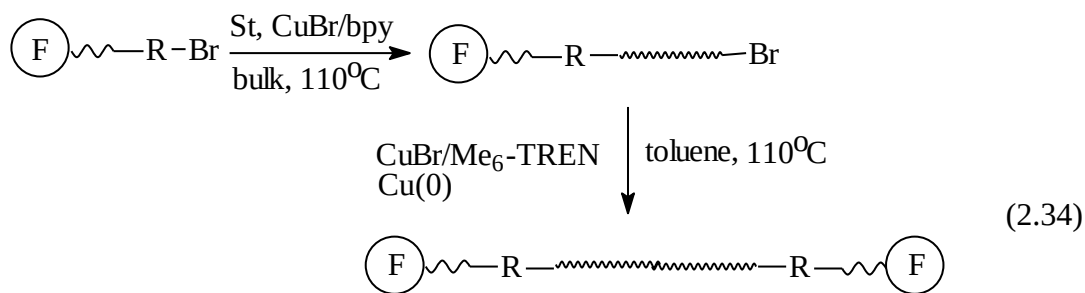
Some other functionalities including biofunctionalities were introduced to polymers by ATRP. Substituted aromatic and alifatic sulphonyl chlorides were shown to be

efficient initiators for ATRP and also used as initiators for the incorporation of functionalities to polystyrenes and polyacrylates. In these applications heterogeneous $\text{CuCl}(\text{Bpy})_3$ system was utilised.

Obviously, ATRP leads to the formation of monofunctional telechelics since the other chain always contains halogen due to the fast deactivation process. Therefore, α - ω - telechelics can only be prepared by transformation of the halide endgroup by means of nucleophilic substitution, free radical chemistry or electrophilic addition of catalyzed by Lewis acids. Typical example of such displacement is represented in reaction 2.33 which illustrates the reactions used to replace the halogens with azides and consequently leading to amino-functional telechelics.



Other examples of halogen atom displacement to produce alcohol, C60, epoxy, maleic anhydride, triphenylphosphine and ketone functionalized polymers. The halide displacement is particularly important to prepare bifunctional hydroxy telechelics which find application in the preparation of segmented polyester and polyurethanes. In such applications the first hydroxy group can be incorporated by using hydroxy-functional initiator derivatives. The second hydroxy group functionalization can then be achieved by direct displacement of halogen group with an amino alcohol or utilising allyl alcohol. Diols can be prepared also by coupling of monohydroxyfunctional polymeric halides. In this connection it is noteworthy to mention the recent work regarding atom transfer coupling process for the synthesis of bifunctional telechelics. Polymers monofunctionalized with aldehyde, aromatic hydroxyl, dimethyl amino groups were obtained by ATRP of styrene using functional initiators in the presence of the CuBr/bpy catalytic complex. Bifunctional telechelics with double molecular weights as compared to the starting materials, were prepared by coupling of monofunctional polymers in atom transfer radical generation conditions, in the absence of monomer, using CuBr as catalyst, tris[2-(dimethylamino)ethyl]amine (Me_6TREN) as ligand, $\text{Cu}(0)$ as reducing agent and toluene as solvent [182]. The overall process is depicted in 2.34.



2.3.2 Controlled Ring-Opening Polymerization (ROP)

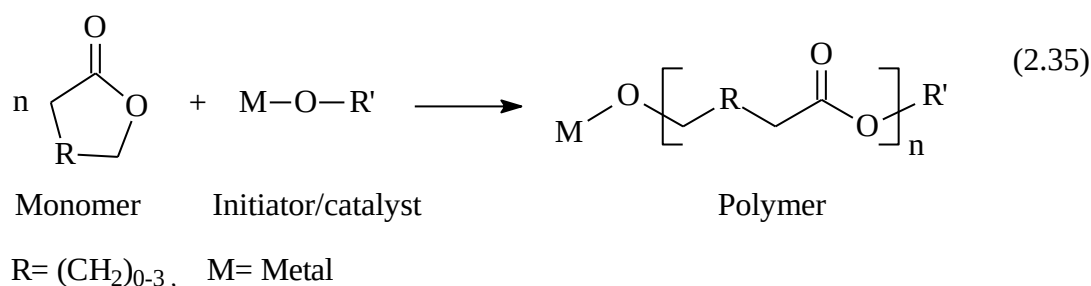
Aliphatic polyesters are an attractive class of polymers that can be used in biomedical and pharmaceutical applications. One reason for the growing interest in this type of degradable polymers is that their physical and chemical properties can be varied over a wide range by, e.g., copolymerization and macromolecular architecture techniques. The synthesis of novel polymer structures through ring-opening polymerization has been studied for a number of years. The development of macromolecules with strictly defined structures and properties, aimed at biomedical applications, leads to complex and advanced architecture and a diversification of the hydrolysable polymers.

Degradable materials with new mechanical properties and modified degradation profiles have been produced and characterized. The increasing demands of a larger number of biomedical applications have resulted in an increasing interest in producing macromolecules through controlled polymerization.

Polylactones and polylactides can be prepared by two different approaches, by the polycondensation of hydroxycarboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique is less expensive than ROP, but it is difficult to obtain high molecular weight polymers, to achieve specific end groups, and to prepare well-defined copolyesters.

2.3.2.1 Ring-Opening Polymerization of Cyclic Esters

Poly lactones and polylactides of high molecular weight are exclusively produced by the ROP of the corresponding cyclic monomers. A polyester is formed when cyclic esters are reacted with a catalyst or initiator. Reaction 2.35 presents the reaction pathway for the ROP of a cyclic ester.



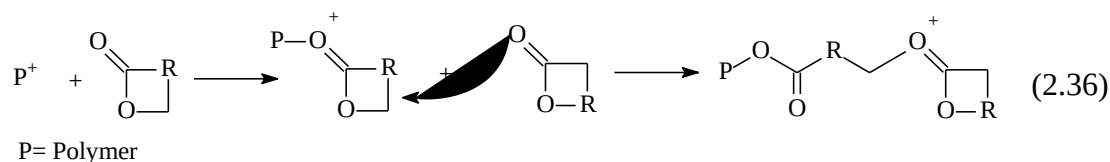
Each macromolecule formed generally contains one chain end-terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. By altering the catalyst or initiator and the termination reaction, the nature of the functional groups can be varied to fit the application of the polymer. The types of initiator and end group play important roles in determining both the thermal stability and hydrolytic stability of the resulting polyester [189]. Functional groups accessible to post-polymerization reactions can also be introduced into the polymer structure in this way.

The ring-opening reaction can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion. A catalyst or initiator is necessary to start the polymerization. Under rather mild conditions, high-molecular weight aliphatic polyesters of low polydispersity can be prepared in short periods of time. Problems associated with condensation polymerization, such as the need for exact stoichiometry, high reaction temperatures, and the removal of low molecular weight by-products (e.g., water) are excluded in ROP.

Depending on the initiator, the polymerization proceeds according to three different major reaction mechanisms [190], *via* cationic, anionic, or “coordination-insertion” mechanisms [191-193]. In addition, radical, zwitterionic [194], or active hydrogen [190] initiation is possible, although such techniques are not used to any great extent.

2.3.2.2 Cationic Ring-Opening Polymerization

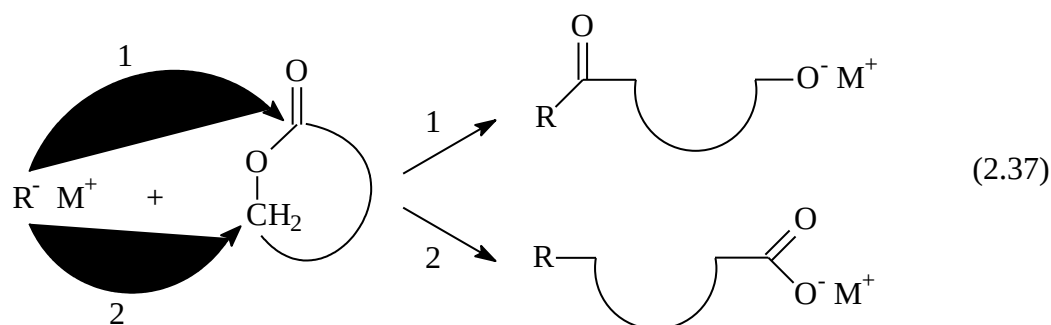
Among the cyclic esters, 4-, 6-, and 7- membered rings form polyesters when reacted with cationic catalysts [190]. The cationic ROP involves the formation of a positively charged species which is subsequently attacked by a monomer as shown in reaction 2.36. The attack results in a ring-opening of the positively charged species through an S_N2 -type process.



The cationic polymerization is difficult to control and often only low-molecular weight polymers are formed. When the bulk and solution polymerization of 1,5-dioxepan-2-one (DXO) with cationic initiators were studied, the highest molecular weight achieved was about 10,000. More detailed reviews on cationic ROP have been published by Penczek and coworkers [195,196].

2.3.2.3 Anionic Ring-Opening Polymerization

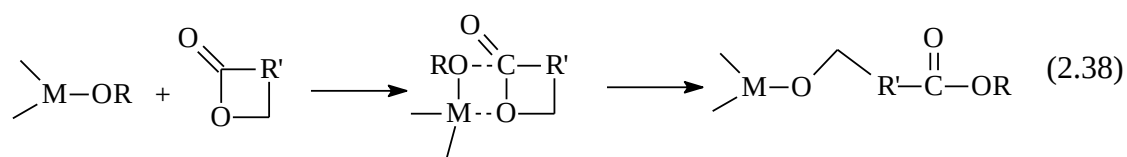
Anionic ROP of cyclic ester monomers takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon atom adjacent to the acyl oxygen, resulting in linear polyester. Reaction 2.37 shows the reaction pathway for the ROP of a cyclic ester by anionic initiation, ring-opening of monomer by 1) acyl-oxygen bond cleavage and 2) alkyl-oxygen bond cleavage [197]. The propagating species is negatively charged and is counter-balanced with a positive ion. Depending on the nature of the ionic propagating chain end and the solvent, the reacting complex varies from completely ionic to almost covalent.



One of the best controlled methods leading to high molecular weight polymers is anionic polymerization carried out in a polar solvent. The Jedlinski group developed living anionic ROP methods for 4- and 5-membered ring lactones and has reported well-defined polymers and copolymers of high molecular weight [198]. The anionic ring-opening of four-membered rings (β -lactones) occurs through alkyl-oxygen or acyl-oxygen cleavage giving a carboxylate or alkoxide. Larger lactones, such as ϵ -caprolactone (ϵ -CL) or lactide, react only by an attack of the anion on the carbonyl carbon atom with acyl-oxygen scission and the formation of an alkoxide as the growing species. A problem associated with the anionic ROP is the extensive back-biting, and in some cases only polyesters of low molecular weight are achieved.

2.3.2.4 Coordination-Insertion Ring-Opening Polymerization

The pseudo-anionic ROP is often referred to as coordination-insertion ROP, since the propagation is thought to proceed by coordination of the monomer to the active species, followed by insertion of the monomer into the metal-oxygen bond by rearrangement of the electrons [191,192]. Reaction 2.38 shows a schematic presentation of the proposed reaction pathway for the ROP of a cyclic ester by the coordination-insertion mechanism. The growing chain remains attached to the metal through an alkoxide bond during the propagation. The reaction is terminated by hydrolysis forming a hydroxy end group. With functional alkoxy-substituted initiators, macromers with end groups active in post-polymerization reactions are produced.

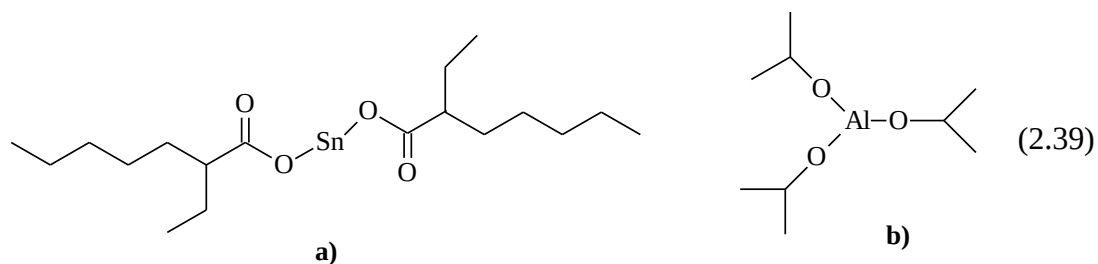


The coordination-insertion type of polymerization has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [192]. When two monomers of similar reactivity are used, block copolymers can be formed by sequential addition to the “living” system.

2.3.2.5 Initiators for the ROP of Lactones and Lactides

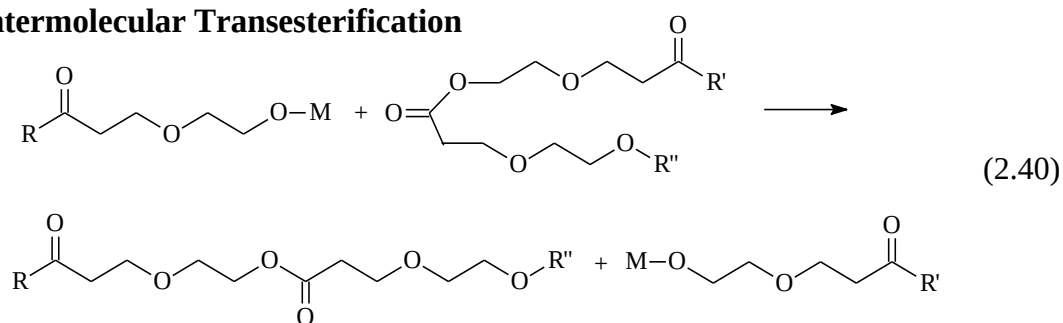
The synthesis of novel initiators and the ROP of existing or new monomers and macromers substituted with functional groups provide a very interesting and promising strategy for producing structurally advanced macromolecules.

A large variety of organometallic compounds, e.g., metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis [199]. Many reactions catalyzed by metal complexes are highly specific and, by careful selection of metal and ligands, reactions can be generated to form a desired polymer structure. The covalent metal alkoxides with free *p* or *d* orbitals react as coordination initiators and not as anionic or cationic initiators. Formulas in 2.39 show some of the most frequently used initiators and catalysts in ROP of lactones. **a)** stannous octoate and **b)** aluminum isopropoxide

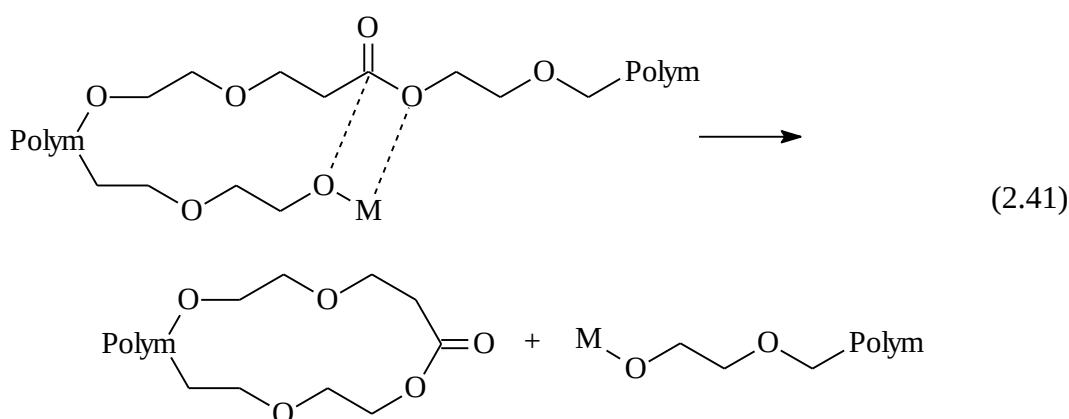


It is well known from the ROP of lactones and lactides that the catalyst or initiator causes transesterification reactions at elevated temperatures [200], or at long reaction times (reactions 2.40 and 2.41) [201].

Intermolecular Transesterification



Intramolecular Transesterification (back-biting)



Intermolecular transesterification reactions modify the sequences of copoly lactones and prevent the formation of block co-polymers. Intramolecular transesterification reactions, i.e., back-biting, cause degradation of the polymer chain and the formation of cyclic oligomers. Both types of transesterification reaction broaden the molecular weight distribution (MWD).

As displayed in the proposed scheme, each intramolecular transesterification randomly breaks the polymer chain. In this way, an attack on the polymer chain leads to a free residual polymer and a new randomized, modified polymer. Consequently, an original copolymer with a block-like structure would be converted to a randomized copolymer after undergoing n transesterifications.

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator [202]. Depending on the metal used, the initiator is more or less active towards side-reactions such as transesterification reactions [202]. The relative reactivity of different metal alkoxide initiators towards chains already formed has been reported to be:



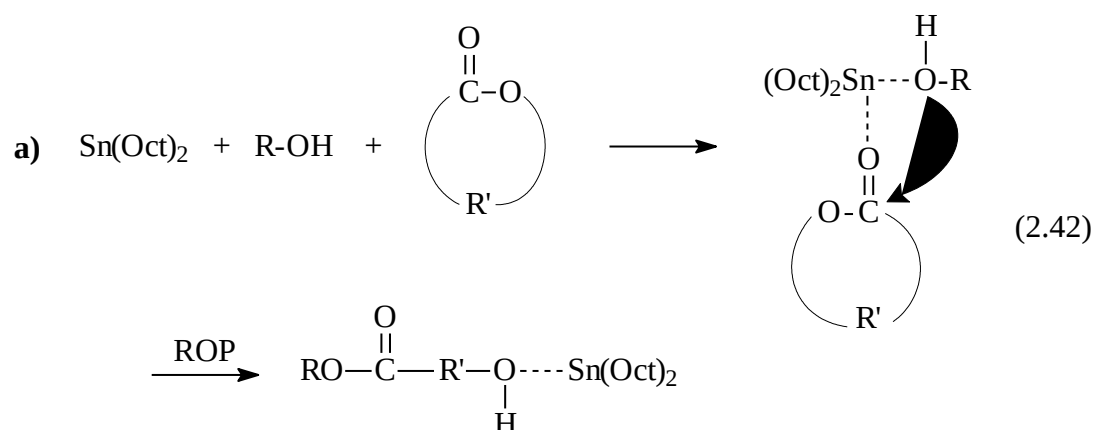
a) Tin(II) 2-Ethylhexanoate

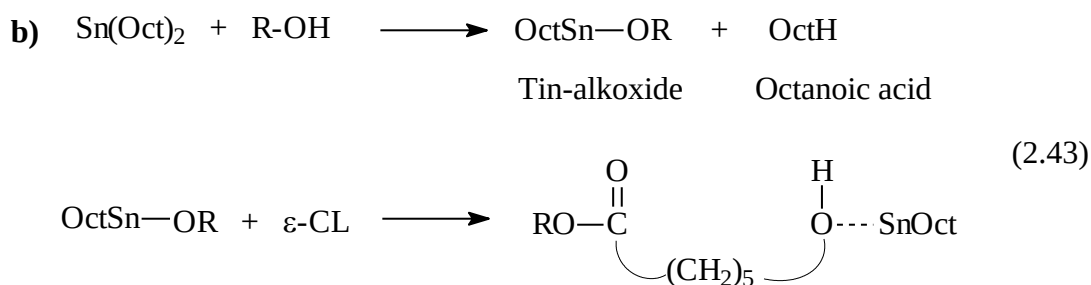
Tin(II) 2-ethylhexanoate, commonly referred to as stannous octoate $[\text{Sn}(\text{Oct})_2]$, is a frequently used catalyst in the ROP of lactones and lactides [203]. $\text{Sn}(\text{Oct})_2$ has been approved as a food additive by the American Food and Drug Administration (FDA). The mechanism of polymerization has been widely discussed. Despite several

proposals [204] over a long period of time, it is not until now that the ROP mechanism is about to be elucidated [205,206]. The $\text{Sn}(\text{Oct})_2$ is not thought to be the actual initiator since the molecular weight does not depend on the monomer-to- $\text{Sn}(\text{Oct})_2$ molar ratio. The most promising mechanism is a “coordination-insertion” mechanism where a hydroxy functional group is thought to coordinate to $\text{Sn}(\text{Oct})_2$, forming the initiating tin alkoxide complex.

Investigations of the coordination-insertion mechanism have resulted in two slightly different reaction pathways. Kricheldorf and coworkers have proposed a mechanism [206] where the co-initiating alcohol functionality and the monomer are both coordinated to the $\text{Sn}(\text{Oct})_2$ complex during propagation. Penczek and coworkers have presented a mechanism [205] where the $\text{Sn}(\text{Oct})_2$ complex is converted into a tin alkoxide before complexing and ring-opening of the monomer. Direct observation of this tin-alkoxide complex has been reported by using MALDI-TOF spectroscopy for both lactide [205] and ϵ -CL polymerization. Reactions 2.42 and 2.43 show the two different proposals. The main ROP mechanism proposals with $\text{Sn}(\text{Oct})_2$ as catalyst, **a)** complexation of a monomer and alcohol prior to ROP and **b)** formation of a tin-alkoxide before ROP of CL.

The $\text{Sn}(\text{Oct})_2$ catalyst is a strong transesterification agent, and the resulting copolymers normally have a randomized microstructure [202]. An increase in reaction temperature or reaction time increases the amount of transesterification reactions.





The ROP of lactide with $\text{Sn}(\text{Oct})_2$ is fairly slow and it is desirable for economic and commercial reasons to increase the rate of polymerization. The addition of an equimolar amount of triphenylphosphine increases the rate and, as an additional advantage, this compound delays the occurrence of the undesirable back-biting reactions.

b) Aluminum Tri-Isopropoxide

ROP initiated with aluminum tri-isopropoxide has been extensively investigated by several research groups since it yields well-defined polymers through living polymerization [207]. A living polymerization is a chain polymerization which proceeds in the absence of the kinetic steps of termination or chain transfer [207].

Polymerization with aluminum tri-isopropoxide is assumed to proceed through a “coordination-insertion” mechanism, which consists of monomer complexation to the active species and insertion by rearrangement of the covalent bonds. The mechanism leads to cleavage of the acyl-oxygen bond of the monomer and of the metal-oxygen bond of the propagating species. The propagation is characterized by the almost total absence of side-reactions such as transesterification reactions, at least until complete monomer conversion has occurred. The initiator is active at low temperatures (reaction temperatures of 0 –25 °C are often reported) and the initiator is preferentially used in solution polymerization.

c) Tin(IV) Alkoxides

Monotin alkoxides, tin dialkoxides and cyclic tin alkoxides have been utilized as initiators in the ROP of cyclic esters. The tin alkoxides are known to form cyclic species during synthesis and the dibutyltin alkoxides are known to exist as monomers and dimers. The cyclic tin alkoxides were originally studied because of their

resistance towards hydrolysis. The tin alkoxides have been reported to be effective transesterification catalysts initiating polymerization at moderate temperatures [208].

The tributyl derivatives have been thoroughly studied since they are easily synthesized by nucleophilic substitution of commercial tributyltin chloride, they are easy to handle due to their moisture resistance, and they are relatively soluble in lactones.

The polymerization of lactones with tin alkoxides is thought to follow the “coordination-insertion” mechanism. The ring-opening of the monomer proceeds through acyl-oxygen cleavage with retention of the configuration. Tin(IV) complexes have been used to produce predominantly syndiotactic poly(b-hydroxybutyrate), macrocyclic poly(b-hydroxybutyrate), poly(ϵ -CL), and polylactide [8]. The cyclic tin alkoxides have the additional advantage of offering a convenient synthetic pathway for the synthesis of macromers, triblock, and multiblock copolymers.

d) Tin(II) Alkoxides

Recently, tin(II) butoxide was used in the polymerization of L,L-lactide [209]. The initiation is fast and quantitative and no transesterification or back-biting reactions are observed. The reaction proceeds with acyl-oxygen bond scission with retention of the configuration, and can be used both in bulk and solution (THF, 20–80 °C) polymerization. It is possible to control the molecular weight in the range of 10^3 to 10^6 with a MWD of 1.15–1.85. The polymerization is very fast, $k_p = 5 \times 10^{-1} \text{ mol}^{-1} \text{ L s}^{-1}$, with only the rare earth alkoxides being faster.

e) Lanthanide Alkoxides

ROP of lactones and lactides using lanthanide alkoxide-based initiators is a relatively recent discovery. The first example of lactones polymerization by lanthanide alkoxide complexes was reported in a DuPont patent written by McLain and Drysdale in 1991 [210].

In general, the activity of these catalysts is much higher than that determined for aluminum alkoxides, especially in lactide polymerization. Polymers of relatively

high molecular weight and narrow MWD are formed. The negative side-reactions such as macrocycle formation, transesterification, and racemization are absent.

Yttrium isopropoxide and yttrium 3-oxapentoxide initiators were the first lanthanide alkoxides described in the literature for the ROP of ϵ -CL [211]. The discovery of lanthanide-based initiator systems allowed the block copolymerization of ϵ -CL with compounds such as ethylene, tetrahydrofuran, L-LA, trimethylene carbonate, and methyl methacrylate. This type of initiator has also been used to prepare poly(b - butyrolactone)s.

2.3.3 Poly(ϵ -Caprolactone) and Copolymers

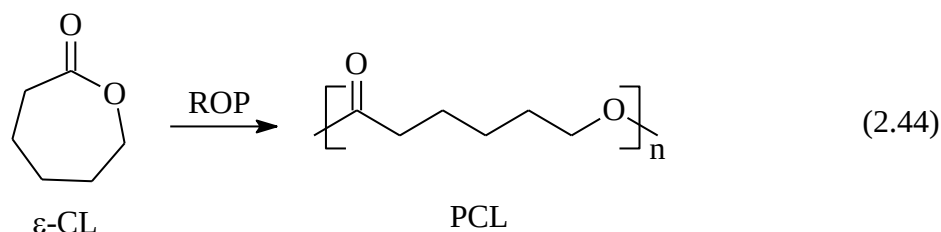
Poly(ϵ -caprolactone) (PCL) is a semi crystalline, biodegradable polymer having a melting point (T_m) of $\sim 60^\circ\text{C}$ and a glass transition temperature (T_g) of $\sim -60^\circ\text{C}$. The repeating molecular structure of PCL homopolymer consists of five non-polar methylene groups and a single relatively polar ester group. This structure gives PCL some unique properties. The mechanical properties are similar to polyolefin because of its high olefinic content, while the presence of the hydrolytically unstable aliphatic-ester linkage causes the polymer to be biodegradable. This combination also gives PCL the unusual property of being compatible with numerous other polymers and PCL has the possibility of blending this aliphatic polyester with a number of commercial polymers such as PVC and bisphenol A polycarbonate. It is of interest as a packaging material and in biomedical applications since it is degradable and its degradation products are non-toxic. In comparison to the other commercially available absorbable materials, PCL is one of the most flexible and easy to process. PCL homopolymers have processing characteristics which are very similar to polyolefins with the exception that the overall processing temperatures are somewhat lower. While the possible range of conditions is actually quite large, injection molded articles can be made. PCL may also be extruded into various profiles and can also be drawn into fibers having tensile strengths of over 60,000 psi and with an elongation of 20-30% [212].

2.3.3.1 Polymerization of ϵ -Caprolactone and copolymers of ϵ -Caprolactone

High molecular weight polymers and copolymers of ϵ -caprolactone are prepared by ring-opening, addition polymerization over a wide range of temperatures. Copolymers can also be prepared with a variety of other lactones, lactides [213] and lactams. In making copolymers, attention to monomer reactivity differences is important and depending on the specific conditions for copolymerization wide differences in copolymer microstructure (sequencing) are possible.

Polymerization temperatures in the range of 140-150°C are typical. The polymerization is normally catalyzed by stannous 2-ethyl hexanoate (stannous octoate) or stannic chloride dihydrate. Other catalysts which have been used include various Lewis acids, alkyl metals and organic acids [214]. Molecular weight is controlled by addition of chain control agents. These chain control agents are usually water, primary alcohols, amines or some other active hydrogen compound. For example, linear polymers can be prepared using alcohols having functionalities less than or equal to two, such as 1-dodecanol or 1,6-hexanediol.

While PCL and its copolymers are subject to biodegradation because of the susceptibility of its aliphatic ester linkage to hydrolysis, biodegradation of the PCL homopolymer is considerably slower than the poly(α -hydroxy acids) such as polylactide because of the combination of its crystallinity and high olefinic character. On the other hand, copolymers with lactides and blends with other degradable polymers and copolymers reduce overall crystallinity increasing the accessibility of ester linkage, and thus significantly enhance the rate of hydrolysis. Therefore, PCL copolymers and polyblends can be prepared having a wide range of physical and mechanical properties with varying rates of biodegradation. The synthesis of PCL is shown in reaction 2.44.



2.3.3.2 Degradation of PCL

The PCL material has a long degradation time, which is usually a disadvantage in medical applications. The *in vivo* degradation of poly(D-LA) was 2.8 times faster than that of the PCL chain cleavage under the same conditions. Different approaches have been used to copolymerize ϵ -CL to increase the degradation rate. Copolymers of ϵ -CL and D-LA of all compositions degraded much more rapidly than their component homopolymers. This observation has been attributed to morphological differences, specifically a reduction in crystallinity and a lowering of the glass transition temperature.

The *in-vitro* and *in-vivo* degradation characteristics of PCL have been characterized by Pitt and coworkers [215]. The authors found the two hydrolytic rates of degradation were essentially similar and concluded that enzymatic involvement was not a factor in the degradation process. The study also reported the observation that the chain scission of PCL was not accompanied by the loss of low molecular weight PCL fragments until the molecular weight had decreased to around 5,000.

Woodward and others [216] have extensively studied the intracellular degradation of PCL. Their work provides perhaps the most comprehensive details on the biocompatibility of PCL throughout the degradation process using an animal model (Sprague-dawley rats). During the first stage (nonenzymatic bulk hydrolysis) the implant became encapsulated by collagen filaments containing only occasional giant cells. After nine months, when the molecular weight decreased to about 5,000, the second stage of the degradation process was observed. During this second stage, the rate of chain scission slowed, the hydrolytic process began to produce short chain oligomers, and weight loss was observed. The authors concluded that intracellular degradation was the primary degradative pathway for the absorption of PCL.

More recently, hydroxyl free radicals have been implicated as a major factor in the degradation of PCL [217,218]. In addition, certain bacteria, yeast and fungi have been shown to possess the ability to degrade PCL.

2.3.3.3 Applications of PCL

Copolymers of PCL with other comonomers (such as glycolide, lactide and 1,5-dioxepan-2-one and blends of PCL with other polymers (such as polyhydroxyvalerate and polyhydroxybutyrate) have been the subject of numerous papers and patents. Applications include suture coatings [219], as well as wide variety of absorbable medical devices, including microporous intravascular stents, as a support to autologous vein grafts [220].

In addition to the above, PCL and other copolymers have been evaluated for other medical uses such as drug delivery systems, an external casting material for broken bones, as a material for use in making custom dental impression trays.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St) (Aldrich)

It was first washed with 5% aq. NaOH solution in order to to remove inhibitors, and then washed with water. It was dried with calcium chloride (CaCl_2) several hours and distilled over calcium hydride (CaH_2) at reduced pressure.

ϵ -Caprolactone (CL) (Aldrich)

It was vacuum distilled over CaH_2 just before use.

3.1.2 Solvents

Diethyl ether (J.T. Baker)

It was dried with CaCl_2 and distilled over sodium wire.

Dichloromethane (J.T. Baker)

It was first washed with conc. H_2SO_4 until the acid layer remained colorless, and then with water, followed by another washing with 5% NaOH (aq.) and finally with water again. It was dried with CaCl_2 and distilled over CaH_2 . It was stored over molecular sieves for use as a solvent in the experiments.

Tetrahydrofuran (THF) (J.T. Baker)

It was dried over potassium hydroxide, distilled over sodium wire, and finally distilled over sodium/benzophenone ketyl.

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

Chloroform (CCl₃) (J.T. Baker)

It was used as received.

Carbontetrachloride (CCl₄) (J.T. Baker)

It was used as received.

Dimethylacetamid(DMAc) (Aldrich)

It was distilled and stored over molecular sieves for use as a solvent in the experiments.

3.1.3 Other Chemicals **α -Bromo-p-toluic acid (Acros)**

It was used without further purification.

2,5-Dibromotoluene (Aldrich)

It was used as received.

3,5-Dibromotoluene (Aldrich)

It was used as received.

Sodium Borohydride (NaBH₄) (Merck)

It was used without further purification.

Copper (I) Bromide (CuBr) (Aldrich)

It was used as received.

2,2-Bipyridine (bpy) (Merck)

It was used as a ligand for ATRP without further purification.

Thionyl chloride (Fluka)

It was distilled over calcium hydride prior to use.

Triethylamine (TEA) (J.T. Baker)

It was distilled over calcium hydride before use.

***p*-xylene (Aldrich)**

It was used as received.

Acetic acid (Aldrich)

It was used without further purification.

Acetic anhydride (Aldrich)

It was used as received.

***N*-Bromosuccinimide, 99% (NBS) (Acros)**

It was used directly.

Triphenylphosphine (PPh₃) (Fluka)

It was used as received.

Pd(PPh₃)₄ (Aldrich)

It was used as a catalyst in Suzuki coupling reactions without further purification.

Tin octoate Sn(Oct)₂ (Sigma)

It was used as an initiator in Ring Opening Polymerization of ϵ -caprolactone as received.

Nickel(II) Chloride (Merck)

It was used as a catalyst in Yamamoto coupling reactions without further purification.

Zn (Merck)

It was used as a catalyst in Yamamoto coupling reactions without further purification.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H -NMR and ^{13}C -NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer using CDCl_3 as a solvent and tetramethylsilane as an internal standart.

3.2.2 Elemental Analysis

Elemental analyses were carried out using a CHNS-932 (LECO) instrument.

3.2.3 Infrared Spectrophotometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.4 UV-visible Spectrophotometer

UV analyses were performed on a Lambda 2 Perkin Elmer Spectrometer from CH_2Cl_2 solutions with the same concentration ($0.044 \text{ g}\cdot\text{L}^{-1}$).

3.2.5 Gel Permeation Chromatography (G.P.C)

GPC measurements were performed with an Agilent1100 RI apparatus equipped with three Waters Styragel columns HR series (4, 3, 2 narrow bore), at a flow rate of

0.3 mL/min and the temperature of the refractive index detector of 30⁰C, and THF as eluent. Molecular weights were calculated using polystyrene standards.

3.2.6 Differential Scanning Calorimeter (D.S.C)

DSC analyses were performed on a Perkin Elmer Differential Scanning Calorimeter DSC-6, in the range 30-300⁰C, under nitrogen, with a scan rate of 10⁰C/min.

3.2.7 Thermogravimetric Analyzer (TGA)

Thermogravimetric data were obtained using a Shimadzu Thermogravimetric Analyzer TGA-50, between 30-600 ⁰C, under nitrogen, with a scan rate of 10⁰C/min.

3.2.8 Fluorescence Spectrometer

Fluorescence measurements were performed using the model LS-50 spectrometer of Perkin&Elmer by using chloroform solutions of the same concentration (0.025g/L).

3.2.9 Atomic Force Microscopy (AFM)

Morphology of polymers in thin films was characterized by NT-MDT Solver P47 AFM in tapping mode.

3.2.10 Ellipsometer

Film thicknesses were measured by Microphotronics ELX-01R Ellipsometer using 632.8 nm laser light at 70⁰ angle.

3.3 Preparation Methods

3.3.1 Synthesis of Initiator for Ring Opening Polymerization (ROP)

3.3.1.1 Synthesis of 1,4-Dibromo-2,5-dimethylbenzene

1,4-dibromo-2,5-dimethylbenzene was obtained by dibromination of *p*-xylene at 2,5-positions with Br₂.

¹H-NMR (**1**) (CDCl₃) (δ, ppm): 7.35 (s, 2H, aromatic), 2.30 (s, 6H, CH₃).

3.3.1.2 Synthesis of 2,5-Dibromoterephthaldehyde

2,5-dibromoterephthaldehyde was obtained by oxidation of *1,4-dibromo-2,5-dimethylbenzene*, in two steps, following a literature [221] procedure: A. 10g (0.0378 mol) of *1,4-dibromo-2,5-dimethylbenzene* was suspended in a mixture of 50 mL of acetic acid and 100 mL of acetic anhydride. 35mL of sulfuric acid was added dropwise at the suspension, maintaining the temperature at 0°C. 21g (0.21 mol) of CrO₃ was added in portions, so the temperature of the reaction mixture didn't exceeded 10°C. The stirring was maintained another 5 hours at 0°C. The greenish slurry was poured into ice water and filtered. The crude diacetate was washed with large amounts of water and finally with cold methanol and is pure enough for the next step. m.p. (DSC): 166-167°C.

¹H-NMR (CDCl₃) (δ, ppm): 7.82 (s, 2H, Ar), 7.72 (s, 2H, Ar-CH-), 2.14 (s, 12H, CH₃).

B. The diacetate was hydrolyzed by refluxing with a mixture of 50 mL ethanol, 50 mL of water and 5mL of sulfuric acid for 5 hours. After cooling, the pale yellow product was separated by filtration and washed with water. The purification was performed by chromatography through a silicagel column using dichloromethane as eluent and two times recrystallization from chloroform, resulting 4.964 g (Yield 45%) yellowish crystals. M.p. (DSC): 190-191°C

¹H-NMR (**2**) (CDCl₃) (δ, ppm): 10.32 (s, 2H, CHO), 8.13 (s, 2H, Ar)

IR (cm⁻¹): 1678 (CHO)

Anal. (C₈H₄Br₂O₂) Calc. C 32.92; H 1.38;

Found C 32.85; H 1.56

3.3.1.3 Synthesis of 2,5-Dibromo-1,4-(dihydroxymethyl)benzene

2,5-Dibromo-1,4-(dihydroxymethyl)benzene was synthesized by reduction of 2,5-Dibromoterephthaldehyde with sodium borohydride:

2,5-dibromoterephthaldehyde (1.38g, 4.72 mmol), and 5 mL of methanol were introduced into a 100 mL round bottom flask equipped with magnetic stirrer, condenser and dropping funnel. 1.512 (40 mmol) NaBH₄ dissolved in 10 mL methanol were added slowly. The mixture was heated to reflux, for 2h, than stirred at room temperature over the night. Than the content of the flask was poured into cold water/HCl (10/1, v/v) and the solution was extracted several times with diethyl ether. The organic solutions were mixed, dried over MgSO₄, and the solvent partially removed at rotaevaporator. Than the concentrated solution was passed through a silicagel column. Final recrystallization from benzene provided a white solid product, m.p. (DSC) = 217-218 °C (yield 92%).

¹H-NMR (**3**) (acetone-d₆) (δ, ppm): 7.74 (s, 2H, Ar), 4.65 (s, 4H, CH₂), 3.29 (s, 2H, OH)

IR (cm⁻¹): 3350 (OH), the peak from 1678 (CHO) from the spectrum of **2** is not present

Anal. (C₈H₈Br₂O₂) Calc. C 32.47; H 2.72;

Found C 32.61; H 2.93

3.3.2 Synthesis of ATRP Initiators

3.3.2.1 Synthesis of 1,4-Dibromo-2-(bromomethyl)benzene

1,4-dibromo-2-(bromomethyl)benzene were prepared by bromination of methyl groups of 3,5-dibromotoluene using N-bromosuccinimide (NBS) in CCl₄.

6.2g (0.0248mol, 4.63g (0.26 mol) N-bromosuccinimide and 0.1g benzoyl peroxide were dissolved in 20mL CCl₄. The solution was maintained at reflux temperature for 4 h. After that time the solution was filtered. The succinimide was washed with a supplementary amount of CCl₄ and finally with a little quantity of CH₂Cl₂. The combined organic solutions were washed several times with water and then dried over MgSO₄. The solvent was removed by rotary evaporator. The product was purified by passing through a silicagel column using diethyl ether as eluent. Finally, the product was obtained as white crystals after recrystallizing twice from petroleum ether.

¹H-NMR (CDCl₃): δ = 7.58 (s, 1H, ArH -3-position), 7.43-7.40 (d, 1H, ArH -5 position), 7.28-7.26 (d, 1H, ArH -6 position), 4.51 (s, 2H, CH₂Br); m.p. (DSC): 94-95°C.

UV (ϵ , L/mol·cm): 216 nm (8400), 235 nm (26100), 284 nm (3700)

Anal. (C₇H₅Br₃) Calc. C 25.57; H 1.53

Found C 25.63; H 1.73

3.3.2.2 Synthesis of 1,3-Dibromo-5-(bromomethyl)benzene

1,3-dibromo-5-(bromomethyl)benzene was prepared in a similar way with 1,4-Dibromo-2-(bromomethyl)benzene from 3,5-dibromotoluene.

¹H-NMR (CDCl₃): δ = 7.58 (s, 1H, ArH -5-position), 7.45 (s, 2H, ArH- 4 and 6 positions), 4.34 (s, 2H, CH₂Br), white crystals, m.p (DSC): 97-98°C

UV (ϵ , L/mol·cm): 232 nm (63500), 281 nm (8900)

Anal. (C₇H₅Br₃) Calc. C 25.57; H 1.53

Found C 25.32; H 1.66

3.3.3 Synthesis of Macromonomers

3.3.3.1 General Procedure for ROP of ϵ -Caprolactone

Appropriate amounts of monomer (ϵ -caprolactone, CL), stannous octoate and bifunctional initiator 2,5-Dibromo-1,4-(dihydroxymethyl)benzene were added under nitrogen in previously flamed and nitrogen-purged Schlenk tubes equipped with magnetic stirrer. The CL polymerizations were carried out in bulk at 110°C. After 24h the mixtures were diluted with CH₂Cl₂ and poured into ten-fold excess of cold methanol. The polymers were collected after filtration and dried at room temperature in vacuum for three days.

IR (cm⁻¹): 3420 (OH), 1720 (broad, C=O)

3.3.3.2 General Procedure for the ATRP Reactions

A round bottom-flask equipped with magnetic stirrer and a lateral neck with a tap was used. The system was vacuumed and back-filled with dry nitrogen several times. A catalyst (CuBr), a ligand bipyridine (bpy), an initiator (1,4-dibromo-2-(bromomethyl)benzene or 1,3-dibromo-5-(bromomethyl)benzene and styrene were added under an inert atmosphere. The flask was placed in an oil bath warmed at 110°C and was stirred at that temperature for a given time, the mixture was diluted with THF and poured into ten-fold methanol. The solid was collected after filtration and drying at 40°C in a vacuo overnight. The polymers were purified by passing through a silicagel column using THF as eluent and reprecipitating into methanol.

3.3.3.3 Synthesis of Block Copolymer Type Macromonomer

3.3.3.3a. Synthesis of 4-Bromomethyl-1-benzenecarbonyl Chloride

α -Bromo-*p*-toluic acid (16.128g, 0.075mol) and 80 mL of thionyl chloride were refluxed for 12h. Thionyl chloride was removed by distillation under reduced pressure and the remained redish liquid was extracted several times with dry hexane. The solution was concentrated and 4-(bromomethyl)-1-benzenecarbonyl chloride was formed upon cooling as pale yellow crystals. A second recrystallization from hexane yielded the pure product as white crystals (63% yield). m.p (DSC): 33-34°C.

$^1\text{H-NMR}$ (CDCl_3) (δ , ppm): 8.12-8.11 (d, 2H, Ar *ortho* to CO), 8.09-8.06 (d, 2H, Ar *ortho* to CH_2), 4.63 (s, 2H, CH_2Br).

$^{13}\text{C-NMR}$ (CDCl_3) (δ , ppm): 167.32 (C=O), 147.93 ($\text{C}_{\text{Ar}}-\text{CH}_2$), 133.87 ($\text{C}_{\text{Ar}}-\text{CO}$), 132.89 (C_{Ar} *ortho* to CO), 132.16 (C_{Ar} *ortho* to CH_2), 33.65 (CH_2).

IR (cm^{-1}): 1772 and 1740 (C=O).

Anal. $\text{C}_8\text{H}_6\text{BrClO}$ Calc. C 41.15; H 2.59;

Found C 41.73; H 1.94

3.3.3.3b. Synthesis of PCL With Benzyl Bromine End-Groups

The PCL macromonomer, (1.5 g, 0.49 mmol), 5 mL dry CH_2Cl_2 and triethylamine (TEA) (0.219g, 21.6 mmol) were added into an 50 mL three-necked round bottom flask fitted with a condenser, a magnetic stirrer, nitrogen inlet-outlet, and an addition funnel containing 4-(bromomethyl)-1-benzenecarbonyl chloride (0.8563g, 3.6 mmol) and 3 mL CH_2Cl_2 mixture. The flask was placed in an ice-water bath. The solution of 4-(bromomethyl)-1-benzenecarbonyl chloride was added dropwise over a period of 1h under nitrogen. Then the mixture was allowed to reach room temperature, and stirred at that temperature for two days. The polymer was precipitated in cold methanol/HCl (10/1 v/v), filtered and washed with big amounts of water and finally with methanol. A second reprecipitation in methanol using CH_2Cl_2 as solvent was performed.

3.3.3.3c. Synthesis of PCL-b-PSt Macromonomer by Transforming ROP in ATRP

A round bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst (CuBr, 0.0631g, 0.44 mmol), ligand bipyridine (bpy, 0.2061g, 1.32 mmol), initiator (PCL with benzylbromine end groups, 0.726g, 0.22mmol) and styrene (St, 2mL) were introduced under inert atmosphere. The flask was placed in an oil bath warmed at 110°C and stirred at that temperature. After 40 min, the mixture was diluted with THF and poured into ten-fold methanol. The solid was collected after filtration and drying at 40°C in a vacuum overnight. The polymer was purified by passing through a silicagel column using THF as eluent and reprecipitation into methanol.

3.3.4 Synthesis of Polyphenylenes by Suzuki and Yamamoto Coupling Methods by Using Macromonomers

3.3.4.1 Synthesis of PPP With Alternating PCL and Hexyl Side Chains by Suzuki Coupling

An 100 ml three neck round bottom flask equipped with a condenser, a rubber septum, nitrogen inlet-outlet, and magnetic stirrer, was charged with 20 mL 1M NaHCO₃ aqueous solution and 30 mL of THF. The solvents were previously degassed by bubbling nitrogen over a period of 30 minutes. The mixture was refluxed under nitrogen, 4 hours, than it was let to arrive at room temperature.

A 20 ml three necks round bottom flask equipped in the same way as the previous one was charged under inert atmosphere 0.4575 g (0.15 mmol) PCL (Table 1), 0.0501g (0.15 mmol) 2,5-dihexylbenzene-1,4-diboronic acid and 0.0026 g (0.00225 mmol) Pd(PPh₃)₄. 1.2 mL of the mixture of solvents was introduced with a syringe through the septum. The reaction was maintained at reflux under vigorous stirring and with the exclusion of oxygen and light. After 24h a supplementary 1 mL of the mixture of solvents was added. After 48h the polymer was obtained by precipitation in methanol. Reprecipitation from THF solution provided a white powder (yield 83 %). ($M_{n, GPC} = 38700$, $M_w/M_n = 1.7$)

3.3.4.2 Synthesis of PPP With PCL Side Chains by Yamamoto Coupling

A 20 ml three necked round bottom flask equipped with condenser, rubber septum, nitrogen inlet-outlet and magnetic stirrer was charged under nitrogen with 0.75g (0.13mmol) **4B**, 0.0033g (0.0125 mmol) PPh_3 , 0.0253g (0.3875 mmol) Zn, 0.001g (0.006mmol) bpy, 0.0008g (0.0063 mmol) NiCl_2 and 0.6 mL of dry dimethyl acetamide. The reaction was performed at 85°C, under nitrogen. After several minutes the color of the solution changed to brown, due to the complex formation. The mixture was stirred at the above-mentioned temperature for 24 hours. Then the polymer was precipitated in a high amount of methanol/HCl mixture (v/v = 9/1), filtered and dried. The polymer was then redissolved in THF, passed through a silicagel column and precipitated in methanol. A white powder (yield 78%) was obtained ($M_{n, \text{GPC}} = 27150$, $M_w/M_n = 1.41$).

3.3.4.3 General Procedure for Suzuki Coupling of Bromine Containing Polystyrene With 2,5-Dihexylbenzene-1,4-diboronic acid

A 100 ml three neck round bottom flask equipped with a condenser, a septum, nitrogen inlet-outlet, and magnetic stirrer, was charged with 20 mL 1M NaHCO_3 solution and 30 mL of THF. The solvents were previously degassed by bubbling nitrogen over a period of 30 minutes. The mixture was refluxed under nitrogen, for 4 hours.

A 20 ml three necks round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with (0.2 mmol) polystyrene (11 and 12), 0.0668g (0.2 mmol) diboronic acid and 0.0035g (0.003 mmol) $\text{Pd}(\text{PPh}_3)_4$. The mixture of solvents (1.8 mL) was introduced with a syringe through the septum. The reaction was maintained under vigorous stirring and with the exclusion of oxygen and light. After 12h a supplementary 1 mL of the mixture of solvents was added. After 3 days the polymer was obtained by precipitation in methanol. The product was filtrated, washed several times with water, dried and than extracted with THF. After concentrating the THF solutions, the polymers were obtained by precipitating in methanol as white powders.

3.3.4.4 Synthesis of PP With Polystyrene Side Chains by Yamamoto Coupling

A 20 ml three necked round bottom flask equipped with condenser, rubber septum, nitrogen inlet-outlet and magnetic stirrer was charged under nitrogen with 0.13 mmol of **PSt**, 0.0033g (0.0125 mmol) PPh_3 , 0.0253g (0.3875 mmol) Zn , 0.001g (0.006mmol) bpy , 0.0008g (0.0063 mmol) NiCl_2 and 0.6 mL of dry dimethyl acetamide. The reaction was performed at 85°C, under nitrogen. After several minutes the color of the solution changed to brown, due to the complex formation. The mixture was stirred at the above-mentioned temperature for 3 days. Then the polymer was precipitated in a high amount of methanol/HCl mixture (v/v = 9/1), filtered and dried. The polymer was then redissolved in THF, passed through a silicagel column and precipitated in methanol.

3.3.4.5 Synthesis of PP With Polystyrene/poly(ϵ -caprolactone) Side Chains by Yamamoto Coupling

The procedure was similar with that described above except that 0.065 mmol of **PSt** and 0.065 mmol of **PCL** were added to the reaction as comonomers.

3.3.4.6 Suzuki Coupling of PCL-b-PSt With 2,5-Dihexyl-1,4-diboronic acid

The procedure was similar with that described previously for Suzuki coupling except that 0.1 mmol of PCL-b-PSt, 0.1 mmol of 2,5-dihexyl-1,4-diboronic acid and 0.0015mmol of $\text{Pd}(\text{PPh}_3)_4$ with 1ml mixture of solvents were added to the reaction.

4. RESULTS and DISCUSSION

4.1 Synthesis of Poly(p-phenylene)-graft-poly(ϵ -caprolactone) Copolymers

Dual functional initiators having both bromine benzyl groups useful for ROP of ϵ -CL or ATRP of styrene and bromine atoms or boronic acid functionalities directly linked to a benzene ring, useful for Suzuki or Yamamoto type reactions were synthesized.

4.1.1 Preparation of Bifunctional Initiator for ROP

The polymerization of ϵ -CL can be initiated using hydroxymethyl functionalites [24, 222-230]. 2,5-Dibromo-1,4-(dihydroxymethyl)benzene (**3**) was prepared following the reaction pathways showed in 4.1. ^1H -NMR of initiator is given in Figure 4.1.

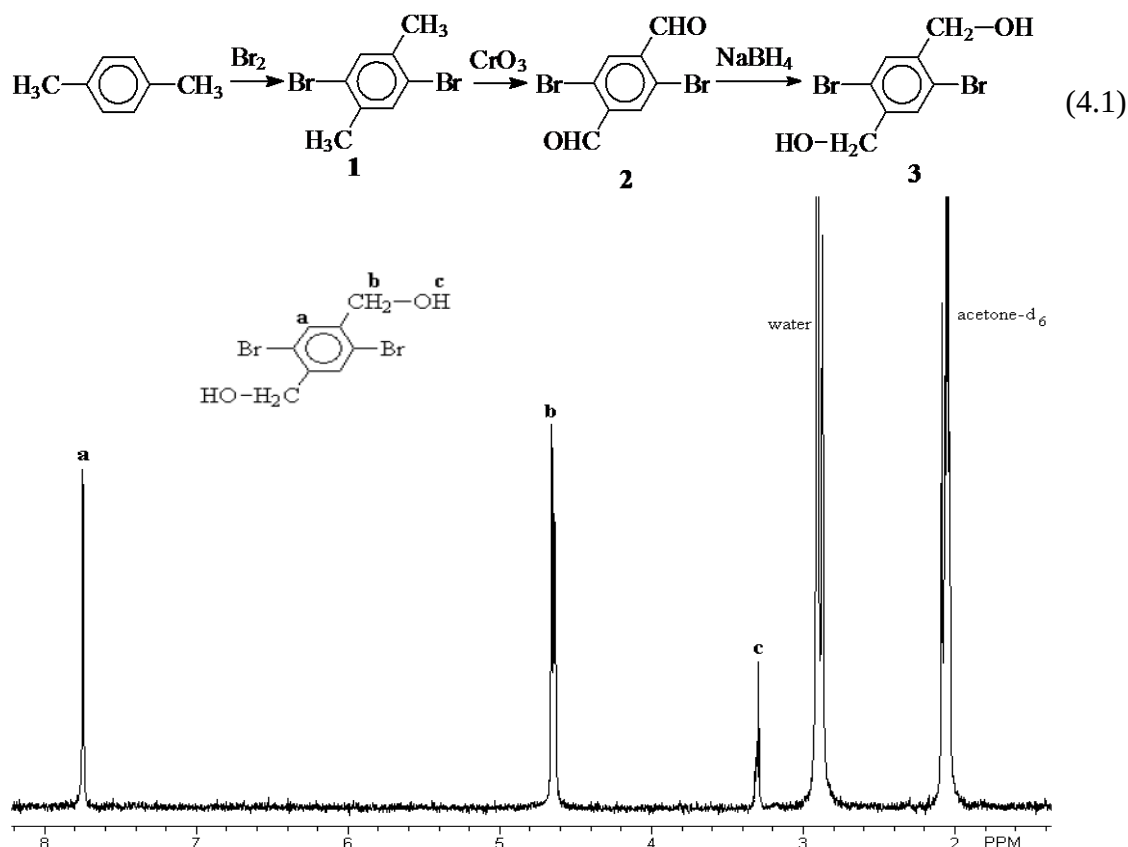


Figure 4.1 : ^1H -NMR spectrum of 2,5-Dibromo-1,4-(dihydroxymethyl)benzene (**3**)

4.1.2 Preparation of Poly(ϵ -CL) Macromonomer by ROP for Suzuki and Yamamoto Methods

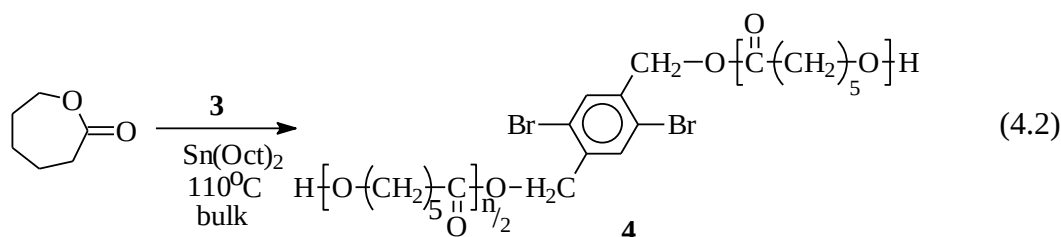
The ROP of ϵ -CL using the initiator above was performed in bulk, in the presence of $\text{Sn}(\text{Oct})_2$ catalyst. In view of the reported role of hydroxyl groups as initiators of the ROP, this reaction was expected to produce polymers containing a 2,5-dibromo-1,4-benzene ring on the middle of the chain (reaction 4.2), derived from the structure of bifunctional initiator 3. Some results of the polymerization are given in Table 4.1.

Table 4.1 : Conditions and results of ROP of ϵ -caprolactone^a

PCL	[CL]/[3] (molar ratio)	M_{nHNMNR}	$M_{\text{nGPC}}^{\text{b}}$	PDI^{b}
4A	40	6000	7722	1.36
4B	20	3050	4270	1.12

^aT=110°C, bulk, 24h, $[\text{OH}]/[\text{Sn}(\text{Oct})_2] = 200/1$ (molar ratio).

^bDetermined by GPC using PSt standards.



As this polymer was intended to be used in further polymerization reactions, the efforts were directed toward obtaining a low molecular weight combined with a low polydispersity. Molecular weights were evaluated both from GPC analysis and ¹H-NMR spectra. Polymerization degrees (50 for **4A** and 24 for **4B**) correspond to the molecular weights indicated in Table 4.1.

Usually determining more precise the molecular weight for PCL a correction formula is used in the literature [231] :

$$M_{\text{nPCL}} = 0.259M_{\text{nGPC}}^{1.073} \quad (1)$$

where M_{nGPC} is the molecular weight determined from GPC using PSt standards.

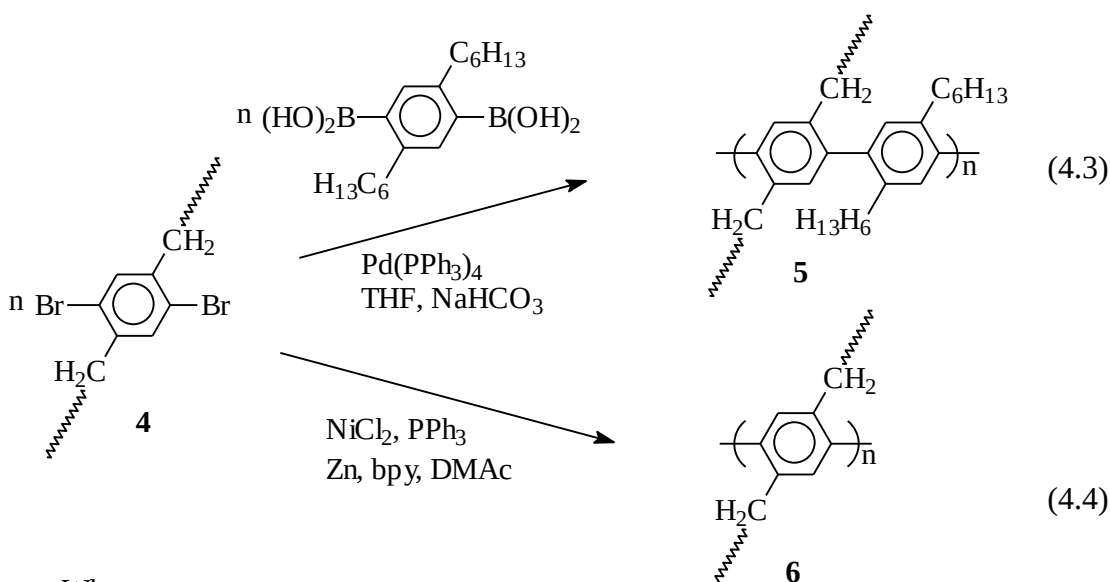
Applying this formula to the GPC values from Table 4.1, molecular weights as 3844 for **4A** and 2036 for **4B** are obtained. The values of molecular weights calculated

from ^1H -NMR spectra were considered to be more reliable and used for further calculations.

PCL **4B** with both lower molecular weight and polydispersity was chosen as macromonomer for transition metal mediated cross-coupling reactions for grafted PPPs syntheses. PCL **4B** macromonomer will be named as **4** in the following steps.

4.1.3 Preparation of PPPs by Suzuki and Yamamoto Methods

The cross-coupling of aryl halides and aryl boronic acids (Suzuki coupling) [8] is one of the most common methods for the synthesis of polyarylenes. Synthesis of PCL grafted PPP by Suzuki (**5**) or Yamamoto (**6**) methods can be seen in reactions 4.3 and 4.4.



In our case the PCL macromonomer **4** was polymerized in combination with 2,5-dihexylbenzene-1,4-diboronic acid and furnished a polymer **5** with $M_{n, \text{GPC}} = 38700$, $M_w/M_n = 1.7$. The ^1H -NMR spectrum of this polymer (Figure 4.2) shows clearly the presence of hexyl groups in the composition of the polymer (**p**, **o** and **q** protons), as well as two types of aromatic protons (**a** and **k**). Moreover, it is verified the relation $I_q/6 = I_g/2(n-1)$, where I_q and I_g are the intensities of the peaks corresponding to the CH_3 protons of hexyl group and the O-CH_2 protons of PCL, respectively and n is the polymerization degree of the starting macromonomer **4**. The result confirms that

PCL chains and hexyl groups are present in equal amounts (alternating) in the PPP structure.

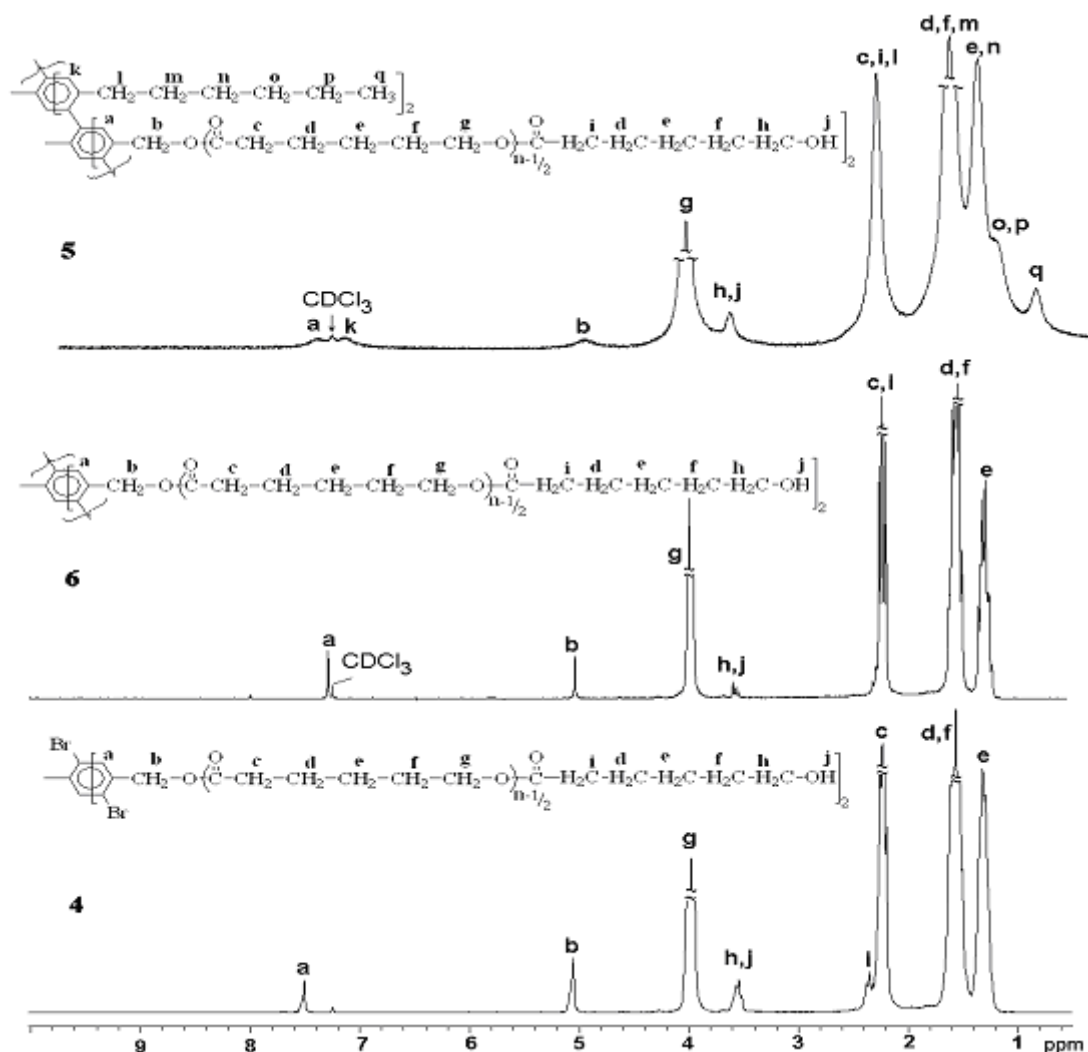


Figure 4.2 : ^1H -NMR (CDCl_3) spectra of PCL **4** and the corresponding PPP **6** and **5**.

The ^1H -NMR spectrum of the product shows only slightly differences as compared with that of the starting macromonomer. The shifting of peak from 7.5 ppm to 7.28 ppm of the aromatic protons is an indication of PPP formation. More evident changes appear in the aromatic region of ^{13}C -NMR spectra of **6** as compared to **4** (Figure 4.3). The peaks from 131.9 ppm and 111.88 ppm corresponding to **a** and **c** carbons respectively, are present in the spectrum of **6** as two broad linked signals at 129.45-127.71 ppm. A broadening of the peaks of aliphatic carbons of PCL is also noticed. This behaviour may be due to the higher polydispersity of PPP **6** as compared to that of the precursor PCL.

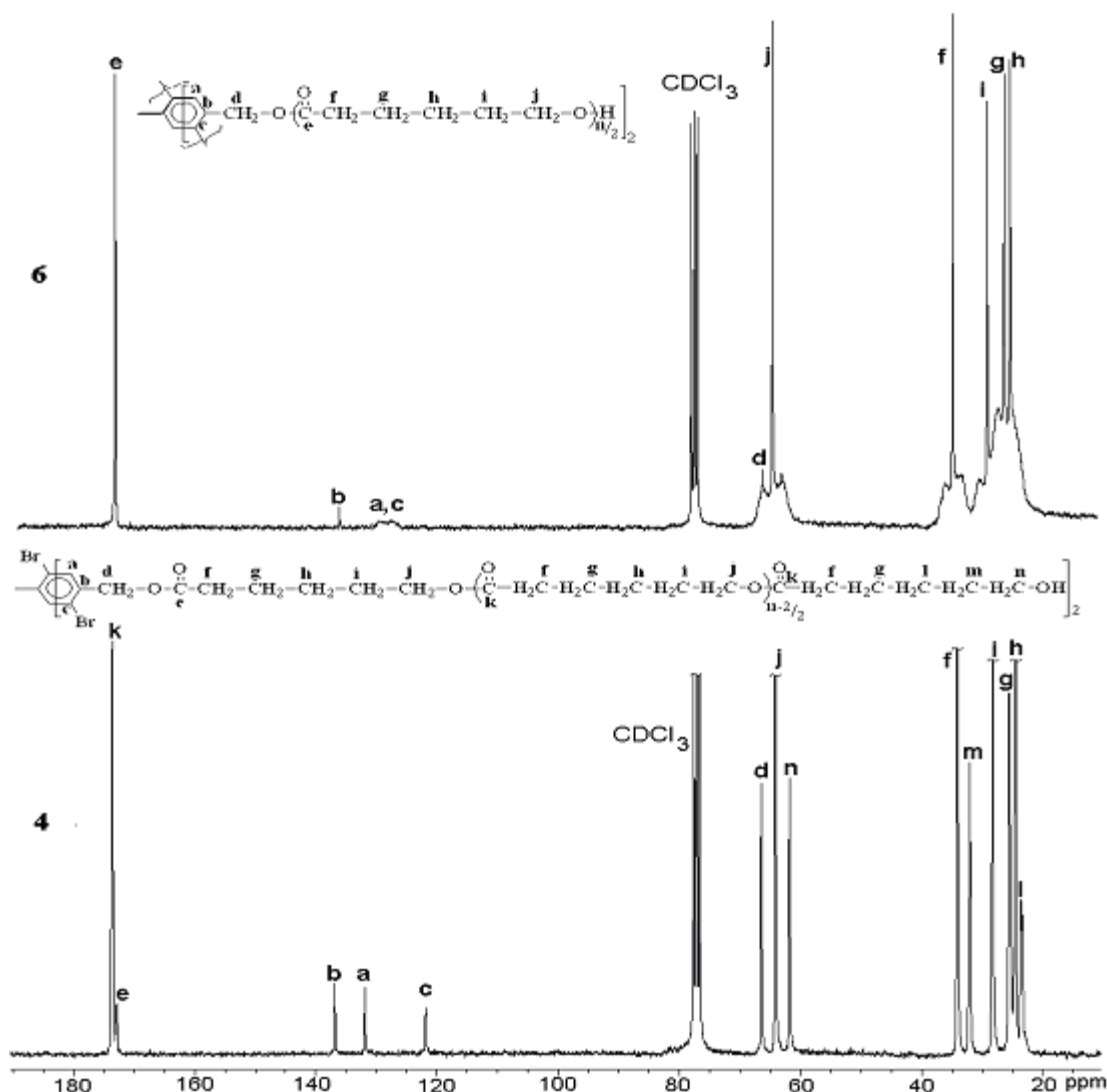


Figure 4.3 : ^{13}C -NMR (CDCl₃) spectra of **4** and the corresponding PPP by Yamamoto method **6**

The polymers have good solubility in usual organic solvents (CHCl₃, THF, DMAc and DMF) similar to PCL macromonomer. The molecular weights measured by GPC based on PS standards, should be taken as the minimum estimation because of the highly branched or comb-like structure of the obtained polyarylenes. Figure 4.4 shows the GPC traces of the obtained polymers. It is interesting to note that the GPC traces of PPPs are broader, but still symmetrical. The lower molecular weight for **6** obtained by Yamamoto method can be due to sterical hindrances. In this case the distance between two adjacent PCL chains is lower as in the case of **5** when the hexyl groups separate the polymeric substituents. As is mentioned in the literature [10], another reason for lower molecular weight of PPP synthesized by Yamamoto method could be due the self-termination of Ni-catalyzed polycondensation, most probably debromination.

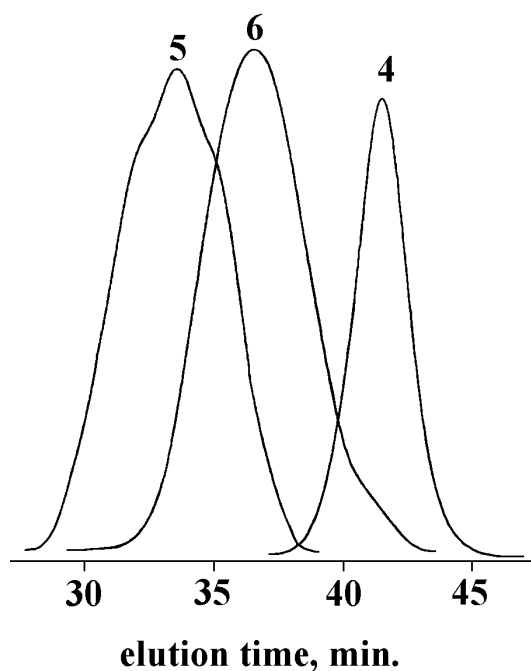


Figure 4.4 : GPC traces of PCL **4** and PPPs **5** and **6**

Figure 4.5 shows important differences in UV absorption spectra of the starting PCL and the corresponding PPPs registered in CH_2Cl_2 solutions with the same concentrations. The absorption with the maximum at 232 nm from macromonomer spectrum is also present with higher intensities in both PPPs spectra. A supplementary shoulder at 250 nm is observed in the UV spectrum **6** indicates polyphenylene formation. In the case of **5**, the appearance of a new broad intense peak with the maximum centered at 271 nm is a further evidence for the presence of PPP based chain.

The thermal behaviour of the polymers was followed by DSC (30-300°C) and TGA (30-600°C), under nitrogen, with a heating rate of 10°C/min. The melting point characteristic to PCL is evidenced at 56°C in DSC traces (Figure 4.6). The PPPs **5** and **6** also showed endothermic peaks characteristic to the melting phenomenon of the PCL side chains at 45°C and 60°C, respectively.

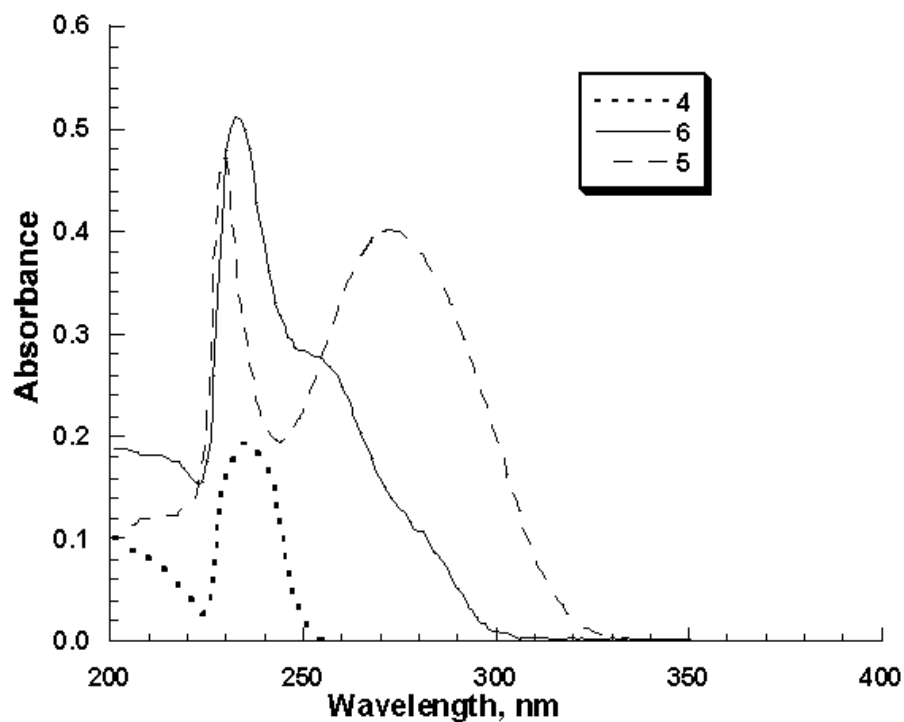


Figure 4.5 : UV spectra of PCL **4** and PPPs **5** and **6**

The decreasing of melting point with 11°C in the case of **5** as compared with the starting macromonomer is probably due to the intercalation of hexyl side groups between PCL pendant chains that have as the effect the shortening of their ordering length.

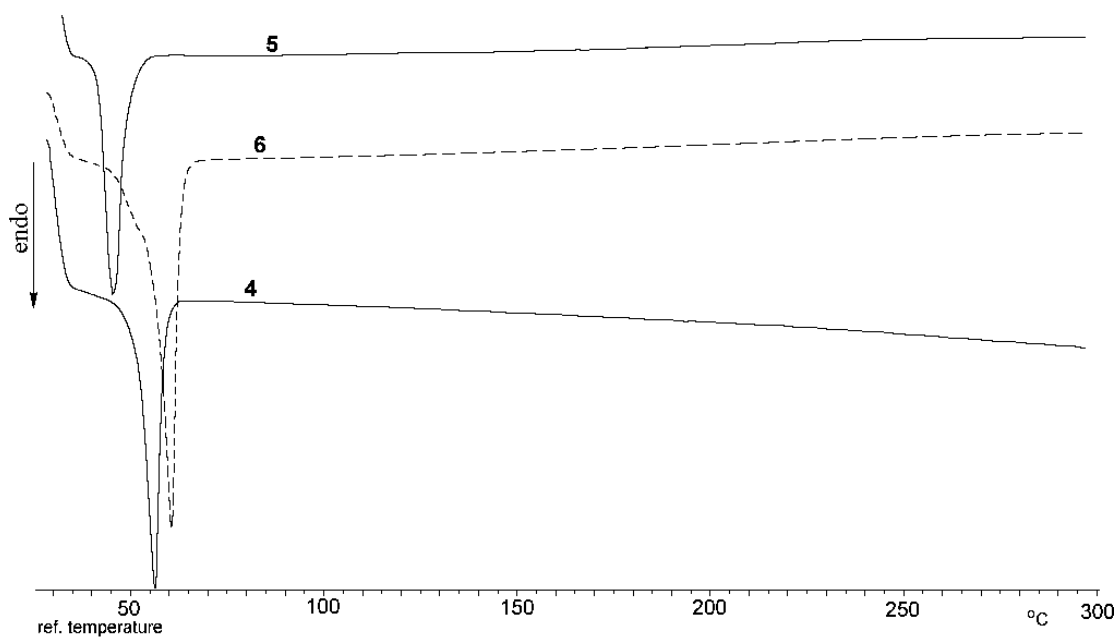


Figure 4.6: DSC traces of PCL **4**, PPPs **5** and **6**

As polymer **4** is thermally stable until 270°C (Table 4.2), the deviation from the linearity of DSC trace of **4** after 70°C, can be due to a very broad and slowly

transition. This effect is not present in the corresponding PPPs, probably due to the decreasing of mobility of PCL segments in the new polymers. All the polymers decompose in two stages, with the main weight loss in the first one. From the data presented in Table 4.2 it can be concluded that the polymer obtained by Suzuki method is the most stable having higher initial degradation temperature and higher char yield at 600°C.

Table 4.2 : The TGA data for macromonomer **4** and synthesized PPPs **5** and **6**

Polymer	First decomposition stage		T _{w10} ^a (°C)	Y _{C600} ^b (%)
	Range (°C)	Weight loss (%)		
4	270-424	91	340	2
5	308-435	89	379	12
6	286-430	93	335	3

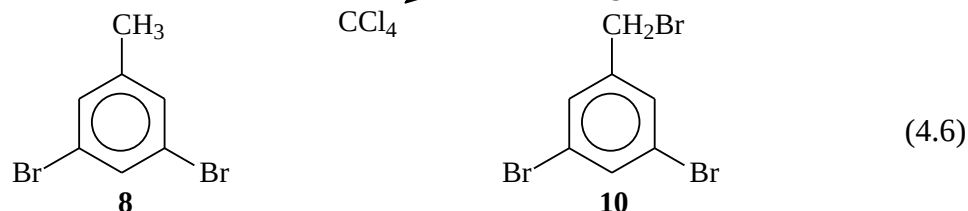
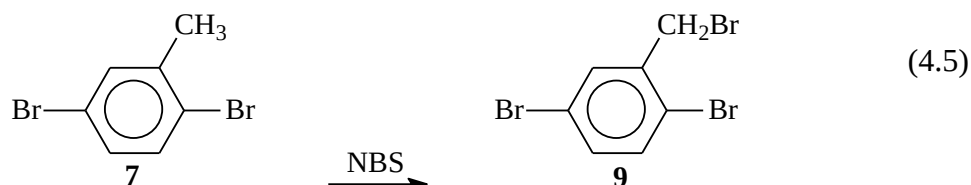
^aTemperature for 10 % weight loss

^bChar yield at 600 °C.

4.2 Synthesis of New Polyphenylene-*g*-Polystyrene and Polyphenylene-*g*-Polystyrene\Poly(ϵ -caprolactone) Copolymers

4.2.1 Preparation of Bifunctional Initiators for ATRP

1,4-dibromo-2-(bromomethyl)benzene (**9**) and 3-dibromo-5-(bromomethyl)benzene (**10**) were synthesized by bromination of methyl groups of commercially available 2,5-dibromotoluene (**7**) and 3,5-dibromotoluene (**8**) (4.5-4.6).



Their structures were proved by ¹H-NMR spectroscopy as shown in Figure 4.7 and 4.8 and elemental analyses.

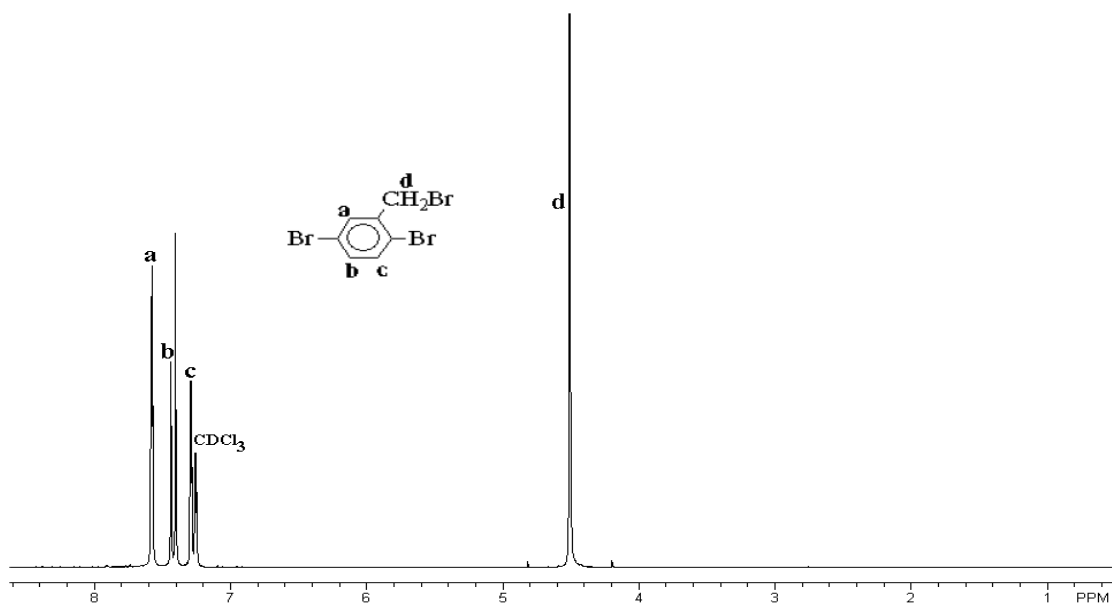


Figure 4.7 : ^1H -NMR spectrum of 1,4-dibromo-2-(bromomethyl)benzene (**9**)

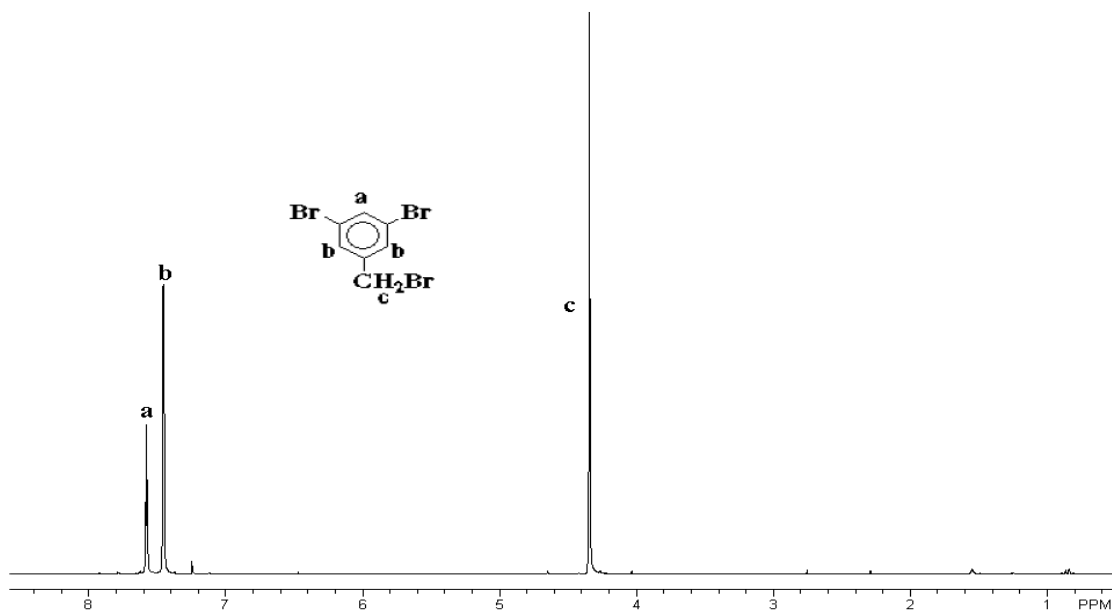
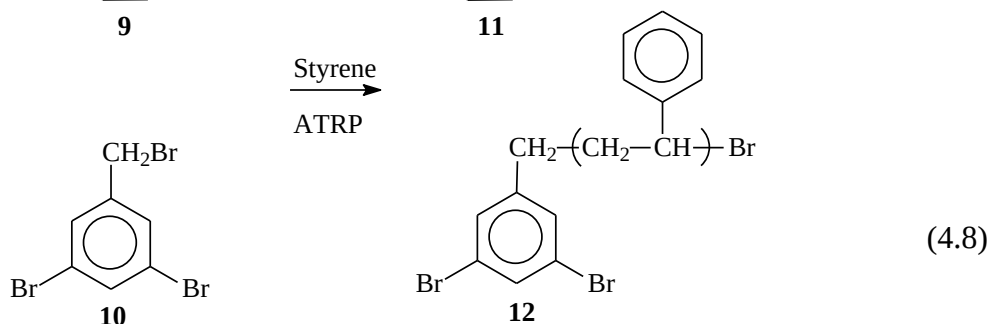
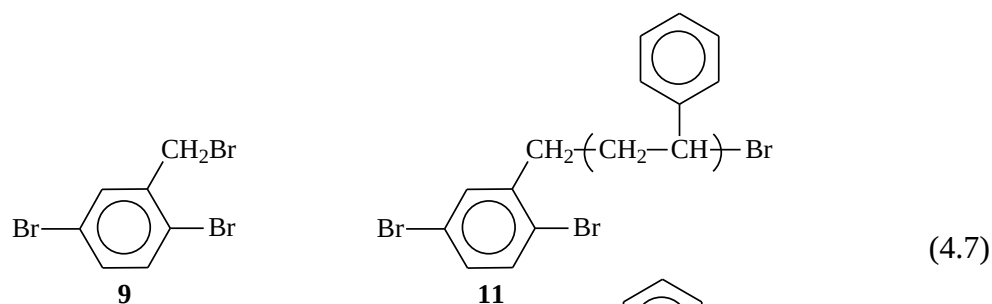


Figure 4.8 : ^1H -NMR spectrum of 3-dibromo-5-(bromomethyl)benzene(**10**)

4.2.2 Preparation of PSt Macromonomers by ATRP

The ATRP of St using 1,4-dibromo-2-(bromomethyl)benzene (**9**) and 3-dibromo-5-(bromomethyl)benzene (**10**) as initiators and the CuBr/bipyridine catalytic system provided precursor polymers **11** and **12**, which had at one end a dibromo-substituted benzene group (4.7-4.8).



As these polymers were intended to be used in further polymerization reactions, the efforts were directed toward obtaining a low molecular weight and low polydispersity along with a convenient yield. Some conditions and results of the ATRP experiments are given in Table 4.3.

Table 4.3 : ATRP of styrene using **9** and **10** as initiators in the presence of CuBr/bpy Complex*

Poly-mer	Initia-tor	$[I]_0 \times 10^2$ $\text{mol} \cdot \text{L}^{-1}$	Time, min	Conver-sion, %	$M_{n,\text{th}}$	$M_{n,\text{GPC}}$	M_w/M_n	$M_{n,\text{H-NMR}}$
11	9	15	55	32.5	2300	2280	1.25	2250
12	10	15	50	36.0	2510	2550	1.25	2500

* $T = 110^\circ\text{C}$; Init./CuBr/bpy mol ratio = 1/2/6, $[St]_0 = 8.7 \text{ mol/L (bulk)}$

As can be seen from Table 4.3, **9** and **10** are effective initiators for ATRP of styrene and the theoretical molecular weights ($M_{n,\text{th}}$), calculated with equation 2, fit the measured ones very well:

$$\overline{M}_{n,\text{th}} = \frac{[M_0]}{[I_0]} (M_w)(\text{conversion}) + M_I \quad (2)$$

Where $[M_0]$ and $[I_0]$ are the initial molar concentrations of the monomer and initiator, and M_w and M_I are the molecular weights of the monomer and initiator, respectively.

Due to the low molecular weights of the polymers, the results could be verified by $^1\text{H-NMR}$ analyses (Figures 4.9 and 4.10). The peak from the final CH-Br protons

appears very clear at about 4.5 ppm (protons k and j respectively). The molecular weights of the polymers were also calculated by ^1H -NMR analyses:

$$\overline{M}_{n,\text{H-NMR}} = M_w \frac{2I_{\text{Ar}} - 2I_{\text{CHBr}}}{5I_{\text{CHBr}}} + M_I \quad (3)$$

where I_{Ar} and I_{CHBr} are the intensities of the peaks from the aromatic region (6.3-7.3 ppm) and from 4.45 ppm, respectively.

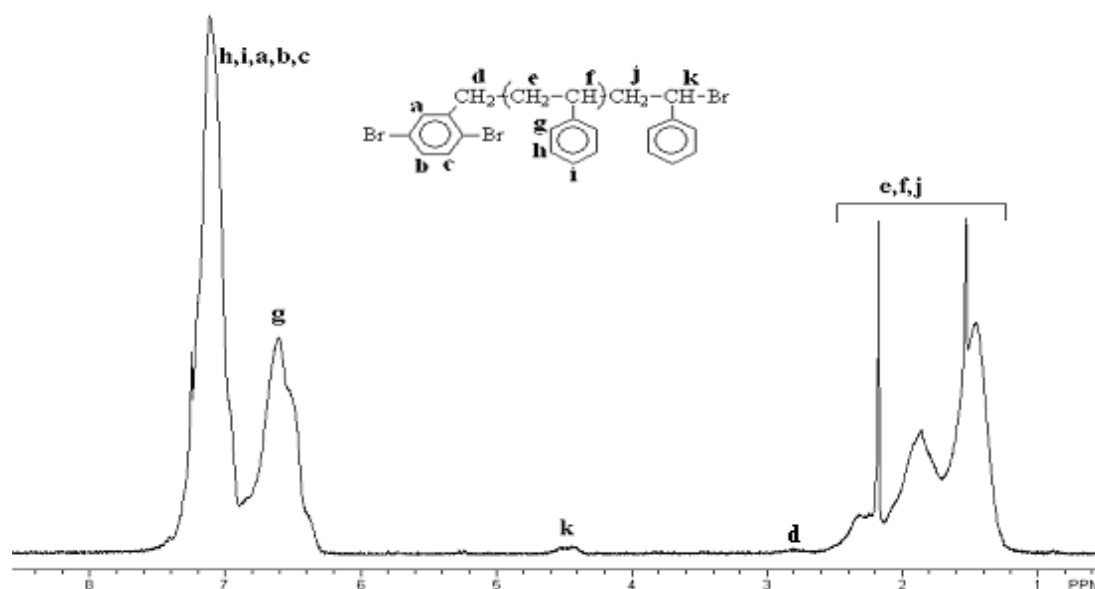


Figure 4.9 : ^1H -NMR spectrum of macromonomer **11**

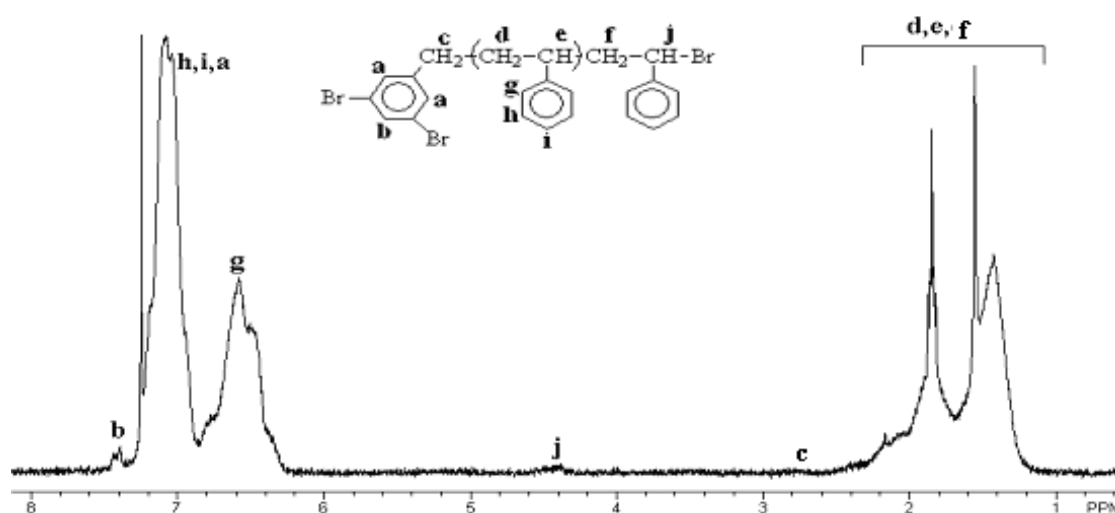


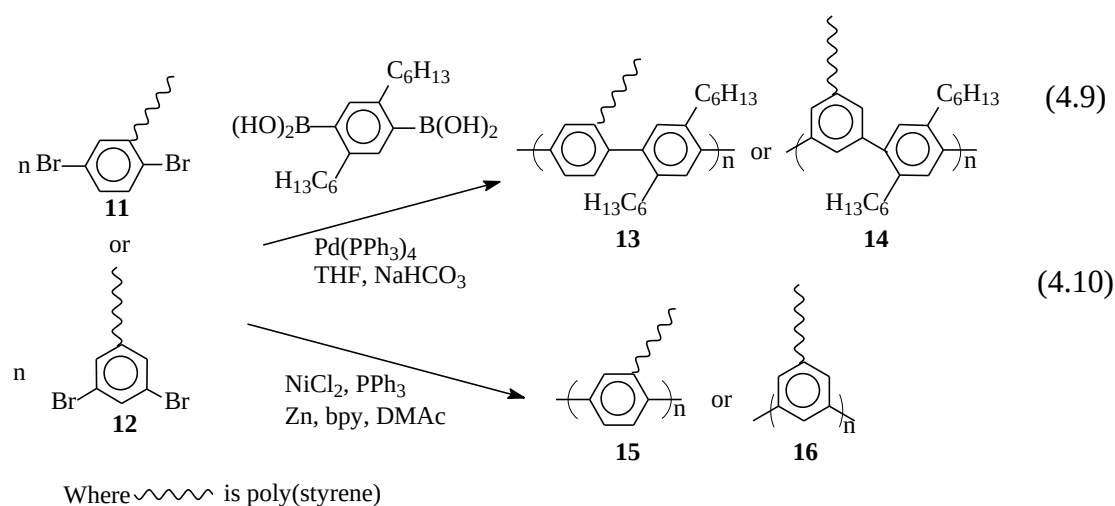
Figure 4.10 : ^1H -NMR spectrum of macromonomer **12**

In the ^1H -NMR spectrum of macromonomer **12** it can be also identified the aromatic proton between the two bromine atoms (proton **b**, Figure 4.10) that belongs to the

rest of initiator **10**. The GPC traces are unimodal and narrow, indicating that no side reaction occurred.

4.2.3 Preparation of PPs by Suzuki and Yamamoto Methods

Both macromonomers possess a dibromo-substituted benzene ring at 2,5 or 3,5 positions, and they were proper for obtaining PPs with side polymeric chains through Suzuki polycondensation in combination with dihexylbenzene-1,4-bisboronic acid, in the presence of a Pd(0) catalyst, or through Yamamoto coupling reactions using Ni based catalysts as seen in reactions 4.9 and 4.10 [232].



In this way, new PPs with PSt side chains were obtained. Some results of the cross-coupling reactions using PSt macromonomers are presented in Table 4.4.

Table 4.4 : Syntheses of PP with PSt side chains by Suzuki and Yamamoto polycondensations using **11** and **12** as macromonomers

Macromonomer	Method of polymerization	Polymer	Conversion, %	$M_{n,\text{GPC}}$	M_w/M_n
11	Suzuki	13	94	58350	3.07
12	Suzuki	14	87	47700	2.76
11	Yamamoto	15	92	17300	1.50
12	Yamamoto	16	89	16439	1.73

The molecular weights measured by GPC based on PSt standards (Table 4.4), should be taken as the minimum estimation because of the highly branched or comb-like structure of the obtained polyarylenes.

The lower molecular weights for **15** and **16** obtained by Yamamoto method could be due to sterical hindrances. In this case the distance between two adjacent PSt chains were lower as in the case of **13** and **14**, when the hexyl groups separated the polymeric substituents.

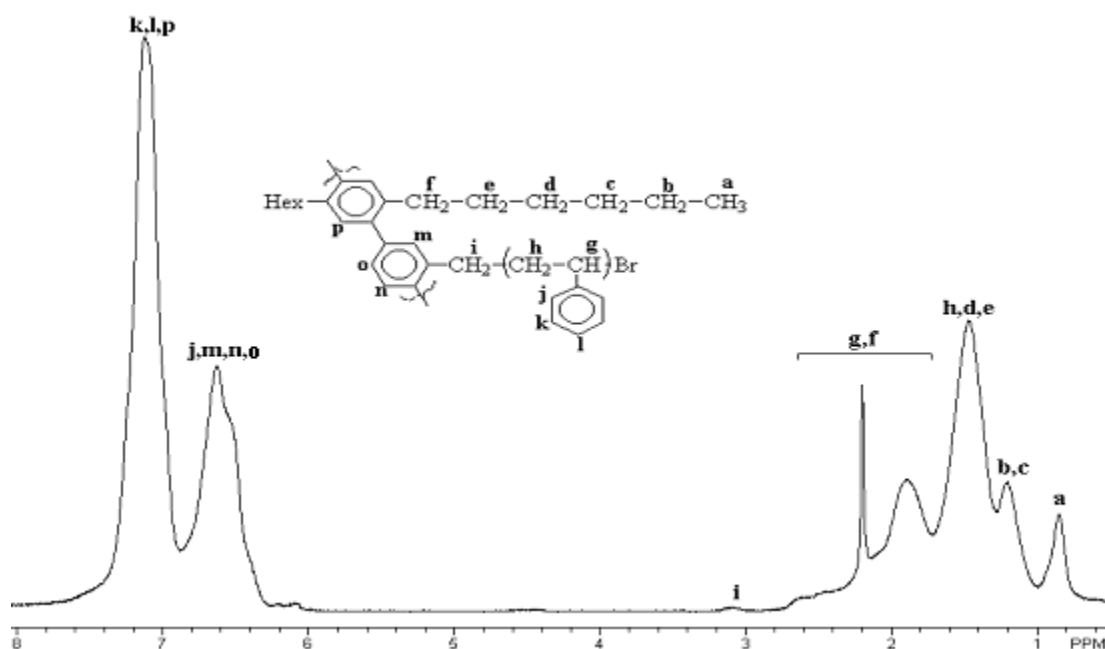


Figure 4.11 : ¹H-NMR spectrum of PPP with alternating PSt/hexyl side chains **13**

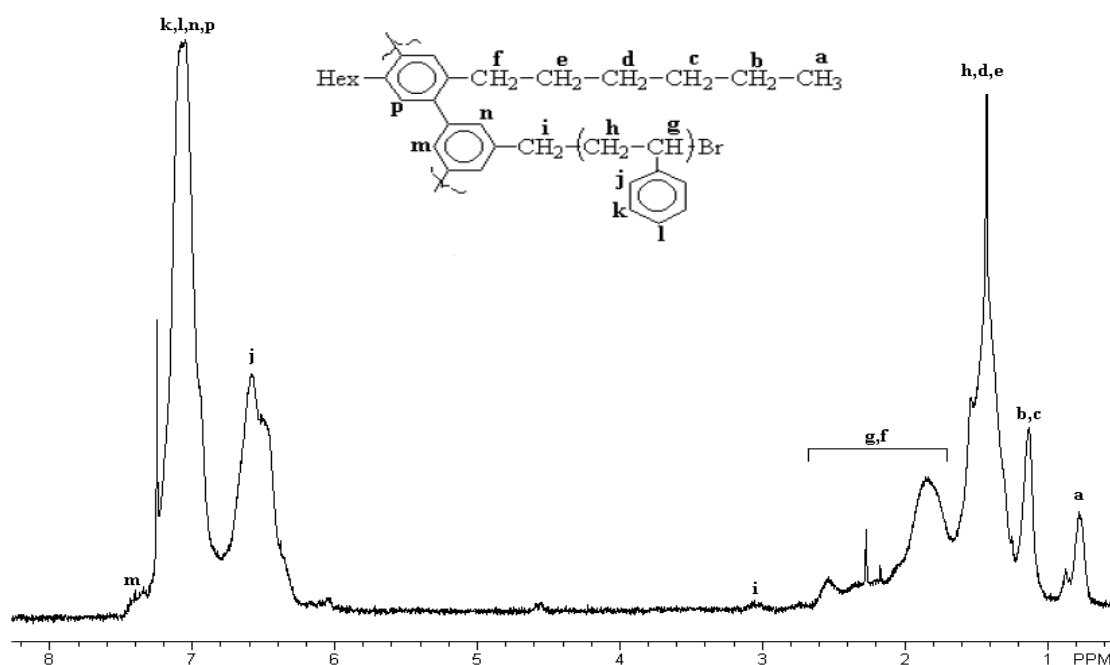


Figure 4.12 : ¹H-NMR spectrum of PMP with alternating PSt/hexyl side chains **14**

The reason for a lower molecular weight of PP synthesized by Yamamoto polycondensation mentioned before [10]. On the other hand, the differences between

molecular weights, of 2-substituted and 3-substituted PPs were minimal, and this indicated that the position of incatenation influenced less the degree of polymerization than the sterical effect of side chains.

The ^1H -NMR spectra of the polymers obtained by Suzuki method Figures 4.11(polymer **13**) and 4.12(polymer **14**) show clearly the presence of hexyl groups in the composition of the polymers (**a**: 0.66-0.99 ppm , **b** and **c**: 1-1.28 ppm). Moreover, it is verified the relation $I_a/6 \approx I_{Ar}/5n$, where I_a and I_{Ar} are the intensities of the peaks corresponding to the CH_3 protons of hexyl groups and the aromatic protons of PSt, respectively and n is the polymerization degrees of the starting macromonomers (**11** and **12**). The result confirms that PSt chains and hexyl groups are present in equal amounts (alternating) in the PPs structures. The protons from the aromatic main chain of PPs are covered by the aromatic protons of PSt side chains excepting proton **m** of **12** (Figure 4.12), that appears separately at about 7.4 ppm.

The presence of hexyl groups in the structures of **13** and **14**, was evidenced also by the ^{13}C -NMR spectra of **13** and **14** (carbons **n** and **o**, Figs. 4.13 and 4.14). Moreover, carbons belonging to the PP main chains (**k**, **i**, **f**, **e** and **m** for **11** in Fig. 3 and **e**, **i**, **g**, **k**, **f**, **j**, **m**, **j** and **h** for **14** in Fig. 4.14) could be identified in both spectra.

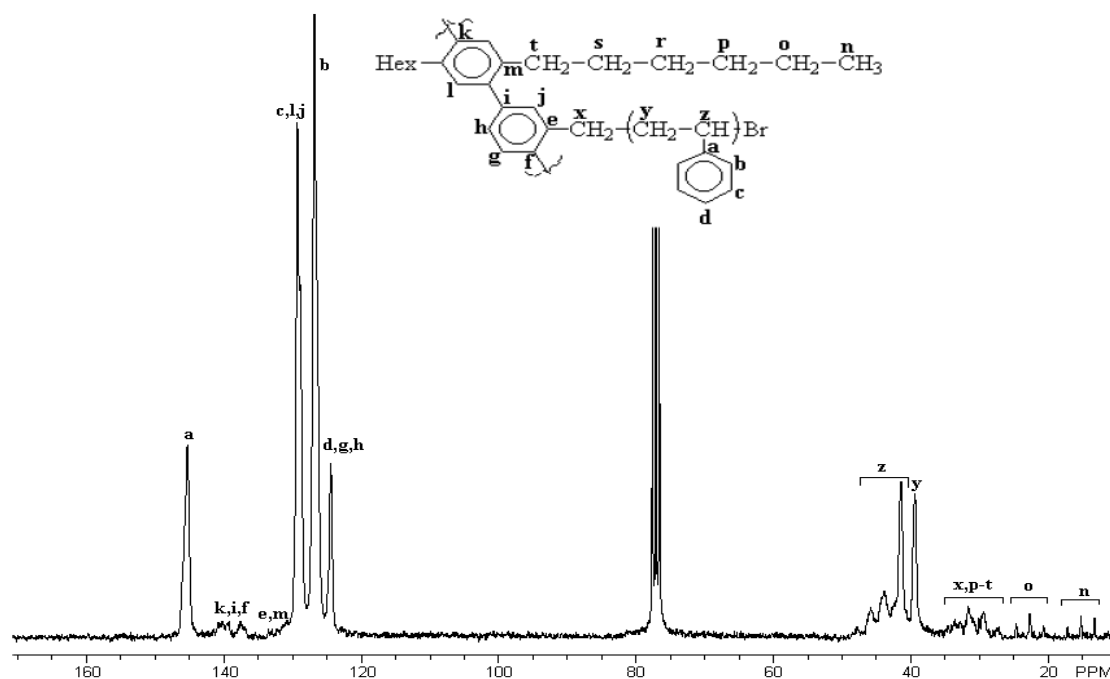


Figure 4.13 : ^{13}C -NMR spectrum of PPP with alternating PSt/hexyl side chains **13**

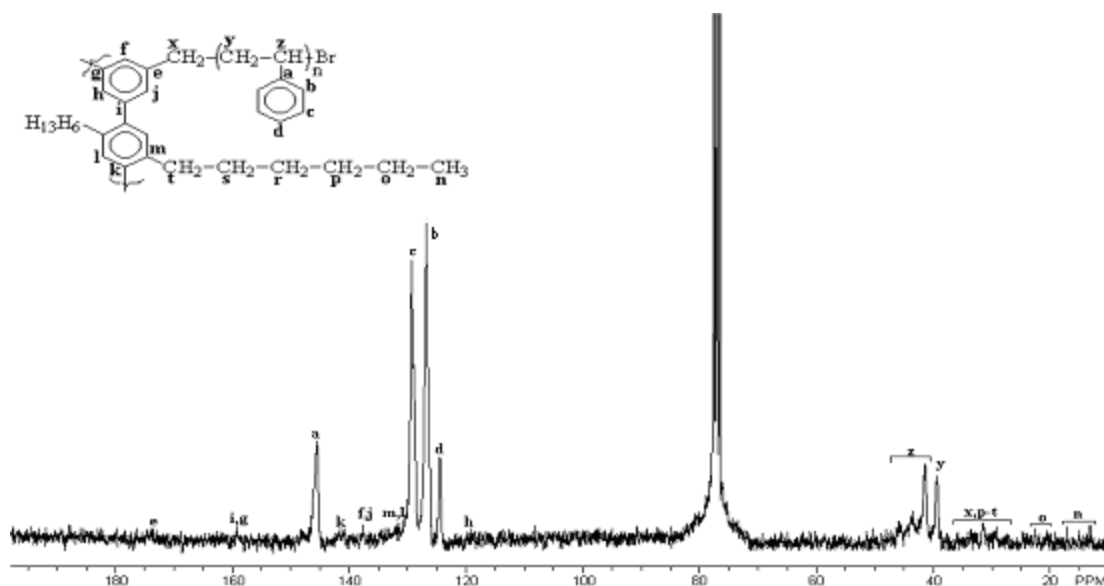
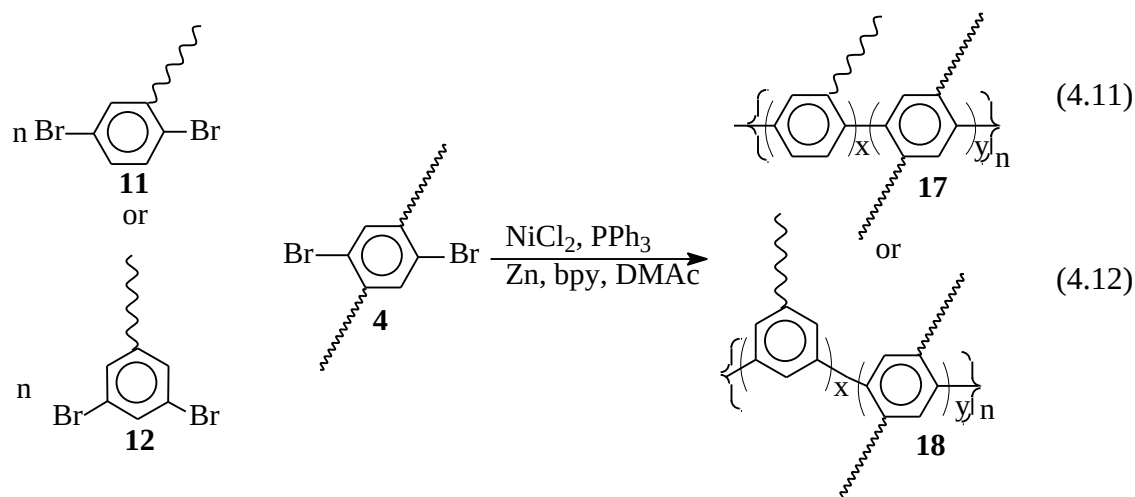


Figure 4.14 : ^{13}C -NMR spectrum of PMP with alternating PSt/hexyl side chains **14**

PPs containing both PSt and PCL side chains could be achieved by Yamamoto copolycondensation of **11** or **12** in combination with the PCL macromonomer **4** as seen in reactions 4.11 and 4.12.

These materials have interesting properties due to microphase separated morphology of crystalline (PCL) and amorphous (PSt) side groups. The ratio between the two types of macromonomers in the feed was 1/1.



Where  is poly(ε-caprolactone)

The results are presented in Table 4.5 and the ^1H -NMR spectra of the products, in comparison with the starting PCL macromonomer are shown in Figure 4.15.

Table 4.5 : Syntheses of PP with polystyrene/poly(ϵ -caprolactone) side chains by Yamamoto co-polycondensation using macromonomers, **11** or **12** and **4**

Macro-monomers	Method of polymerization	Poly-mer	Con-versi-on (%)	M _n	M _w /M _n	Content of PSt chains in copolymer (%) ^{a,b}	Content of St r.u. in copolymer (%) ^b
11 and 4	Yamamoto	17	74	23400	1.35	42.1	35.6
12 and 4	Yamamoto	18	83	19720	1.50	49.2	45.7

a: Initial ratio of the co-macromonomers was 1:1 (mol/mol)

b: Calculated from ¹H-NMR spectra

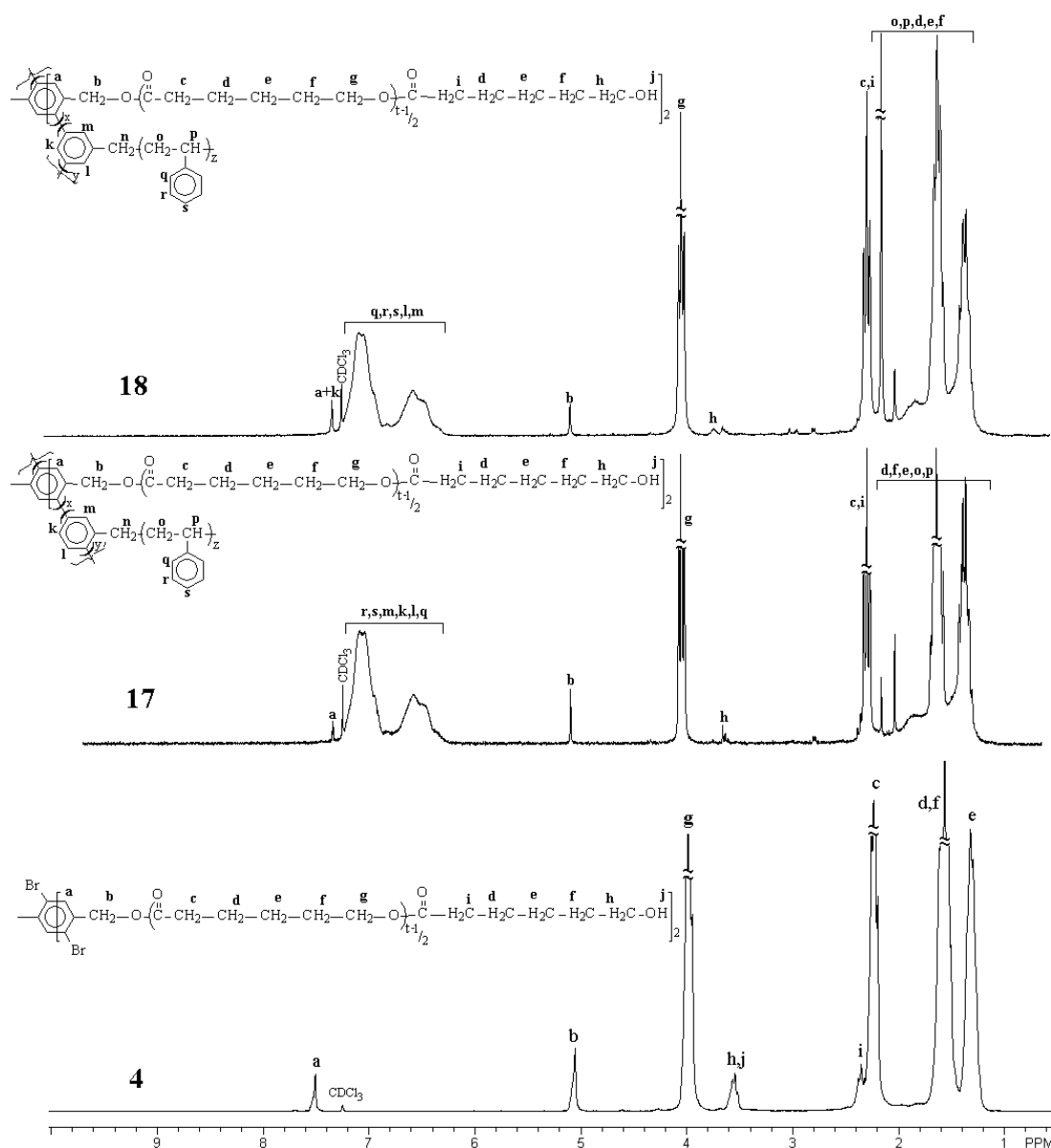


Figure 4.15 : ¹H-NMR spectra of PCL macromonomer **4** and copolymers with PSt **17** and **18**

As shown in Figure 4.15 and from the Table 4.5, the two components (PSt and PCL) are present almost in equal amounts according to the number of chains. The lower value for PSt in the case of **17**, could be due to the higher steric hindrances, when the PSt chains are linked to the 2 position of the 1,4-phenylene ring. In the case of **18**, the substitution of 1,3-phenylene ring at the fifth position could be more favorable for the reaction from this point of view. As PCL chains are longer, the PSt content is lower in copolymers (35.6-45.7%)

In the ^{13}C -NMR spectrum of **17** (Figure 4.16), near the strong peaks corresponding to the carbons belonging to both PCL and PSt side chains, some peaks due to of the PPP main chain could be identified, as well.

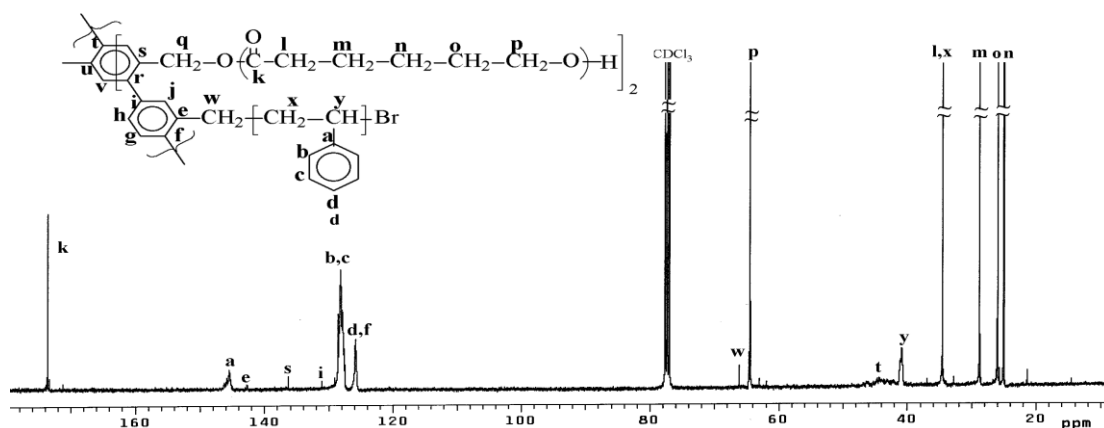


Figure 4.16 : ^{13}C -NMR spectrum of copolymer **17**

For these polymers, also, because of the expected shape of the macromolecules GPC could not give valuable information about the polymerization degree.

Despite this, Figures 4.17 and 4.18 show that the GPC traces of the new polymers (**17** and **18** respectively) are shifted to higher molecular weights, in comparison with that of the starting macromonomers. It is also interesting to notice that the GPC traces of the polyphenylenes, even though they are broader, are still symmetrical.

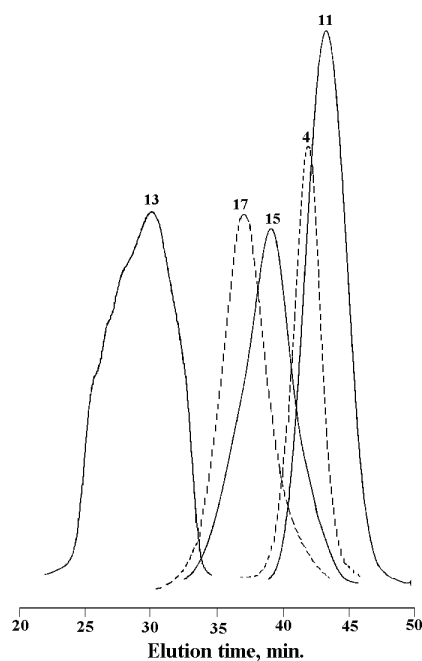


Figure 4.17 : GPC traces of macromonomers **11** (p-PSt) and **4** (PCL) and the corresponding PPs: **13** (Suzuki method) **15** (Yamamoto method) and **17** (Yamamoto method, PSt-PCL copolymer)

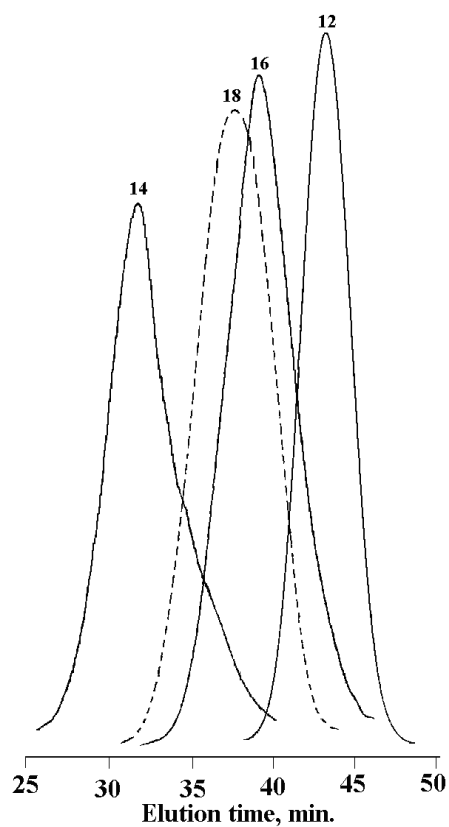


Figure 4.18 : GPC traces of macromonomer **12** (m-PSt) and the corresponding PPs: **14** (Suzuki method), **16** (Yamamoto method) and **18** (Yamamoto method, PSt-PCL copolymer)

The IR spectra of the macromonomers **4** and **12** as well as of the copolymers **17** and **18** are given in Figure 4.19. The PP IR spectra also shows the presence of both components (PSt and PCL) in the structures of **17** and **18**. Peaks from 1720 cm^{-1} , 1362 cm^{-1} , 1290 cm^{-1} , 1240 cm^{-1} , 1195 cm^{-1} , 1105 cm^{-1} , 960 cm^{-1} and 735 cm^{-1} are due to PCL chains. Absorptions from 1595 cm^{-1} , 1490 cm^{-1} , 840 cm^{-1} , 750 cm^{-1} and 700 cm^{-1} are specific to PSt component, whereas peaks that could be attributed to both polymers are also present at: 1450 cm^{-1} , 1045 cm^{-1} and 540 cm^{-1} .

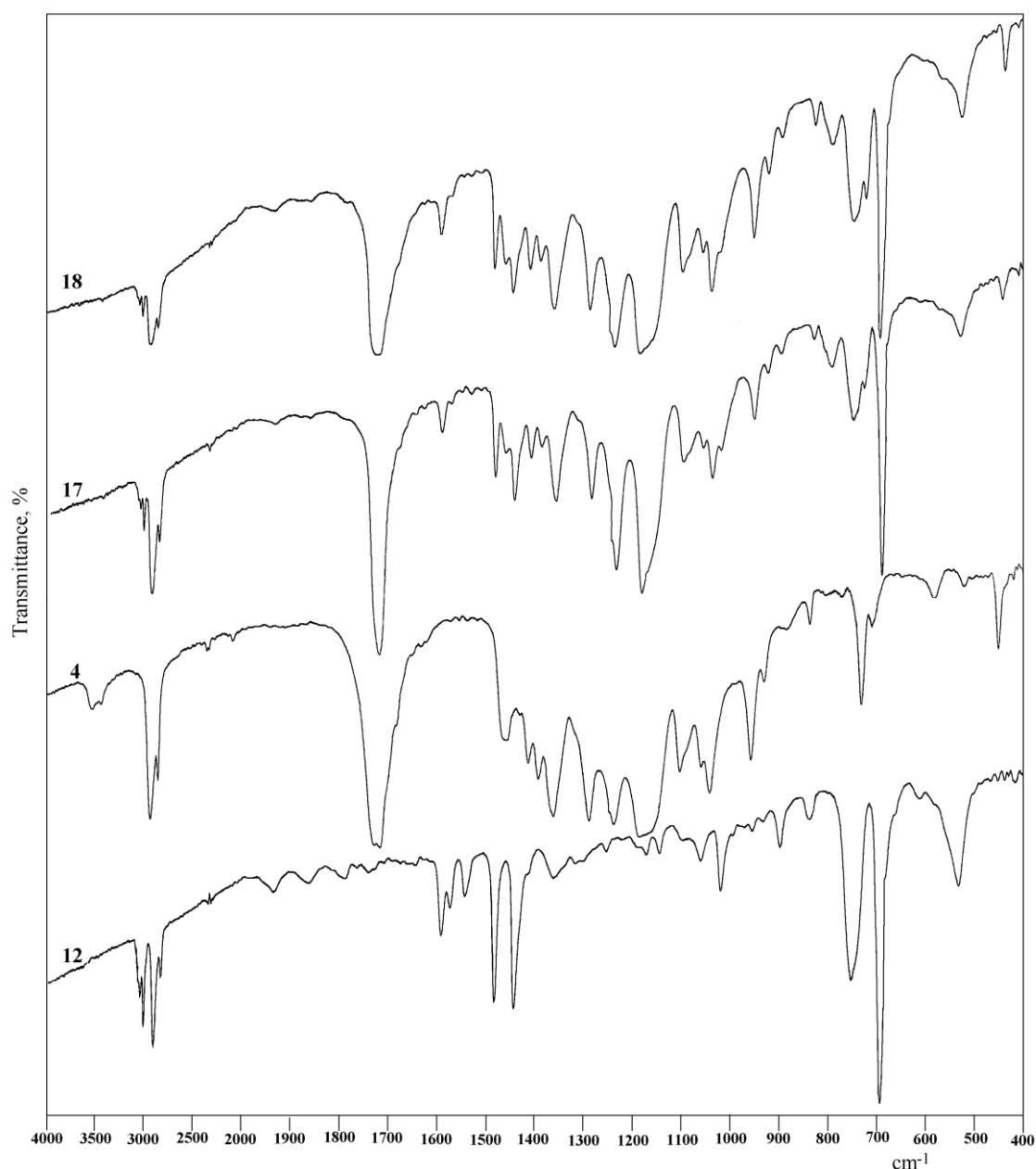


Figure 4.19 : IR spectra of macromonomers **4** and **12** and copolymers **17** and **18**

UV absorption spectra of macromonomers **4** and **11** and the corresponding PPs registered in CH₂Cl₂ solutions with the same concentrations are shown in Figure 4.20. PSt macromonomer has an absorption at 230 nm and a smaller one at 262 nm while PCL macromonomer **4** has an absorption at 238 nm. PPs UV spectra present also two maxima of absorption at wavelengths close to that of the macromonomer **11**, at 225-230 nm and at 252-257 nm. Both peaks have higher intensity as comparing with that of **11**, but a more accentuated difference can be noticed in the second one. The second strong absorption band of each PP is due to the presence of supplementary phenylene rings in the main chain. Normal and alkyl substituted PP has two absorptions in UV in the same region (200-300 nm) [233].

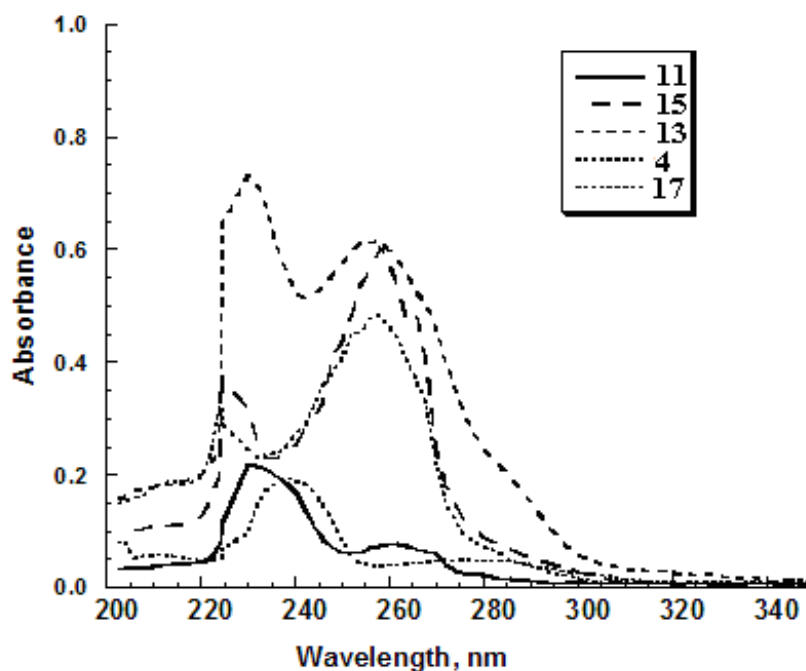


Figure 4.20 : UV spectra of the starting macromonomers **11** and **4** and the corresponding PPs **13**, **15** and **17**

In the case of **13**, the PP obtained by Suzuki reaction and possessing in its structure the 2,5-dihexyl-1,4-phenylene moiety, a supplementary shoulder can be noticed at about 285 nm. Figure 4.21 shows the UV spectra of the macromonomer **12** and the corresponding PPs **14**, **16** and **18**. The same tendency of increasing the absorbance with the maximum at 225-230 nm of PPs as comparing to that of **12**, is observed in this case, too. Also the shoulder of absorption from the PSt macromonomer spectrum becomes strong absorption peaks in the case of **14**, **16** and **18** in the range 258-262 nm. A shoulder at 285 nm can be noticed in the spectrum of the polymer obtained by

Suzuki method (**14**), similar with **13**, due to the presence of 2,5-dihexyl-1,4-phenylene groups in its structure.

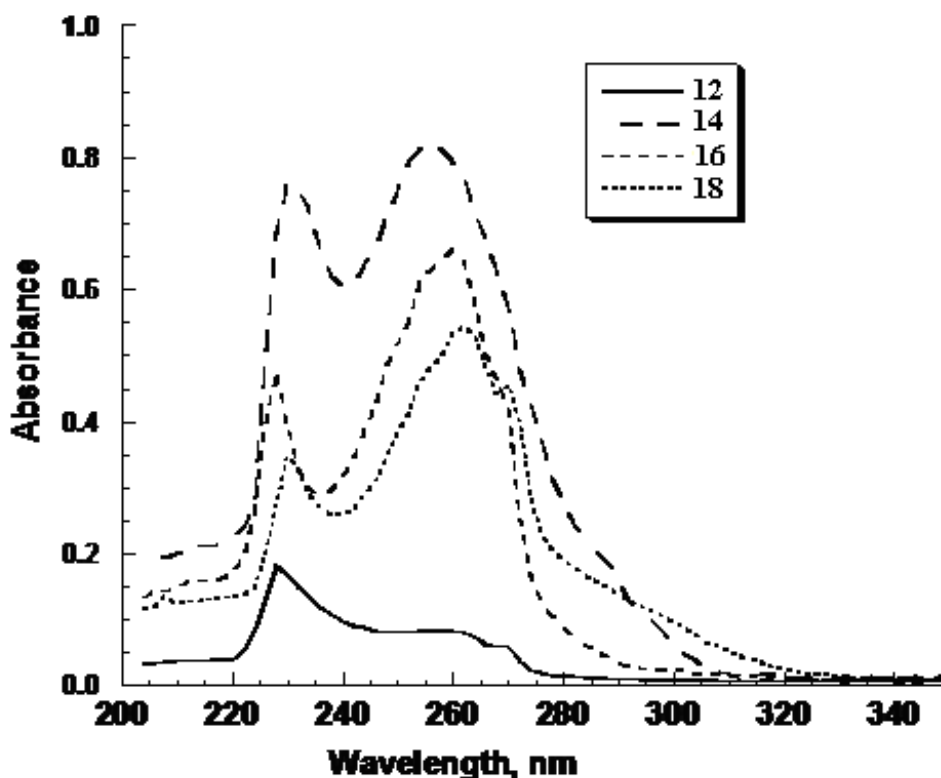


Figure 4.21 : UV spectra of the macromonomer **12** and the corresponding PPs **14**, **16** and **18**

In Figures 4.22 and 4.23 are given the fluorescence spectra of PPs obtained by Suzuki method, as well as of copolymers with PCL, in comparison with the starting PSt macromonomers. The measurements were performed in CHCl_3 solutions with the concentration of 0.025g/L. The fluorescence of PCL macromonomer **4** has very weak peaks at this concentration so it was presumed that its influence is very low in the fluorescence spectra of copolymers **17** and **18**. The excitation spectrum of **11** has the maximum at 306 nm and the emission spectrum obtained for excitation wavelength at this value has a maximum at 361 nm. The emission spectrum of **13** for excitation at wavelength of 294.5 nm presents a maximum at 359 nm, very close to that of **11**. In the case of **17**, the maximum intensity of emission spectrum for excitation at 314 nm is at 378.5 nm. As it was expected a shift to higher wavelengths for PPs, the result suggests that the influence of PSt in PPs structures is stronger than that of the PP main chain. A shift is produced only in the case of copolymer with PCL, when the concentration of PSt in the material is reduced. In the case of macromonomer **12**, the maximum intensity of emission spectrum for excitation at 299 nm is at 321 nm.

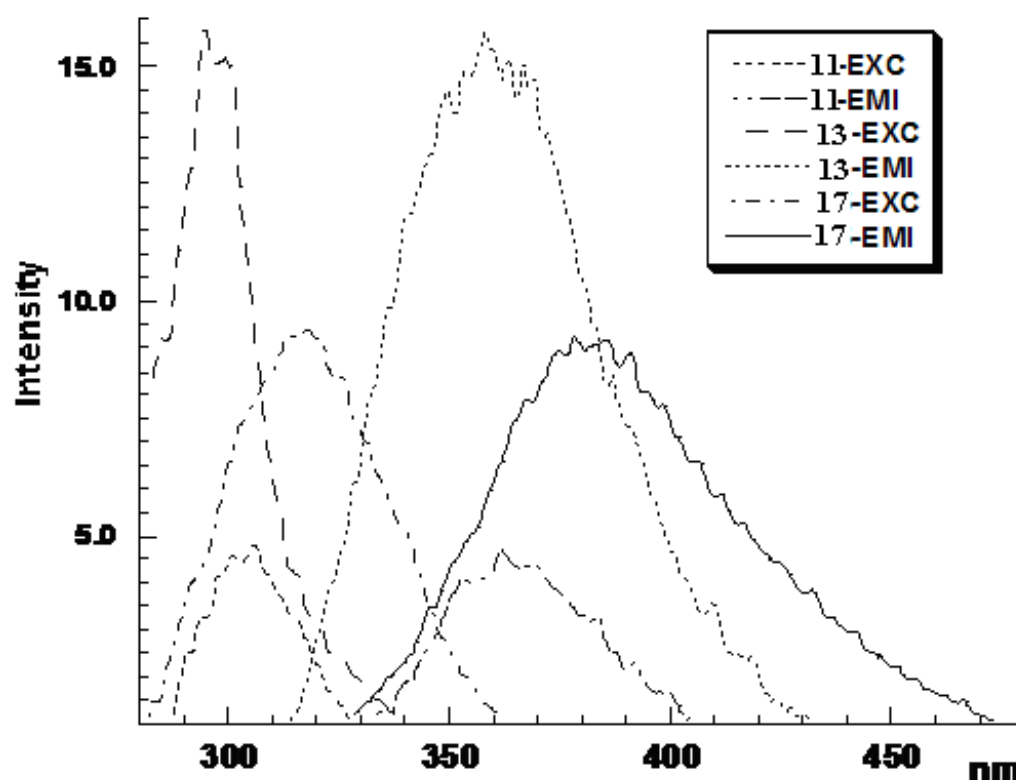


Figure 4.22 : Fluorescence spectra of macromonomer **11**, the PP obtained by Suzuki method (**13**) and the copolymer with PCL (**17**)

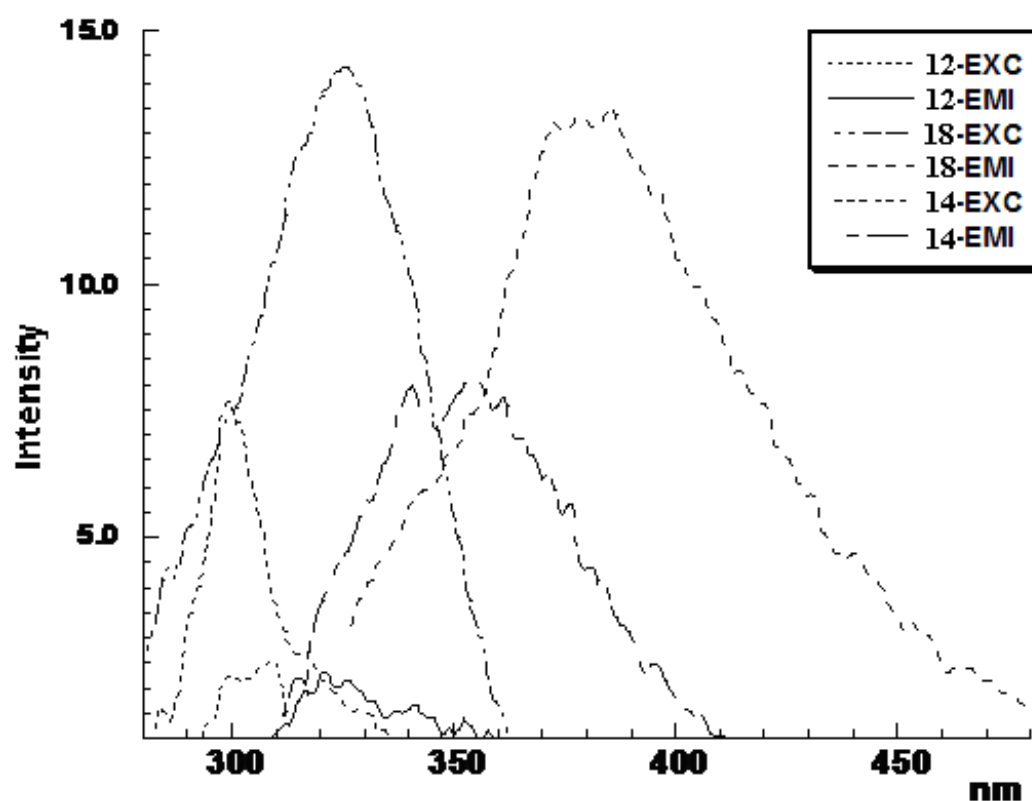


Figure 4.23 : Fluorescence spectra of macromonomer **12**, the PP obtained by Suzuki method (**14**) and the copolymer with PCL (**18**)

The maxima for emission spectra of PPs **14** and **18** are found at 354.5 nm and 390 nm, respectively, for excitation at 299.5 nm and 325.5nm, respectively. In this case a shift of the maximum intensity is observed in both cases, but the higher one is also found in the case of PCL copolymer **18**. (Figure 4.23).

Thermal behaviour of polymers

The thermal behaviour of starting macromonomers and derived polymers was followed by differential scanning calorimetry (DSC) (30-300°C), the heating rate being 10°C/min. In the DSC trace of PCL macromonomer **4**, the endothermic peak characteristic to melting phenomena of this polymer is seen at 56°C (Figure 4.24). PSt based macromonomers **11** (Figure 4.24) and **12** (Figure 4.25) show endothermic peaks centred at 79°C and 86 °C, respectively. These can be attributed to the well known enthalpic relaxation at the glass transition of polystyrene. The higher value for **12** as comparing to **11** can be due to the slightly higher molecular weight of the first one. The corresponding PPs obtained from **11** or **12** shows also the T_g characteristic to PSt blocks. Thus, the respective T_g values appear for the polymers obtained by Suzuki method, **13** and **14** at 90°C and 91°C, and for the polymers obtained by Yamamoto polycondensation, **15** and **16**, at 92°C and 76°C.

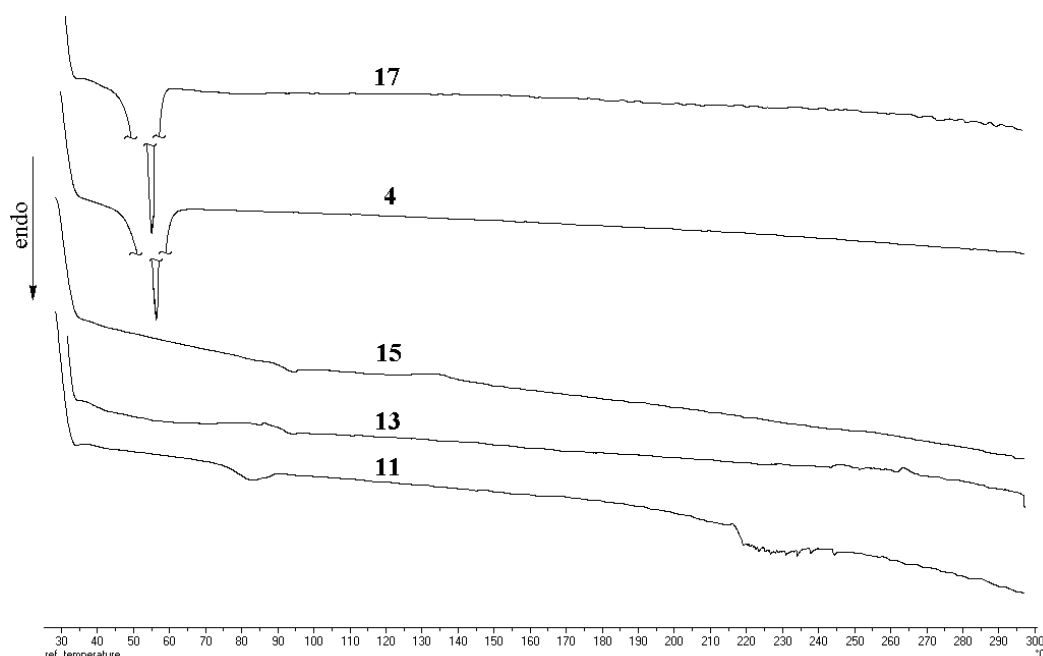


Figure 4.24 : DSC traces of macromonomers **11** and **4** and the corresponding PPs **13**, **15** and **17**

We can notice, generally, an increase of T_g of these polymers, probably due to the lowering of mobility of the PSt chains linked to the PP main chain. The lower value found for **16** can be due to the less steric hindrances when 1,3-phenylene rings are substituted to the 5th position.

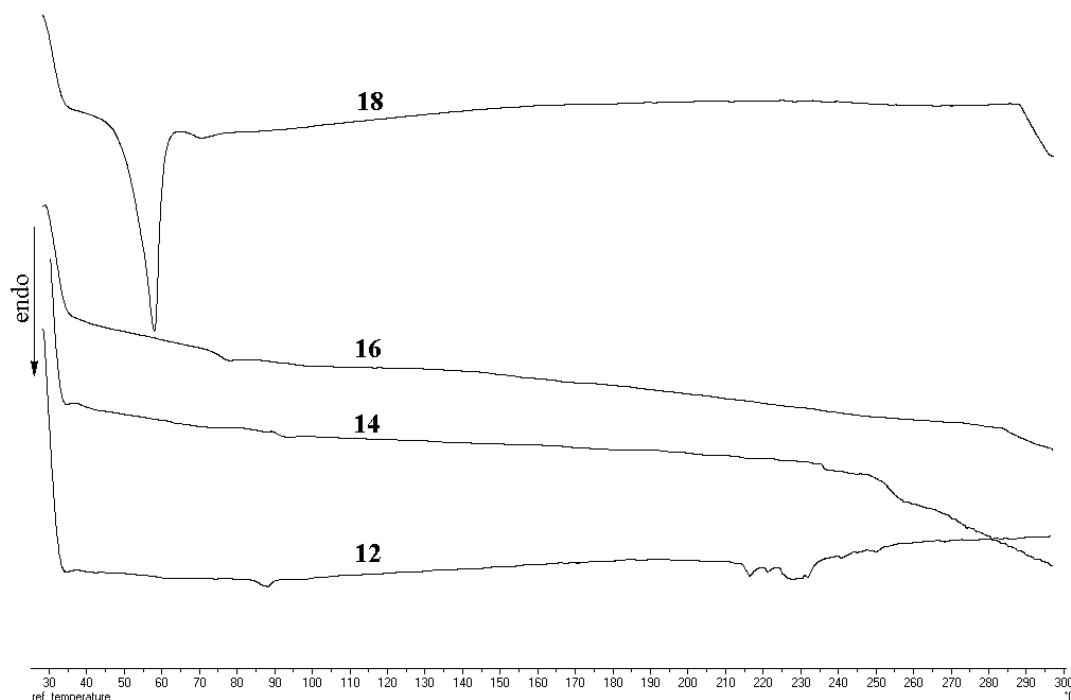


Figure 4.25 : DSC traces of macromonomer **12** and the corresponding PPs **14**, **16** and **18**

Interesting behaviour was encountered for the PCL containing PPs, **17** and **18**. In the DSC traces of both polymers the endothermic peaks corresponding to melting points of PCL blocks can be observed at 55°C and 58°C, respectively. In the case of **18**, a very small inflexion at 68°C, that can be attributed to PSt blocks glass transition, can be observed. In the DSC trace of **17** the T_g of PSt component could not be identified. Even though 42.1% of the side chains were composed of PSt as was calculated from $^1\text{H-NMR}$ spectrum. The polymerization degree of PCL side chain is higher than that of PSt side chains. Moreover, each repeating unit of PCL is longer than that of PSt. We can suppose that an inclusion phenomenon of PSt chains inside of PCL ones can take place, leading to a decreasing of freedom for PSt segments and hindering their thermal mobility. A similar behavior was noticed, when a PP with perfectly alternating polytetrahydrofuran (PTHF)/ polystyrene side chains was obtained and both melting point characteristic to PTHF and T_g characteristic to PSt were missing from the DSC trace [234]. In the present case, on one hand, the PCL and PSt side

chains are not in alternating structure and on the other, the PCL chains are sufficiently long, so their crystallinity is preserved and the melting peak appears in the DSC trace of this polymer. The presence of T_g peak in the DSC of **18** can be explained also by the higher mobility of PSt chains in this polymer, due to the more favorable position of substitution at PP chain, from the steric point of view.

Morphology of polymers in thin films

The polymers have good solubility in usual organic solvents (benzene, chlorinated solvents, THF, DMAc and DMF) similar to PSt macromonomers and thin films could be easily prepared by spin-coating for AFM measurements.

The morphology of starting macromonomer **4** and derived polymers **17** and **18** in thin films was observed by Atomic Force Microscopy (AFM). Fig. 4.26 shows the AFM height images of thin films of macromonomer **4**. After spin coating on SiO₂ surfaces, crystalline domains containing mostly perpendicular lamellae (edge-on lamellae) were observed in the films (Fig. 4.26a). The size of these domains varied between 7-30 μm . Films were heated under optical microscope and melting was observed around 55 $^{\circ}\text{C}$ in consistent with DSC melting peak. When thinner films were coated on hydroxylated SiO₂ surfaces, lamellae were parallel to the substrate (flat-on lamellae) and layered morphology was observed (Fig. 4.26b).

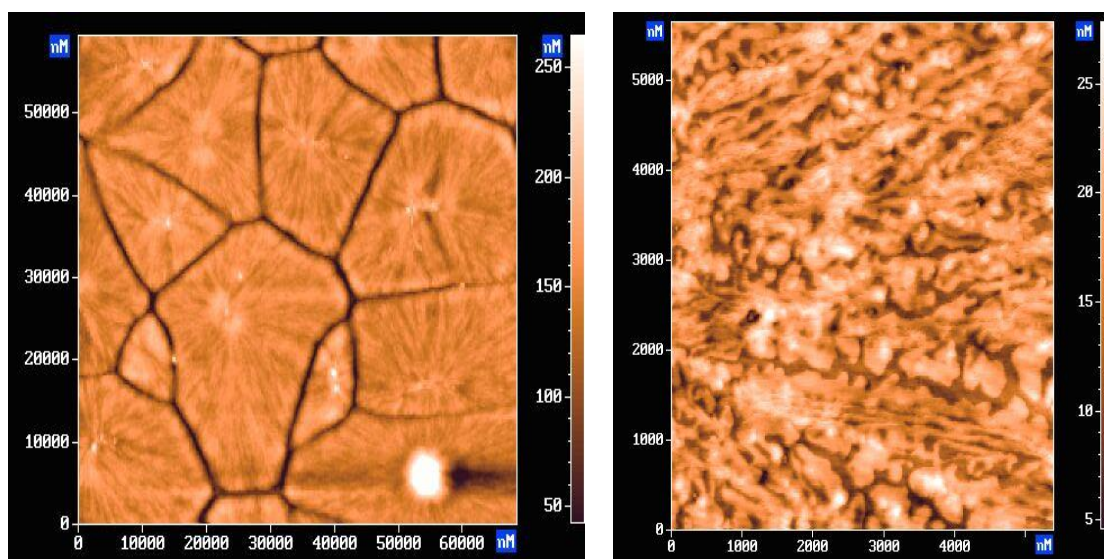


Figure 4.26 : AFM height images of thin films of macromonomer **4**: a) 60 nm thick film on SiO₂ surface after spin coating, b) 40 nm thick film on hydroxylated SiO₂ surface after melting and recrystallizing.

The thickness of these layers (fold length of PCL crystals) was 8-10 nm. Film thickness was ~40 nm as measured by ellipsometry, indicating a total of 4-5 layers in the film. Such layering can be attributed to the ordering effect of –OH end groups of PCL on –OH coated SiO₂ surface.

PPs containing both PSt and PCL side chains, **17** and **18**, showed microphase separated morphology after annealing. 40 nm thick film of polymer **17** already showed some layering after spin coating on hydroxylated surface. Annealing this film at 75 °C (above T_m of PCL and expected T_g of PS) for 45 minutes resulted in the microphase separated morphology shown in Fig. 4.27a.

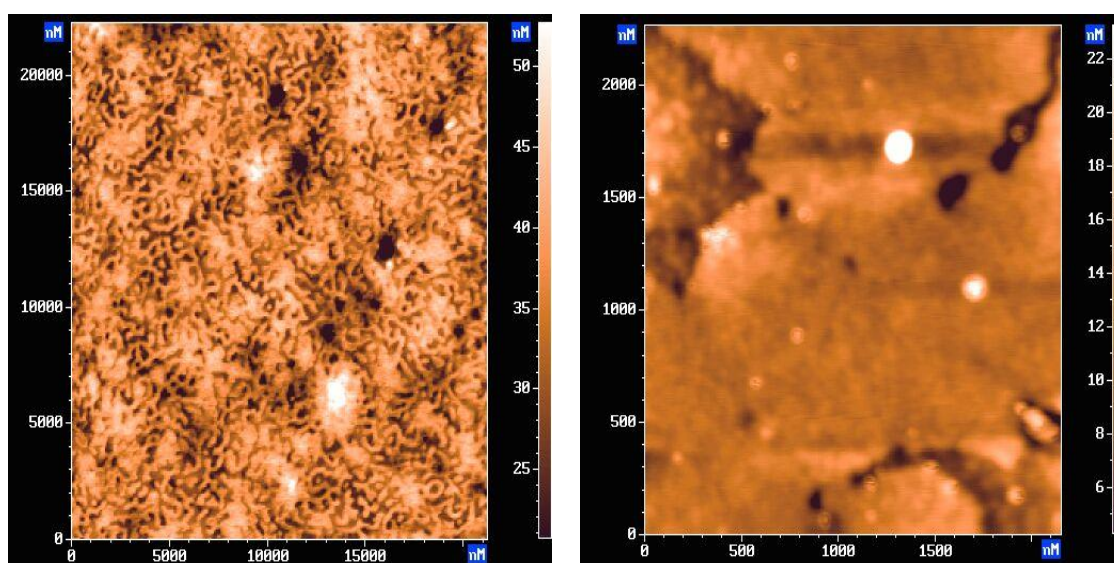


Figure 4.27 : AFM height images of thin films of PP **17**: a) 40 nm thick film on hydroxylated SiO₂ surface after annealing at 75 °C for 45 min, b) 20 nm thick film on hydroxylated SiO₂ surface after annealing at 130°C for 60 min.

The incomplete top layer is ~10 nm thick. The depth of the holes in the AFM picture indicates at least 4 layers which is consistent with the film thickness of ~40 nm as measured by ellipsometry. This layered morphology should have PCL on the substrate as the –OH end groups of PCL would prefer hydroxylated surface and PSt on top because of its lower surface energy. Bending of PCL and PSt side blocks in opposite directions of the backbone is entropically costly, but enthalpically favored. Because of alternating PCL and PSt on the backbone, the density of both PCL and PSt layer will be low after bending and this will allow significant interdigitation of the same components in the neighbouring layers. Thus, it is reasonable to assume that the film morphology consists of alternating layers of PCL and PSt, the period in the normal direction to the substrate being equal to the sum of thicknesses of PCL

layer and PSt layer. MW of PSt side block in **17** is 2300 g/mole. Radius of gyration, R_g , of PSt side block is only 1.3 nm.

So in one period of layers (PCL+PSt), PCL fold length of 8-10 nm will be dominant, with amorphous PSt forming a very thin (1.3 nm thick) layer. Layered morphology is very stable in thin films. Even after annealing a 20 nm thick film at 160 °C for 1 hour, layered structure with layer thickness of 10 nm is still seen (Fig. 4.27b). This is also an indication of strong interaction between –OH end groups of PCL and the substrate.

Polymer **18** also showed similar layered morphology in thin films.

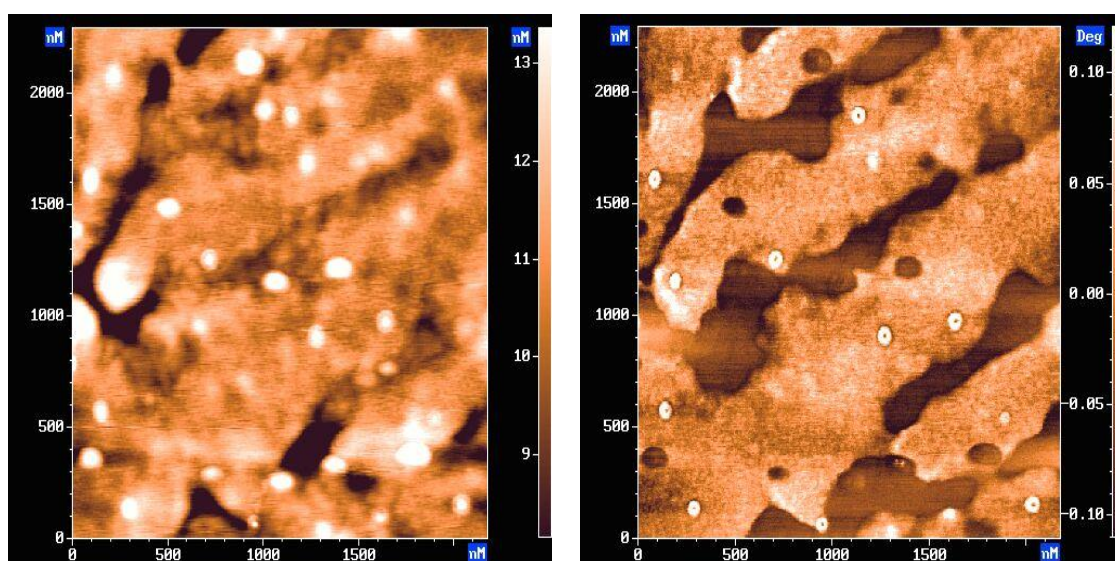


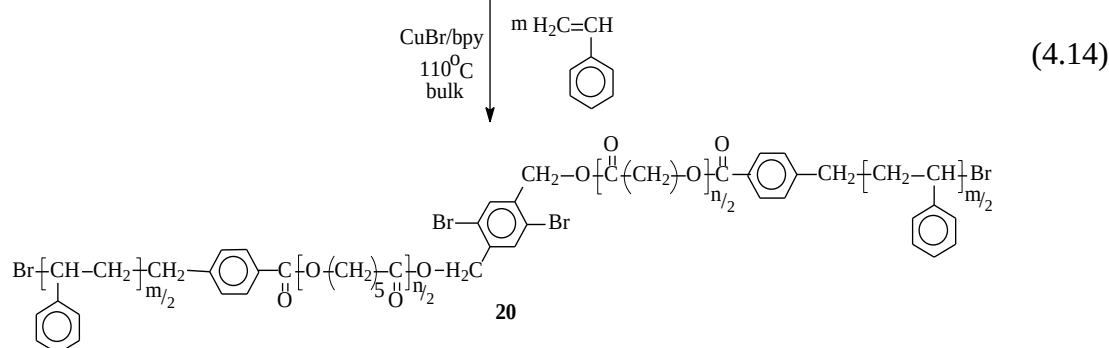
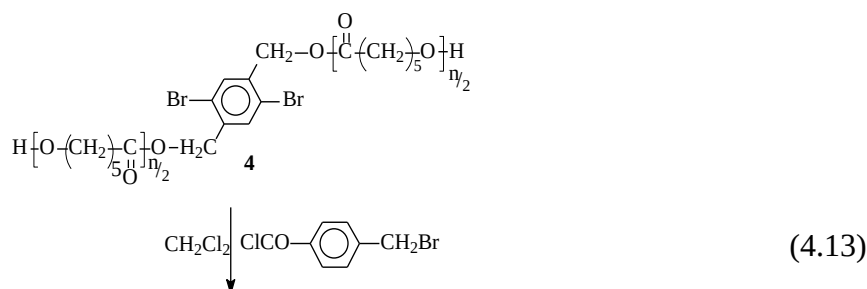
Figure 4.28 : AFM images of 24 nm thick film of PP **18** on hydroxylated SiO₂ surface after annealing at 130 °C for 60 min: a) height image, b) phase image.

Fig. 4.28 shows the height and phase image of a 20 nm (2 periods) thick film on hydroxylated substrate after annealing at 160 °C for 1 hour. In the height image (Fig. 4.28a) 2-3 nm thick top layer is seen on top of underlying layer. The thickness of this top layer is close to R_g of PSt side blocks and can be attributed to PSt layer. As described above, PSt is also favored to be on top due to its lower surface energy. Phase image (Fig. 4.28b) shows very nice contrast between the top layer and the underlying layer which indicates a significant difference in the viscoelasticity of these two layers. The underlying layer is the PCL layer.

4.3 Synthesis of Polyphenylenes with PCL-b-PSt Side Chains

4.3.1 Preparation of PCL-b-PSt Macromonomer

The strategy for synthesis of PCL-*b*-PSt macromonomer was to transform the final OH groups of the PCL **4** synthesized by ROP, in initiating sites for ATRP (4.13-4.14). The reaction of **4** with 4-bromomethyl benzoyl chloride provided a macromolecular bifunctional initiator **19** (4.13), with final benzyl bromine groups [235].



In order to assure a complete functionalization of the polymer, a high excess of 4-bromomethyl benzoyl chloride and long reaction time was used. The ^1H -NMR spectrum of **19** (Figure 4.29) registered in CDCl_3 shows very clear the presence of the new groups at 8.13-7.91 ppm (**l**), 7.55-7.34 ppm (**m**) and 4.60-4.52 (**n**). In the same time the $\text{CH}_2\text{-O}$ protons from 5.09-5.02 ppm (**b**) belonging to the initiator used in ROP of CL and present in the spectrum of PCL, can be also identified in the spectrum of **19**. Moreover, the $\text{CH}_2\text{-OH}$ protons (**h**) appeared in the PCL spectrum at 3.64-3.45 ppm are not present in the case of **19**. A new peak at 4.30-4.22 (**k**) appears

in the spectrum of **19**, corresponding to the new vicinity (ester group) of the last CH_2 protons of PCL.

A slight increase in the molecular weight is noticed in both GPC measurements and ^1H NMR calculations for **19** as compared to the precursor **4**, while the polydispersity is maintained at the same low value (Table 4.6). This can be the consequence of partial fractionation during the purification of **19**.

Table 4.6 : Molecular weight characteristics of the PCL based polymers

Polymer	Mn_{HNMR}	Mn_{GPC}	PDI
4	3050 ($n_{\text{CL}}=24$)	4270	1.12
19	3300 ($n_{\text{CL}}=24.6$)	5300	1.11
20	5200 ($n_{\text{CL}}=25$, $m_{\text{St}}=19$)	11500	1.07

The next step for obtaining the PCL-*b*-PSt macromonomer was the ATRP of styrene using **19** as bifunctional macroinitiator. A polymer with average polymerization degree $\text{GP}_{\text{n,PCL}} = 25$ and $\text{GP}_{\text{n,PSt}} = 19$ was obtained (values calculated from ^1H -NMR spectrum) (Table 4.6). Conversion of styrene was determined gravimetrically (22%) and $\text{M}_{\text{n,th}}$ (5120) was calculated with the formula given before in equation 2.

The difference observed in molecular weight values determined by ^1H -NMR and GPC measurements may be due to the influence of PCL component of the copolymer since GPC is calibrated with PSt standards. However, the value of $\text{M}_{\text{n,th}}$ is closer to that found from the ^1H -NMR spectrum. In the ^1H -NMR spectrum of the copolymer **20**, registered in CDCl_3 (Figure 4.29), can be identified the peaks belonging to both PSt and PCL blocks. Moreover, the peaks originating from 2,5-dibromo-1,4-(dihydroxymethyl)benzene, the bifunctional initiator for ROP of ϵ -caprolactone (7.61-7.52 ppm (**a**) and 5.21-5.08 ppm (**b**)) are still present in the spectrum of **20**. Additionally, these peaks made it possible to evaluate the polymerization degree of PCL block in a similar way as for **4** and **19**. The value $n_{\text{CL}} = 25$ is only very slightly higher than that calculated for **19** (Table 4.6). The same calculation could also be performed for the PSt block, and a value of $n_{\text{St}} = 19$ was obtained. Therefore, the value of 5200 obtained from the integrals of ^1H -NMR spectrum was considered to be the most reliable one and was taken in account for further calculations. It is interesting to note that the polydispersity of the polymer decreased from 1.11 to 1.07 after the ATRP reaction.

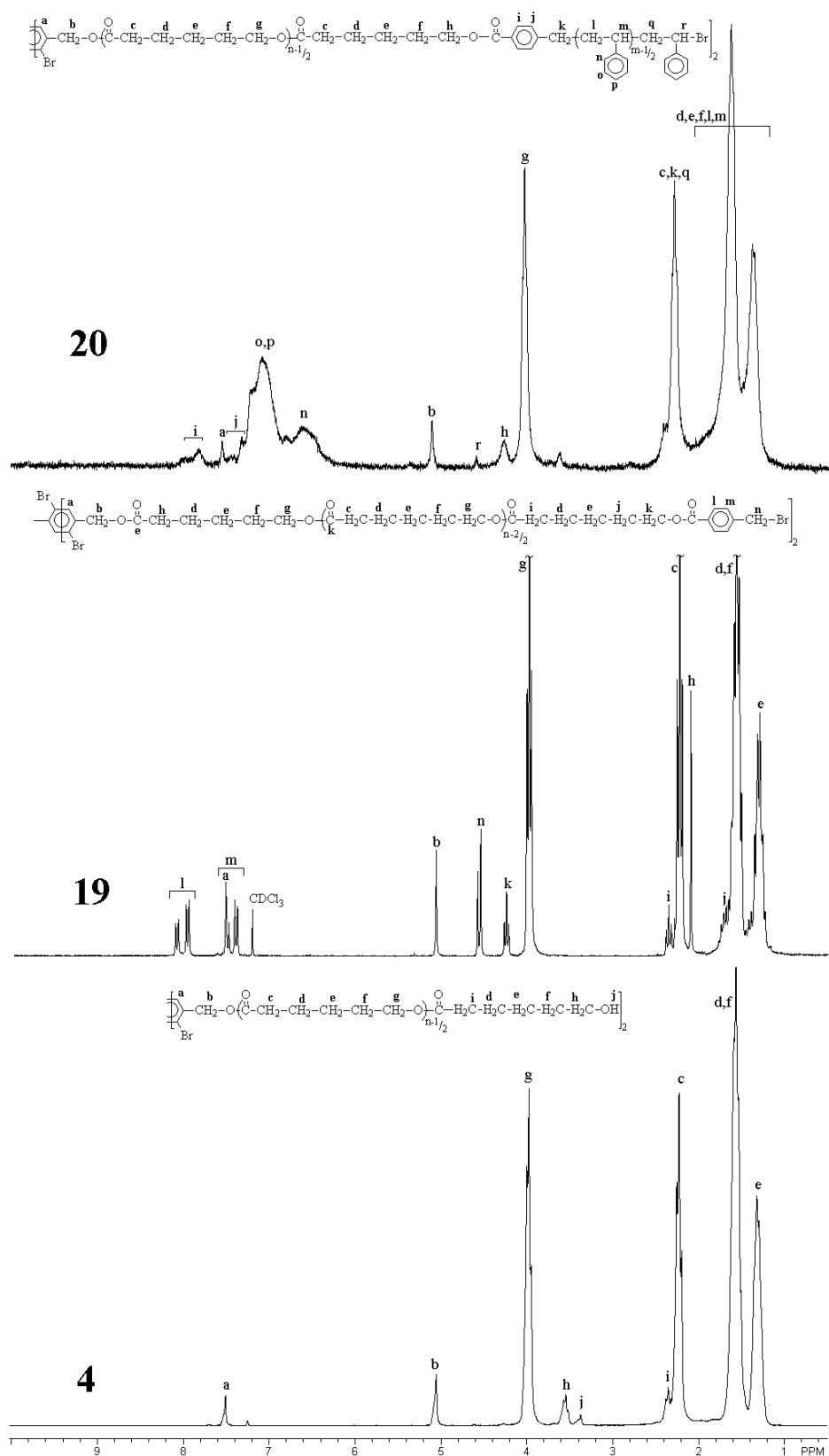


Figure 4.29 : ^1H -NMR spectra of initial PCL macromonomer **4**, the PCL functionalized with benzyl bromide **19**, and the copolymer PCL-b-PSt **20**.

The ^{13}C -NMR spectrum of **20** in CDCl_3 (Figure 4.30), also shows peaks characteristic to both components. For example at 174.29-172.77 ppm (**e**) and 31.03-20.09 ppm (**i**, **g**, **h**) appear the signals due to the carbons belonging to the PCL component, while the peaks from 145.51-144.83 ppm (**s**), 132.70-123.45 ppm (**t**, **x**, **y**, **m**, **n**, **l**), 47.86-37.60 ppm (**r**) are due to PSt carbons. Signals attributed to the end groups could be also identified at 166.71 ppm (**k**), 144.50 ppm (**o**), 142.13 (**w**), 137.08 (**b**), 132.88 (**a**), 121.93 (**c**), confirming the proposed structure.

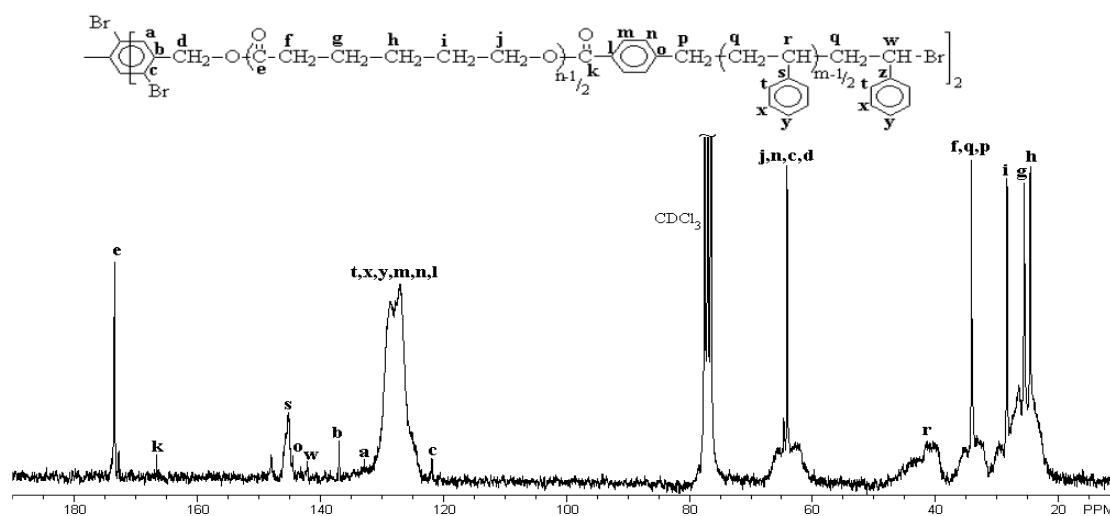
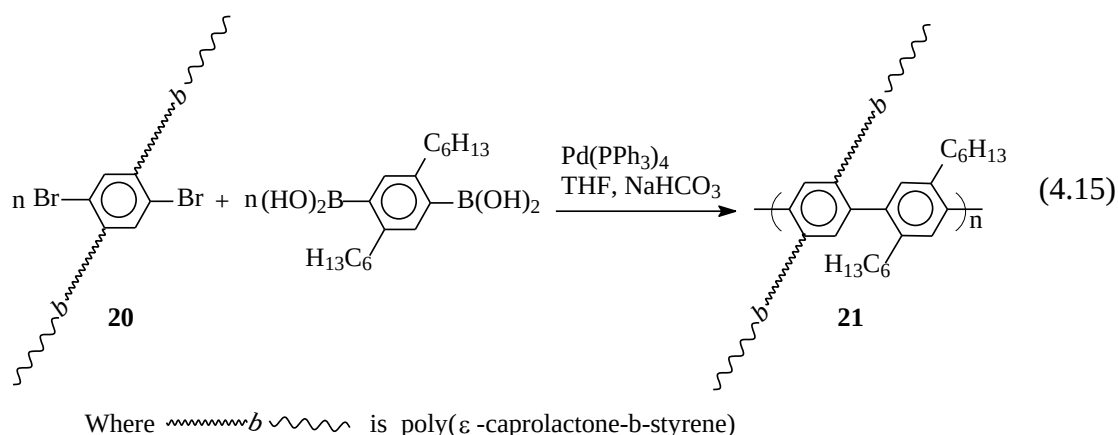


Figure 4.30 : ^{13}C -NMR spectrum of PCL-*b*-PSt macromonomer **20**.

4.3.2 Preparation of PPs with PCL-*b*-PSt Side Chain

As block copolymer **20** still contains the central 2,5 dibromo-1,4-phenylene moiety, it is appropriate to use it as macromonomer in coupling reactions in the presence of transition metals catalysts (Suzuki or Yamamoto type polycondensations) for the synthesis of grafted PPPs. The subsequent step was to use the macromonomer in a Suzuki type polymerization in combination with 2,5-dihexylbenzene-1,4-diboronic acid as reaction partner (4.15).



A polymer with solubilities similar to those of the starting block-copolymers (THF, chlorinated solvents) and good film-forming properties was obtained.

The $^1\text{H-NMR}$ spectrum of the polymer **21** obtained by Suzuki method (Figure 4.31) shows clearly the presence of hexyl groups in the composition of the polymer as the signal of aliphatic CH_3 (**q**) group appears separately at 0.66-0.95 ppm. Moreover, it is verified the relation $I_q/6 \approx I_g/2n_{\text{CL}}$, where I_q and I_g are the intensities of the peaks corresponding to the CH_3 protons of hexyl groups and the of $\text{CH}_2\text{-O}$ protons of PCL block, respectively and n_{CL} is the polymerization degree of PCL. This result confirms that PSt chains and hexyl groups are present in equal amounts (alternating) in the PPs structures. The same relation is also obtained when the integrals of aromatic protons of the PSt blocks are used in the calculation, instead of those of **g** protons.

Due to the high molecular weight and polydispersity of the polymer **21**, consequently further broadening of the peaks, the identification of other end groups in the $^1\text{H-NMR}$ spectrum was not possible.

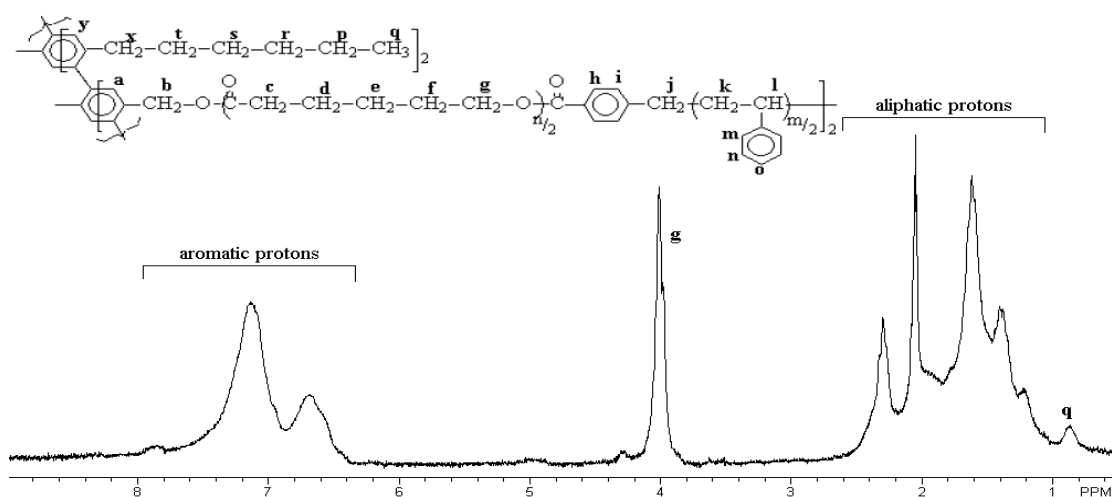


Figure 4.31 : ^1H -NMR spectrum of PPP with PCL-*b*-PSt side chains **21**

The value of molecular weight of polymer **21** measured by GPC reported in Table 4.7 can not be very reliable. On one hand, the polymer contains PCL blocks that make imprecise the evaluation of M_n by GPC using PSt standards, on the other hand, because of the highly branched or comb-like structure of the obtained polyarylenes the value should be taken only as a minimum estimation. In any case, the GPC trace of polymer **21** (Figure 4.32) shows a very significant shift to higher molecular weights as comparing with macromonomer **20**, proving that the new polymer was readily formed. In the Figure 4.32 are also presented the GPC traces of the starting PCL **4** as well as the benzyl bromide functionalized one, **19**.

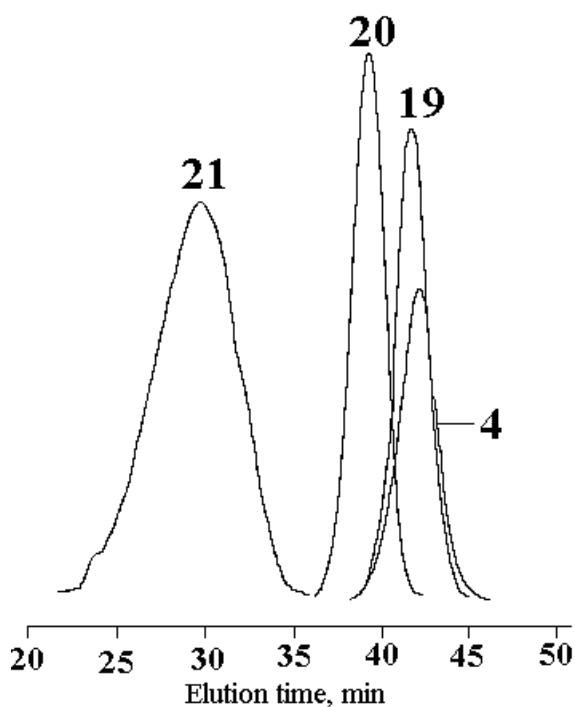
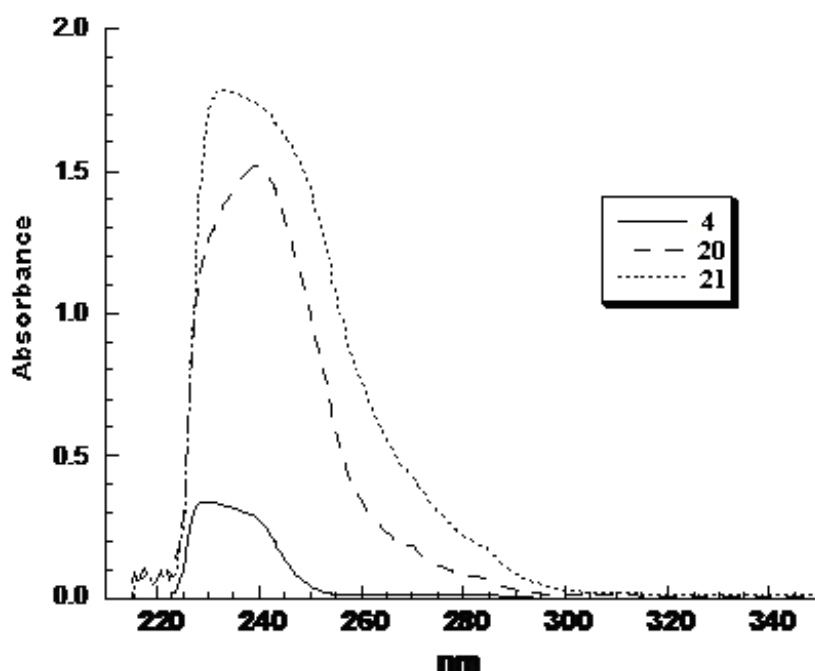


Figure 4.32 : GPC traces of PCL macromonomer **4**, the PCL functionalized with benzyl bromide **19**, and the copolymer PCL-*b*-PSt **20**.

Table 4.7 : Molecular weight characteristics of the PCL based polymers

Polymer	Mn _{HNMR}	Mn _{GPC}	PDI
20	5200 (n _{CL} =25, m _{St} =19)	11500	1.07
21	-	62800	2.87

Figure 4.33 shows important differences in the UV absorption spectra of the starting PCL **4** as comparing with the block-copolymer **20** and the corresponding PPP **21**, registered in CH₂Cl₂ solutions with the same concentrations. The maximum of absorptions between 225-250 nm have increased intensities in the order of **4**<**20**<**21**. While the difference between **4** and **20** is attributed to the aromatic rings of the new added PSt component, the higher absorption for **21** can be due to the PPP main chain. Moreover, absorption shoulders at 270 nm and 285 nm are a further evidence for the presence of PPP based chain.

**Figure 4.33** : UV spectra of starting PCL **4**, the block-copolymer **20** and the PPP with polymeric substituents **21**.

The thermal behavior of the polymers was followed by DSC (30-300°C) under nitrogen, with a heating rate of 10°C/min. The DSC thermograms (Figure 4.34) showed endothermic peaks characteristic to the melting phenomenon of the PCL is present in all the cases at 48°C (**4**), 44°C (**19**), 40°C (**20**) and 36°C (**21**). A decrease of the melting temperature of PCL with the increasing of complexity of the polymers was also noted. The introducing PSt component into polymer **20** can disturb the

length of ordering of PCL chains. In the case of PPP, the intercalation of hexyl side groups between PCL-*b*-PSt pendant chains can cause not only a decrease of in the melting temperature, but also the corresponding endothermic peak has lower intensity.

In this connection, it is worth to mention previous works on the thermal behavior of PPPs with polystyrene/polytetrahydrofuran (PTHF) side chains [234] or with PSt/PCL ones mentioned above [232]. Interestingly, the T_g of PSt component was missing. This unusual observation was explained in terms of inclusion phenomenon of PSt chains inside the PCL or PTHF segments. This leads to a decreased freedom of PSt segments and consequently hinders their thermal mobility. In the present case, however, the T_g of PSt block is present at about 76°C for both PSt-*b*-PCL **20** and PPP **21**. As the the PSt blocks are at the end of the PPP side chains, their mobility is not disturbed by PCL chains and as a consequence, the T_g of polystyrene in polymer **21** can successfully be identified.

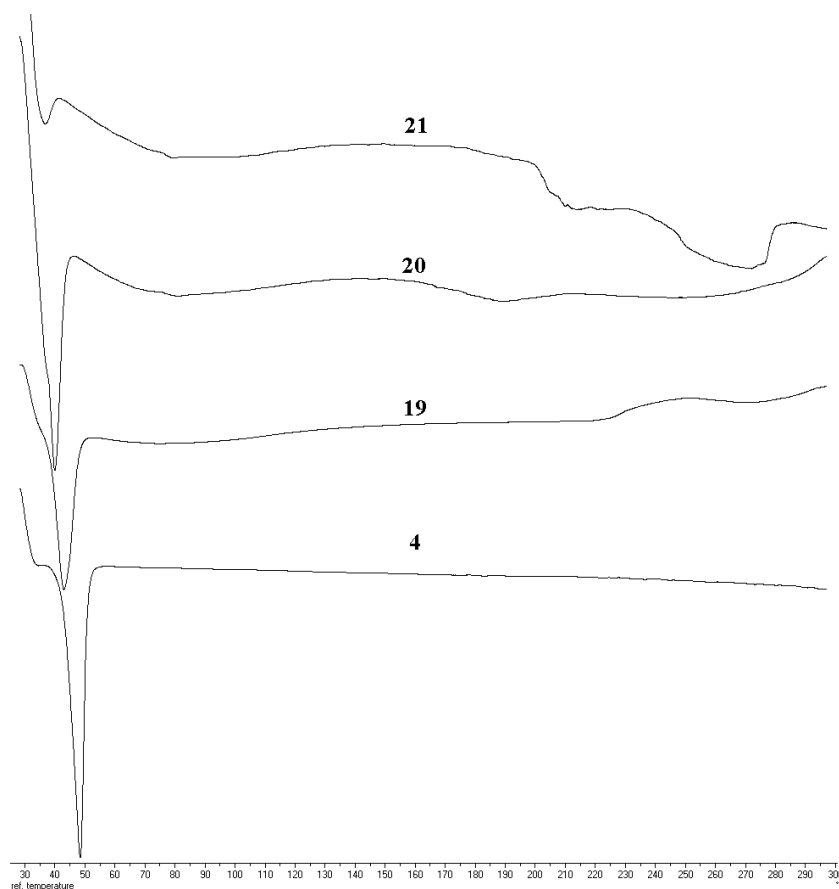


Figure 4.34 : DSC traces of PCL macromonomer **4**, the PCL functionalized with benzyl bromide **19**, and the copolymer PCL-*b*-PSt **20**.

5. CONCLUSIONS

In the present thesis, special macromolecular architectures were successfully designed, by combining polyphenylation process with controlled polymerization methods such as ATRP or ROP. Precursor polymers synthesized by ATRP or ROP were, in the next step, employed in Suzuki or Yamamoto type cross-coupling reactions, affording the designed architecture.

Effective bifunctional initiators for ROP of ϵ -CL and ATRP of styrene, were designed and synthesized. Dual functional initiator having hydroxymethyl functionalities was used in the polymerization of ϵ -CL in the presence of $(\text{SnOct})_2$ catalyst while the compounds with benzyl bromine moities initiated ATRP of St by using $\text{CuBr}/2,2'$ -bipyridine. By these polymerization methods, polymeric precursors that posses designed molecular weights with narrow molecular weight distributions were prepared.

The presence of a central benzene ring, 2,5-disubstituted with bromine atoms in the structure of these polymers, make them proper for using them as macromonomers for synthesis of PPs, by subsequent Suzuki or Yamamoto type reactions. Poly(p-phenylene)-*graft*-poly(ϵ -caprolactone) copolymers were obtained by combining ROP and cross-coupling processes. The new comb like PPP with PCL side substituents have very good solubility in common organic solvents at room temperature. 2,5-dibromo- or 3,5-dibromo- phenylene moities at one end of the macromonomers permitted to obtain PPs with PSt lateral chains. The Yamamoto co-polycondensation of the these macromonomers with a PCL one provided PPs with both PSt and PCL side chains.

On the other hand, in order to get another novel architecture, a bifunctional macroinitiator for ATRP was obtained by reaction of OH end groups a PCL macromonomer and 4-bromomethyl benzoyl chloride. The polymerization of styrene in the presence of this macroinitiator, in conjunction with $\text{CuBr}/2,2'$ -bipyridine as

catalyst, provided a well defined block-macromonomer with the structure PCL-*b*-PSt and low polydispersity. The presence of a central 2,5 dibromo-1,4-phenylene moiety in the structure of block copolymer provides possibility for further use in a Suzuki type polycondensation in conjugation with 2,5-dihexylbenzene-1,4-diboronic acid. In this way a PPP bearing as side chains PCL-*b*-PSt units was obtained.

The structures of the synthesized polymers were proved by spectral methods (^1H (^{13}C)-NMR, IR) and by GPC measurements. Optical properties were studied by UV and fluorescence spectroscopy and the thermal behaviour was studied by DSC and TGA. Spin coated thin films of macromonomers and polymers showed morphological transitions after annealing at temperatures above T_m and T_g of the components, in consistent with DSC characterization. Morphological characterization by AFM confirmed crystalline structure of PCL macromonomer. A layered microphase separated morphology was observed for PPs containing PSt and PCL blocks. The resulting morphology was consistent with the chemical structure of alternating PSt and PCL side blocks along the backbone.

This work clearly demonstrates that further complex macromolecular structures based on polyphenylenes can readily be synthesized by using the synthetic strategy followed above. The present research opens new pathways for obtaining new materials useful in many high-tech applications such in bioapplication or light-emitting diodes. For example, PCL is known to be a biocompatible and biodegradable polymer. The incorporation of such segment in a regular manner to PPs may create novel functional polymers.

REFERENCES

- [1] **Meredith, P.L.**, 2000. Life sciences and materials: A Successful Marriage is Possible, *J. Polym. Sci.; Part A: Polym. Chem.*, **38(4)**, 667-678.
- [2] **Tovar, J.D. and Swager, T.M.**, 2003. Cofacially Constrained Organic Semiconductors, *J. Polym. Sci.; Part A: Polym. Chem.*, **41(22)**, 3693-3702.
- [3] **Qiu, H. and Wan, M.**, 2001. Synthesis, Characterization and Electrical Properties of Nanostructural Polyaniline Doped with Novel Sulfonic Acids (4-{n-[4-(4-nitrophenylazo)phenoxy]alkyl}aminobenzene sulfonic acid), *J. Polym. Sci.; Part A: Polym. Chem.*, **39(20)**, 3485-3497.
- [4] **De Risi, F. R., D'Ilario, L. and Martinelli, A.**, 2004. Synthesis and Characterization of Epoxidized Polybutadiene/Polyaniline Graft Conducting Copolymer, *J. Polym. Sci.; Part A: Polym. Chem.*, **42(12)**, 3082-3090.
- [5] **Cacialli, F., Li, X.C., Friend, R.H., Moratti, S.C. and Holmes, A.B.**, 1995. Light- Emitting Diodes Based On Poly(methacrylates) With Distyrylbenzene and Oxadiazole Side, *Synth. Met.* **75(2)**, 161-168.
- [6] **Hochfilzer, C., Tasch, S., Winkler, B., Huslage, J. and Leising, G.**, 1997. Electroluminescent Nanostructures in New Polystyrene-Oligo (phenylene-vinylene) Graft Copolymer, *Synth. Met.*, **85(1)**, 1271-1272.
- [7] **Ivory, D.M., Miller, G.G., Sowa, J.M., Shacklette, L.W., Chance, R.R. and Baughmann, R.H.**, 1979. Highly Conducting Charge-Transfer Complexes of Poly(p-phenylene), *J. Chem. Phys.*, **71**, 1506.
- [8] **Schluter, A.D.**, 2001. The Tenth Anniversary of Suzuki Polycondensation (SPC). *J. Polym. Sci. Part A. Polym. Chem.*, **39**, 1533-1556.
- [9] **Gin, D.L. and Conticello, P.V.**, 1996. Poly(p-phenylene): New directions in Synthesis and Application, *Trip.Reviews.*, **4(7)**, 217-223.
- [10] **Schluter, A.D. and Wegner, G.**, 1993. Palladium and Nickel Catalyzed Polycondensation- The Key to Structurally Defined Polyarylenes and Other Aromatic Polymers, *Acta. Polym.*, **44(2)**, 59-69.
- [11] **Witteler, H., Lieser, G., Wegner G. and Schulze, M.**, 1993. Textures of Liquid-crystalline Phases of Substituted Poly(p-phenylene)s, *Makromol. Chem. Rapid Commun.* **14(8)**, 471-480.
- [12] **Grem, G., and Leising, G.**, 1993. Electroluminescence of wide-band gap Chemically Tunable Cyclic Conjugated Polymers, *Synth. Metals.*, **57**,. 4105-4110.

- [13] **Berlin, A. and Zotti, G.**, 2000. Self-assembly of Mono- and Multilayers of Polyconjugated Conducting Polymers, *Macromol. Rapid Commun.* **21(7)**, 301-318.
- [14] **Li, X.G., Zhou, H.J., Huang, M.R., Zhu, M.F. and Chen, Y.M.**, 2004. Facile synthesis and characterization of the copolymers and their pure nanoparticles from aniline with 4-sulfonic diphenylamine, *J. Polym. Sci. Part A. Polym. Chem.*, **42(13)**, 3380-3394.
- [15] **Guijun, Y., Boqiu, W., Yuping, D., Maofeng, Z., Zhaohui, Y., Qiaoling, Y., Yip, L.J.W. and Benzhong, T.** 2004. Self-assembly and photovoltaic properties of multilayer films based on partially doped polyaniline and poly(4-carboxyphenyl)acetylene, *J. Polym. Sci., Part A. Polym. Chem.*, **42(13)**, 3091-3394.
- [16] **Berresheim, A.J., Muller, M., Mullen, K.**, 1999. Polyphenylene Nanostructures, *Chem. Rev.* **99(7)**, 1747-1785.
- [17] **Lauter, U., Meyer, W.H. and Wegner, G.**, 1997. Molecular Composites from Rigid-Rod Poly(*p*-phenylene)s with Oligo(oxyethylene) Side Chains as Novel Polymer Electrolytes, *Macromolecules*, **30(7)**, 2092-2101.
- [18] **Francois, B., Widawski, G., Rawiso, M., and Cesar, B.**, 1995. Block-Copolymers with Conjugated Segments - Synthesis and Structural Characterization, *Synth. Met.*, **69(1)**, 463-466.
- [19] **Yamamoto, T.**, 1992. Electrically Conducting and Thermally Stable π -conjugated Poly(arylene)s Prepared by Organometallic Processes, *Prog. Polym. Sci.*, **17(6)**, 1153-1205.
- [20] **Matyjaszewski, K.**, 1998. Controlled Radical Polymerization, Vol. 685, *Acs Symposium Series*, American Chemical Society, Washington DC.
- [21] **Webster, O.W.**, 1991. Living Polymerization Methods, *Science*, **251(4996)**, 887-893.
- [22] **Wang, J.S. and Matyjaszewski, K.**, 1995. Controlled Living Radical polymerization Atom Transfer Radical Polymerization in the Presence of Transition-metal Complexes, *J. Am. Chem. Soc.*, **117(20)**, 5614-5615.
- [23] **Gaynor, S.G., Edelman, S. and Matyjaszewski, K.**, 1996. Synthesis of Branched and Hyperbranched Polystyrenes, *Macromolecules*, **29(3)**, 1079-1081.
- [24] **Storey, R.F., Wiggins, J.S. and Puckett, A.D.**, 1994. Hydrolyzable Poly(ester-urethane) Networks From L-Lysine Diisocyanate and D,L-Lactide Epsilon-Caprolactone Homopolyester and Copolyester Triols, *J. Polym. Sci., Part A. Polym. Chem.*, **32(12)**, 2345-2363.

- [25] **Degirmenci, M., Izgin, O. and Yagci, Y.,** 2004. Synthesis and Characterization of Cyclohexene Oxide Functional Poly(ϵ -caprolactone) Macromonomers and Their Use In Photoinitiated Cationic Homo- and Copolymerization, *J. Polym. Sci., Part A. Polym. Chem.*, **42(13)**, 3365-3372.
- [26] **Wang, Y., Lu, G. and Huang, J.,** 2004. Copolymerization of the Macromonomer Poly(ethylene oxide) With Styryl End Group and Styrene in the Presence of Poly(ϵ -caprolactone) With 2,2,6,6- Tetramethylpiperidiny-1-oxy End Group by Controlled Radical Mechanism, *J. Polym. Sci., Part A. Polym. Chem.*, **42(9)**, 2093-2099.
- [27] **Joubert, M., Delaite, C., Bourgeat-Lami, E. and Dumas, P.,** 2004. Ring-Opening Polymerization of ϵ -Caprolactone and L-Lactide from Silica Nanoparticles Surface, *J. Polym. Sci., Part A. Polym. Chem.*, **42(8)**, 1976-1984.
- [28] **Kovacic, P. and Jones, M.B.,** 1987. Dehydro Coupling of Aromatic Nuclei by Catalyst-Oxidant Systems: Poly(p-phenylene), *Chem.Rev.*, **87**, 357-379.
- [29] **Natta, G., Mazzanti, G. and Corradini, P.,** 1958. Stereospecific Polymerization of Acetylene, *Atti. Accad. Naz. Lincei Rend. Cl. Sci. Fis. Mat. Nat.*, **25**, 3-12; *Chem. Abstr.* 1959,**53**,139851.
- [30] **Watson, Jr.W.H., McMordie, Jr.W.C. and Lands, L.G.,** 1961. Polymerization of Alkynes by Ziegler-type Catalyst, *J. Polym. Sci.*, **55**, 137-144.
- [31] **Hatano, M., Kambara, S. and Okamoto, S.,** 1961. Paramagnetic and electric properties of polyacetylene, *J. Polym. Sci.*, **51**, S26.
- [32] **Berets, D.J. and Smith, D.S.,** 1968. Electrical Properties of linear Polyacetylene, *Trans. Faraday Soc.*, **64**, 823.
- [33] **Kleist, F.D. and Byrd, N.R.,** 1969. Preparation and properties of polyacetylene, *J. Polym. Sci. A-1*, **7**, 3419.
- [34] **Shirakawa, H. and Ikeda, S.,** 1971. Infrared Spectra of Poly(acetylene), *Polym. J.*, **2(2)**, 231.
- [35] **Shirakawa, H., Ito, T., and Ikeda, S.,** 1973. Raman-Scattering and Electronic-Spectra of Poly(acetylene), *Polym. J.*, **4**, 460.
- [36] **Ito, T., Shirakawa, H., and Ikeda, S.,** 1974. Simultaneous Polymerization and Formation of Poly(acetylene) Film on Surface of Concentrated Soluble Ziegler-Type Catalyst Solution, *J. Polym. Sci. Polym. Chem.*, **12(1)**, 11-20.
- [37] **Ito, T., Shirakawa, H., and Ikeda, S.,** 1975. Thermal Cis-Trans Isomerization and Decomposition of Poly(acetylene), *J. Polym. Sci. Polym. Chem.*, **13(8)**, 1943-1950.

- [38] **Shirakawa, H., Ito, T., and Ikeda, S.,** 1978. Electrical Properties of Poly(acetylene) with Various Cis-Trans Compositions, *Macromol.Chem.Phys.*,**179(6)**, 1565-1573.
- [39] **Bott, D.C.,** Structural Basis for Semiconducting and Metallic Polymers, *Handbook of Conducting Polymers*,**Vol.2(33)**.
- [40] **Kovacic, P. and Kyriakis, A.,** 1963. Polymerization of Benzene to p-Polyphenyl by Aluminum Chloride-Cupric Chloride , *J. Am. Chem. Soc.*, **85**, 454.
- [41] **Ried, W. and Freitag, D.,** 1968. Oligophenyls, Oligophenylenes, and Polyphenyls, a Class of Thermally Very Stable Compounds *Angew. Chem. Int. Ed.*, **7(11)**, 835-844.
- [42] **Shacklette, L.W., Chance, R.R., Ivory, D.M., Miller, G.G. and Baughmann, R.H.,** 1980. Electrical and Optical Properties of Highly Conducting Charge-Transfer Complexes of Poly(p-phenylene), *Synth.Met.*, **1(3)**, 307-320.
- [43] **Jones, M.B., Kovacic, P. and Lanska, D.,** 1981. Polymerization of Aromatic Nuclei 26. Poly(p-phenylene)- Friedel-Crafts Alkylation, Molecular-Weight, and Propagation Mechanism, *J. Polym. Sci.Polym. Chem.*, **19**, 89.
- [44] **Tieke, B., Bubeck, C. and Lieser, G.,** 1982. Redox Reactions of Poly(1,4-Phenylene)- A Spectroscopic Study of Thin Transparent Films, *Macromol. Chem. Rap. Commun.*, **3(5)**, 261-268.
- [45] **Froyer, G., Maurice, F., Mercier, J.P., Riviere, D., Le Cun, M. and Auvray, P.,** 1981. Morphology of Poly(p-phenylene) Powders and Pellets, *Polymer*, **22(7)**, 992-994.
- [46] **Lerner, N.R.,** 1974. ESR and Chemical Study of Poly(p-phenylene) Formed by Using an $\text{AlCl}_3\text{-CuCl}_2$ Catalyst. *J. Polym. Sci. Polym. Chem.*, **12(11)**, 2477-2495.
- [47] **Bredas, J.L., Chance, R.R. and Silbey, R.,** 1982. Comparative Theoretical Study of the Doping of Conjugated Polymers-Polarons in Poly(acetylene) and Poly(p-phenylene), *Phys. Rev. B*, **26(10)**, 5843-5854.
- [48] **Gin, D.L., Avlyanov, J.K. and MacDiarmid, A.G.,** 1994. Synthesis and Processing of Poly(p-phenylene) via the Phosphoric Acid-Catalyzed Pyrolysis of a Stereoregular Precursor Polymer- a Characterization Study, *Synth. Met.* **66(2)**, 169-175.
- [49] **Komaguchi, K., Morita, M., Tsutsumi, H. and Matsuda, Y.,** 1990. Characteristics of Poly(p-Phenylene) Films Prepared by Electropolymerization of Benzene , *Chemistry Express*, **Vol.5**, 961-964.

- [50] **Morita, M., Komaguchi, K., Tsutsumi, H. and Matsuda, Y.,** 1992. Electrosynthesis of Poly(p-phenylene) Films and Their Application to the Electrodes of Rechargeable Batteries, *Electrochim. Acta*, **37(6)**, 1093-1099.
- [51] **Sato, K., Noguchi, M., Demachi, A., Oki, N. and Endo, M.,** 1994. A Mechanism of Lithium Storage in Disordered Carbons, *Science*, **264(5158)**, 556-558.
- [52] **Grem, G., Leditzky, G., Ulrich, B. and Leising, G.,** 1992. Realization of a Blue-Light-Emitting Device Using Poly(p-phenylene), *Adv. Mater.*, **4(1)**, 36-37.
- [53] **Grem, G., et al.,** 1995. Stable Poly(p-phenylene) and Their Application in Organic Light-Emitting Devices, *Synth. Met.*, **71(1-3)**, 2193-2194.
- [54] **Rubinson, J.F., Neff, S., Mark, H.B., Galal, A. and Atta, N.F.,** 1995. Characterization and Investigation of the Electrocatalytic Properties of Poly(p-phenylene) Modified Electrodes, *J. Electroanal. Chem.*, **384(1-2)**, 19-23.
- [55] **Kim, H.K. and Ober, C.K.,** 1992. Acid-Catalyzed Photoaromatization of Poly(cyclohexadiene-1,2-Diol) Derivatives into Polyphenylene, *Polym. Bull.*, **28**, 33.
- [56] **Nehring, J., Amstutz, H., Holmes, P.A. and Nevin, A.,** 1987. High-Pretilt Polyphenylene Layers for Liquid-Crystal Displays, *Appl. Phys. Lett.*, **51(16)**, 1283-1284.
- [57] **Shibata, T., Kabumoto, A., Shiragami, T., Ishitani, O., Pac, C. and Yanagida,** 1990. Novel Visible-Light-Driven Photocatalyst- Poly(p-phenylene)- Catalyzed Photoreductions of Water, Carbonyl-Compounds and Olefins, *J. Phys. Chem.*, **94(5)**, 2068-2076.
- [58] **Bilow, N. and Jones, J.R.,** 1973. Solid Lubricants and Method, *U.S. Patent* 3 730 893; 1973. *Chem. Abstr.*, **79**, 44192.
- [59] **Agnew, R.J. and Dille, K.L.,** 1966. Solid lubricant compositions, *U.S. Patent* 3 278 429; 1967. *Chem. Abstr.*, **66**, 12765.
- [60] **Martinek, T.W., Haines, R.M., Weichman, R.L. and Trainer, W.J.,** 1969. High temperature grease, *U.S. Patent* 3 476 687; 1970. *Chem. Abstr.*, **72**, 14472.
- [61] **Gale, D.M.,** 1977. Toughened Linear Aromatic Polymers, *U.S. Patent* 4 011 293; 1977. *Chem. Abstr.*, **86**, 141175.
- [62] **Wang, C.S.,** 1978. Branched polyphenylene-mica composites, *U.S. Patent* 4 066 604; 1978. *Chem. Abstr.*, **88**, 122227.
- [63] **Tang, C.W. and Vanslyke, A.S.,** 1987. Organic Electroluminescent Diodes, *Appl. Phys. Lett.*, **51**, 913-915.

- [64] **Adachi, C., Tokito, S., Tsutsui, T. and Saito, S.,** 1988. Electroluminescence in Organic Films with Three Layer Structure, *Jap. J. Appl. Phys.*, **27**, L269-L271.
- [65] **Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burns, P.L. and Holmes, A.B.,** 1990. Light-emitting Diodes Based on Conjugated Polymers, *Nature*, **347**, 539.
- [66] **Braun, D. and Heeger, A.J.,** 1991. Visible Light Emission From Semiconducting Polymer Diodes., *Appl. Phys. Lett.*, **58**, 1982-1984.
- [67] **Ohmori, Y., Uchida, M., Muro, K. and Yoshino, K.,** 1991. Visible-Light Electroluminescent Diodes Utilizing Poly(alkylthiophene), *Jap. J. Appl. Phys.*, **30**, L1938-L1940.
- [68] **Ohmori, Y., Uchida, M., Muro, K. and Yoshino, K.,** 1991. Blue Electroluminescent Diodes Utilizing Poly(alkylfluorene), *Jap. J. Appl. Phys.*, **30**, L1941-L1943.
- [69] **Grem, G., Leditzky, G., Ullrich, B. and Leising, G.,** 1992. Realization of a Blue-light-emitting Device Using Poly(p-phenylene), *Adv. Mater.*, **4**, 36-37.
- [70] **Grem, G., Leditzky, G., Ullrich, B. and Leising, G.,** 1992. Blue Electroluminescence Device Based on a Conjugated Polymer, *Synth. Metals.*, **51**, 383-389.
- [71] **Scherf, U. and Mullen, K.,** 1991. A Soluable Ladder Polymer via Bridging of Functionalized Poly(p-phenylene)-Precursors, *Macromol. Chem. Rapid. Comm.*, **12**, 489-497.
- [72] **Rehan, M., Schluter, A.D. and Wegner, G.,** 1990. Soluble Poly(p-phenylene)s 3. Variation of the Length and the Density of the Solubilizing Side-Chains *Macromol. Chem.*, **191(9)**, 1991-2003.
- [73] **Ballard, D.G.H., Courtis, A., Shirley, I.M. and Taylor, S.C.,** 1988. Synthesis of Polyphenylene from a Cis-Dihydrocatechol, a Biologically Produced Monomer, *Macromolecules*, **21(2)**, 294-304.
- [74] **Stamm, M.,** 1984. Synthesis and Characterization of Conducting Oriented Fibers of Poly(p-phenylene), *Mol. Cryst. Liq. Cryst.*, **105(1-4)**, 259-271.
- [75] **Shi, G., Xue, G., Li, C., Jin, S. and Yu, B.,** 1994. Uniaxial Oriented Poly(p-phenylene) Fibrils and Films, *Macromolecules*, **27(13)**, 3678-3679.
- [76] **Feast, W.J., Tsibouklis, J., Pouwer, K.L., Groenendaal, L. and Meijer, E.W.,** 1996. Synthesis, Processing and Material Properties of Conjugated Polymers, *Polymer*, **37(22)**, 5017-5047.
- [77] **Milosevich, S., Saichek, K., Hinchey, L., England, W.B. and Kovacic, P.,** 1983. Coordination in benzene dimer cation radical, *J. Am. Chem. Soc.*, **105(5)**, 1088-1090.

- [78] **Soma, Y., Soma, M. and Harada, I.**, 1983. Resonance Raman-Spectra of Benzene Adsorbed on Cu^{+2} Montmorillonite-Formation of Poly(p-phenylene) Cations in the Interlayer of the Clay Mineral, *Chem. Phys. Lett.*, **99(2)**, 153-156.
- [79] **Aldissi, M. and Lepins, R.**, 1984. Synthesis of Soluble Conducting Polymers- Poly(acetylene)s and Polyaromatics, *J. Chem. Soc. Chem. Commun.*, **4**, 255-256.
- [80] **Aeiyaich, S., Soubiran, S., Lacaze, P. C., Froyer, J. and Pelous, Y.**, 1989. A New Method for Obtaining Poly(p-phenylene) Films by Electrochemical Oxidation of (Benzene- SbF_5) PI-Complexes in SO_2 Medium, *Synth. Met.*, **32**, 103.
- [81] **Levi, M.D., Pisarevskaya, E.Yu., Molodkina, E.B. and Danilov, A.I.**, 1993. Electrochemical-Behaviour and Structural Characterization of Highly Crystalline Poly(p-phenylene) Films Obtained by Oxidation of Benzene in a Concentrated Sulfuric-Acid Emulsion, *Synth. Met.*, **54(1-3)**, 195-201.
- [82] **Oshawa, T., Inoue, T., Takeda, S., Kaneto, K. and Yoshino, K.**, 1986. Electrochemical Polymerization of Benzene with $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ as Electrolyte, *Polym. Commun.*, **27(8)**, 246-247.
- [83] **Bhadani, S.N., SenGupta, S.K., Gupta, M.K. and Prasad, J.**, 1993. Electrolysis of Conducting Poly(p-phenylene), *J. Appl. Polym. Sci.*, **47(7)**, 1215-1218.
- [84] **McKean, D.R. and Stille, J.K.**, 1987. Electrical-Properties of Poly(5,6-dihydroxy-2-cyclohexen-1,4-ylene) Derivatives, *Macromolecules*, **20(8)**, 1787-1792.
- [85] **Braham, J.N., Hodgins, T., Katto, T., Kohl, R.T. and Stille, J.K.**, 1978. Polyphenylenes via Bis(2-pyrones) and Diethynylbenzenes-Effect of m-Phenylene Units in Chain, *Macromolecules*, **11(2)**, 343-346.
- [86] **Laird, T., Ollis, W.D. and Sutherland, I.O.**, 1980. Base-catalyzed Rearrangements Involving ylide intermediates. 5. Thermal Rearrangements of 3-dimethylaminohex-5-en-1-ynes, *J. Chem. Soc., Perkin Trans 1*(7), 1473-1476.
- [87] **Unroe, M.R., Reinhardt, B.A. and Soloski, E.J.**, 1987. The Insitu Formation of Polyphenylenes via the Thermal Cyclization of Substituted Dimethylaminohex-5-en-1-ynes, *J. Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **28**, 193.
- [88] **Hayashi, T., Konishi, M., Kobori, Y., Kumada, M., Higuchi, T. and Hirotsu, K.**, 1984. Dichloro[1,1'-bis (diphenylphosphino) ferrocene]palladium (II): An Effective Catalyst for Cross-coupling of Secondary and Primary Alkyl Grignard and Alkylzinc Reagents with Organic Halides, *J. Am. Chem. Soc.*, **106(1)**, 158-163.

- [89] **Corriu, J. P. and Masse, J.P.**, 1972. Activation of grignard-reagents by transition-metal complexes - New and simple synthesis of trans-stilbenes and polyphenyls, *J. Chem. Soc., Chem. Commun.*, **3**,144.
- [90] **Tamura, M. and Kochi, J. K.**, 1971. Vinylation of Grignard reagents. Catalysis by iron, *J. Am. Chem. Soc.*, **93(6)**, 1487-1489.
- [91] **Yamamura, M., Moritani, I. and Murahashi, S.I.**, 1975. Reaction of sigma-vinylpalladium complexes with alkyllithiums - Stereospecific syntheses of olefins from vinyl halides and alkyllithiums, *J. Organomet. Chem.*, **91(2)**, C39-C42.
- [92] **Negishi, E.**, 1978. Aspects of Mechanism and Organometallic Chemistry, p. 285, Ed. Brewster, J.H., Plenum Press, New York.
- [93] **Miyaura, N. and Suzuki, A.**, 1995. Palladium-catalyzed cross-coupling reactions of organoboron compounds, *Chem. Rev.*, **95**, 2457-2483.
- [94] **Tatsumi, K., Nakamura, A., Komiya, S., Yamamoto, T. and Yamamoto, A.**, 1984. An Associative Mechanism for Reductive Elimination of D8 NIR2(PR3)2, *J. Am. Chem. Soc.*, **106(26)**, 8181-8188.
- [95] **Komiya, S., Abe, Y., Yamamoto, A. and Yamamoto, T.**, 1983. Phosphine-Induced Reductive Elimination From Cis-Arylmethylnickel(II) Complexes Having a 1,2-Bis(Dimethylphosphino)ethane Ligand, *Organometallics*, **2(10)**, 1466-1468.
- [96] **Collman, J.P., Hegedus, L.S., Norton, J.R. and Finke, R.G.** 1987. Principles and Applications of Organotransition Metal Chemistry, p.322, University Science Books : Mill Valley, CA.
- [97] **Yamamoto, A.**, 1986. Organotransition Metal Chemistry, p.244, John Wiley: New York.
- [98] **Morrell, D.G. and Kochi, J.K.**, 1975. Mechanistic Studies of Nickel Catalysis in Cross Coupling of Aryl Halides with Alkylmetals-Role of Arylalkylnickel(II) Species as Intermediates, *J. Am. Chem. Soc.*, **97(25)**, 7262-7270.
- [99] **Iyoda, M., Sakitani, M., Otsuka, H. and Oda, M.**, 1985. Reductive Coupling of Benzyl Halides Using Nickel(0)-Complex Generated Insitu in the Presence of Tetraethylammonium Iodide, a Simple and Convenient Synthesis of Bibenzyls. *Chem. Lett.*, **1**, 127-130.
- [100] **Yamamoto, T., Morita, A., Miyazaki, Y., Maruyama, T., Wakayama, H., Zhou, Z., Nakamura, Y. and Kanbara, T.**, 1992. Preparation of π -Conjugated Poly(thiophene-2,5-diyl), Poly(p-phenylene) and Related Polymers Using Zerovalent Complexes. Linear Structure and Properties of the π -Conjugated Polymers. *Macromolecules*, **25**, 1214-1223.

- [101] **Yamamoto, T., Hayashi, Y. and Yamamoto A.**, 1978. Novel Type of Polycondensation Utilizing Transition Metal-Catalyzed C-C Coupling .1. Preparation of Thermostable Polyphenylene Type Polymers, *Bull. Soc. Chem. Japan.*, **51(7)**, 2091-2097.
- [102] **Yamamoto, T., Maruyama, T., Ikeda, T. and Sisido, M.**, 1990. Excimer Like Emission From Linear π -Conjugated Poly(pyridine-2,5-diyl), *J. Chem. Soc. Chem. Commun.*, **19**, 1306-1307.
- [103] **Yamamoto, T., Maruyama, T. and Kubota, K.**, 1989. Polarizing Film Prepared by Using Linear Poly(2,5-pyridinediyl), *Chem. Lett.*, **11**, 1951-1952.
- [104] **Wirth, H.O., Riehl, N. and Kallmann, H.P.**, 1966. In Physik und Chemie der Scintillatoren Eds.; K. Thiernig Verlag: Munchen, p. 44.
- [105] **Kern, W., Seibel, M. and Wirth, O.**, 1959. *Makromol. Chem.*, **29**, 164-189. Über die Synthese methylysubstituierter P-Oligopenylene. 5. Mitteilung.
- [106] **Kern, W., Ebersbach, H.W. and Ziegler, I.**, 1959. *Makromol Chem*, **31**, 154-180. Über die synthese methoxylsubstituierter p-oligophenylene. 6. Mitteilung.
- [107] **Ringsdorf, H., Tschirner, P., Hermann-Schönherr, O. and Wendorff, J.H.**, 1987. Synthesis, Structure and Phase-Behaviour of Liquid-Crystalline Rigid-Rod Polyesters and Polyamides with Disk-Like Mesogens in the Main Chain, *Makromol. Chem. Phys.*, **188(6)**, 1431-1445.
- [108] **Ballauff, M.** 1989. Stiff- Chain Polymers Structure, Phase-Behaviour and Properties, *Angew. Chem. Int. Ed. Engl.*, **28(3)**, 253-267.
- [109] **Rehahn, M., Schluter, A.D. and Feast, W. J.** 1988. A High Yield Route to 2,5-Di-N-alkyl-1,4-Benzenedicarboxylic Acids, *Synthesis*, **5**, 386-388.
- [110] **Blatter, K., Schluter, A.D.** 1989. Model Studies for the Synthesis of Ribbon-Shaped Structures by Repetitive Diels-Alder Reaction, *Chem. Ber.*, **122(7)**, 1351-1356.
- [111] **Schluter, A. D.** 1991. Ladder Polymers the New Generation, *Adv. Mater.*, **3(6)**, 282-291.
- [112] **Rehahn, M., Schluter, A.D., Wegner, G. and Feast, W. J.**, 1989. SolublePoly(p-phenylene)s 1. Extension of the Yamamoto Synthesis to Dibromobenzenes Substituted with Flexible Side Chains, *Polymer*, **30(6)**, 1054-1059.
- [113] **Kreyenschmidt, M., Uckert, F. and Mullen, K.**, 1995. A New Soluble Poly(p-phenylene) with Tetrahydropyrene Repeating Units, *Macromolecules*, **28(13)**, 4577-4582.

- [114] **Suzuki, A.**, 1999. Recent Advances in the Cross-coupling Reactions of Organoboron Derivatives with Organic Electrophiles, 1995–1998, *J. Organomet. Chem.*, **576**, 147–168.
- [115] **Suzuki, A.**, 1994. New Synthetic Transformations via Organoboron Compounds, *Pure Appl. Chem.*, **66(2)**, 213-222.
- [116] **Kramer, A.V. and Osborn, J.A.**, 1974. Mechanistic Studies of Oxidative Addition to Low Valent Metal Complexes. IV. CIDNP Effects in Platinum(0) and Palladium(0) Reactions, *J. Am. Chem. Soc.*, **96(25)**, 7832-7833.
- [117] **Tour, J.M.**, 1994. Soluble Oligophenylenes and Polyphenylenes, *Adv. Mater.*, **6(3)**, 190-198.
- [118] **Schluter, A.D.**, 1998. Progress In Handbook of Conducting Polymers, Skotheim, T. A., Elsenbaumer, R.L. and Reynolds, J.R., p.209, Eds. Marcel Dekker, New York.
- [119] **Cowie, J.M.G.**, 1973, Polymers: Chemistry and Physics of Modern Materials; International Textbook: Aylesbury, England,; p. 4–5.
- [120] **Bo, Z. and Schluter, A.D.**, 2000, Entering a New Level of Use for Suzuki Cross-Coupling: Poly(p-phenylene)s with Fourth-Generation Dendrons, *Chem. Eur. J.*, **6(17)**, 3235-3241.
- [121] **Matos, K. and Soderquist, J.A.**, 1998, Alkylboranes in the Suzuki-Miyaura Coupling: Stereochemical and mechanistic studies, *J. Org. Chem.*, **63(3)**, 461-470.
- [122] **Frahn, J., Karakaya, B., Schafer, A. and Schluter, A.D.**, 1997, Suzuki polycondensation: On Catalyst Derived Phosphorus Incorporation and Reproducibility of Molecular Weights, *Tetrahedron*, **53(45)**, 15459-15467.
- [123] **Schluter, S., Frahn, J., Karakaya, B. and Schluter, A.D.**, 2000, Improved Suzuki Polycondensation: A Diiodo Versus a Dibromo Monomer, *Macromol. Chem. Phys.* **201(1)**, 139-142.
- [124] **Wang, C.S., Kilitziraki, M., MacBride, J.A.H., Bryce, M.R., Horsburgh, L.E., Sheridan, A. K., Monkman, A.P. and Samuel, I.D.W.**, 2000, Tuning the optoelectronic properties of pyridine-containing polymers for light-emitting devices, *Adv. Mater.*, **12(3)**, 217.
- [125] **Groger, H.**, 2000, Modern Methods of the Suzuki Cross Coupling: The Long Expected General Synthetic Routes Using Aryl Chlorides, *J. Prakt. Chem.*, **342(4)**, 334-339.
- [126] **Gronowitz, S. and Peters, D.**, 1990, Convenient Synthesis of Various Terheterocyclic Compounds by Pd(0) Catalyzed Coupling Reactions, *Heterocycles*, **30(1)**, 645-658.

- [127] **Miyaura, N., Yanagi, T. and Suzuki, A.,** 1981. The Palladium Catalyzed Cross-Coupling Reaction of Phenylboronic Acid with Haloarenes in the Presence of Bases, *Synth. Commun.*, **11(7)**, 513-519.
- [128] **Szwarc, M.,** 1956. Living Polymers, *Nature.*, **178**, 1168-1169.
- [129] **Quirk, R. and Lee, B.,** 1992. Experimental Criteria for Living Polymerizations, *Polym. Int.*, **27(4)**, 359-367.
- [130] **Matyjaszewski, K.,** 1995. Introduction to Living Polymerization, Living and/or Controlled Polymerization, *J. Phys. Org. Chem.*, **8(4)**, 197-207.
- [131] **Litvinenko, G. and Muller, A.H.E.,** 1997. General Kinetic Analysis and Comparison of Molecular Weight Distributions for Various Mechanisms of Activity Exchange in Living Polymerizations, *Macromolecules*, **30(5)**, 1253-1266.
- [132] **Matyjaszewski, K. and Gaynor, S.G.,** 2000. In Applied Polymer Science, p. 929, Craver, C.D. and Carraher, C.E., Pergamon Press, Oxford.
- [133] **Swarc, M.,** 1960. Termination of Anionic Polymerization, *Adv. Polym. Sci.*, **2**, 275-306.
- [134] **Matyjaszewski, K.,** 2000. *Controlled / Living Radical Polymerization: Progress In ATRP, NMP, and RAFT*, Vol. 768, Ed. American Chemical Society, Washington DC.
- [135] **Matyjaszewski, K. and Xia, J.,** 2001. Atom Transfer Radical Polymerization, *Chem. Rev.*, **101**, 2921-2990.
- [136] **Hawker, C.J., Bosman, A.W. and Harth, E.,** 2001. Approaches to Nanostructures for Advanced Microelectronics Using Well-defined Polymeric Materials, *Abstracts of Papers of The American Chemical Society*, **222**, 52-Poly Part 2.
- [137] **Mayadunne, R.T.A., Rizzardo, E., Chiefari, J., Chong, Y.K., Moad, G. and Thang, S.H.,** 1999. Living Radical Polymerization with Reversible Addition-fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents, *Macromolecules*, **32 (21)**, 6977-6980.
- [138] **Patten, T.E. and Matyjaszewski, K.,** 1998. Atom transfer radical polymerization and the synthesis of polymeric materials, *Adv. Mater.*, **10(12)**, 901.
- [139] **Patten, T.E. and Matyjaszewski, K.,** 1999. Copper(I)-catalyzed atom transfer radical polymerization, *Acc. Chem. Res.*, **32(10)**, 895-903.

- [140] **Matyjaszewski, K. and Xia, J.**, 2002. Fundamentals of Atom Transfer Radical Polymerization, in *Handbook of Radical Polymerization*, Chapter 11, Eds. Matyjaszewski, K. and Davis, T.P., John Wiley and Sons, Inc., New York.
- [141] **Fischer, H.**, 1999. The persistent radical effect in controlled radical polymerizations, *J. Polym. Sci.; Part A: Polym. Chem.*, **37(13)**, 1885-1901.
- [142] **Pryor, W.A., Tang, F.Y., Tang, R.H. and Church, D.F.**, 1982. Chemistry of the tert-butyl radical - polar character, rho value for reaction with toluenes, and the effect of radical polarity on the ratio of benzylic hydrogen abstraction to addition to aromatic rings *J. Am. Chem. Soc.*, **104 (10)**, 2885-2891.
- [143] **Kotani, Y., Kamigaito, M. and Sawamoto, M.**, 2000. Living radical polymerization of para-substituted styrenes and synthesis of styrene-based copolymers with rhenium and iron complex catalysts, *Macromolecules*, **33(18)**, 6746-6751.
- [144] **Kotani, Y., Kamigaito, M. and Sawamoto, M.**, 1999. Re(V)-mediated living radical polymerization of styrene: ReO₂I(PPh₃)(2)/R-I initiating systems, *Macromolecules*, **32(8)**, 2420-2424.
- [145] **Destarac, M., Matyjaszewski, K. and Boutevin, B.**, 2000. Polychloroalkane initiators in copper-catalyzed atom transfer radical polymerization of (meth)acrylates, *Macromol. Chem. Phys.*, **201(2)**, 265-272.
- [146] **Percec, V., Kim, H.J. and Barboiu, B.**, 1997. Scope and limitations of functional sulfonyl chlorides as initiators for metal-catalyzed "living" radical polymerization of styrene and methacrylates, *Macromolecules*, **30(26)**, 8526-8528.
- [147] **Wang, J.S. and Matyjaszewski, K.**, 1995. Living controlled radical polymerization - transition-metal-catalyzed atom-transfer radical polymerization in the presence of a conventional radical initiator, *Macromolecules*, **28(22)**, 7572-7573.
- [148] **Singha, N.K. and Klumperman, B.**, 2000. Atom-transfer radical polymerization of methyl methacrylate (MMA) using CuSCN as the catalyst, *Macromol. Rapid Commun.*, **21(16)**, 1116-1120.
- [149] **Xia, JH. and Matyjaszewski, K.**, 1997. Controlled/"living" radical polymerization. Homogeneous reverse atom transfer radical polymerization using AIBN as the initiator, *Macromolecules*, **30(25)**, 7692-7696.
- [150] **Klumperman, B.**, 2004. Living Radical Polymerization, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc., New York.
- [151] **Teodorescu, M., Gaynor, S.G. and Matyjaszewski, K.**, 2000. Halide anions as ligands in iron-mediated atom transfer radical polymerization, *Macromolecules*, **33(7)**, 2335-2339.

- [152] **Moineau, G., Minet, M., Teyssie, P. and Jerome, R.,** 2000. Synthesis of fully acrylic thermoplastic elastomers by atom transfer radical polymerization (ATRP), 2 - Effect of the catalyst on the molecular control and the rheological properties of the triblock copolymers, *Macromol. Chem. Phys.*, **201(11)**, 1108–1114.
- [153] **Kato, M., Kamigaito, M., Sawamoto, M. and Higashimura, T.,** 1995. Polymerization of methyl-methacrylate with the carbon-tetrachloride dichlorotris (triphenylphosphine) ruthenium(ii) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization, *Macromolecules*, **28(5)**, 1721–1723.
- [154] **Wakioka, M., Baek, K.Y., Ando, T., Kamigaito, M. and Sawamoto, M.,** 2002. Possibility of living radical polymerization of vinyl acetate catalyzed by iron(I) complex, *Macromolecules*, **35(2)**, 330–333.
- [155] **Haddleton, D.M., Jasieczek, C.B., Hannon, M.J. and Shooter, A.J.,** 1997. Atom transfer radical polymerization of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper (I) complexes, *Macromolecules*, **30 (7)**, 2190-2193.
- [156] **Matyjaszewski, K., Patten, T.E. and Xia, J.,** 1997. Controlled/"living" radical polymerization. Kinetics of the homogeneous atom transfer radical polymerization of styrene, *J. Am. Chem. Soc.*, **119(4)**, 674-680.
- [157] **Matyjaszewski, K., Davis, K., Patten, T. and Wei, M.,** 1997. Observation and analysis of a slow termination process in the atom transfer radical polymerization of styrene, *Tetrahedron*, **53(45)**, 15321-15329.
- [158] **Yagci, Y., Nuyken, O. and Graubner, V.M.,** 2004. Telechelic Polymers, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc., New York. **12**, 57-130.
- [159] **Haddleton, D.M. and Waterson, C.,** 1999. Phenolic ester-based initiators for transition metal mediated living polymerization, *Macromolecules*, **32(26)**, 8732-8739.
- [160] **Matyjaszewski, K., Coca, S., Nakagawa, Y. and Xia, J.,** 1997. Functional Polymers by Atom Transfer Polymerization, *Polym. Mater. Sci. Eng.*, **76**, 147.
- [161] **Matyjaszewski, K., Coessens, V., Nakagawa, V., Xia, Y., Qiu, J., Gaynor, S. G. Coca, S. and Jasieczek, C.,** 1998. Functional polymers : modern synthetic methods and novel structures, *Am. Chem. Soc. Symp. Ser.*, **704**, 16.

- [162] **Gaynor, S.G. and Matyjaszewski, K.,** 1997. Advances in Free Radical Polymerization, *Am. Chem. Soc. Symp. Ser.* **685**, 396.
- [163] **Zhang, X., Xia, J. and Matyjaszewski, K.,** 2000. End-Functional Poly(tert-butyl acrylate) Star Polymers by Controlled Radical Polymerization. *Macromolecules*, **33(7)**, 2340-2345.

- [164] **Matyjaszewski, K., Jo, S.M., Paik, H.J. and Gaynor, S. G.,** 1997. Synthesis of Well-Defined Polyacrylonitrile by Atom Transfer Radical Polymerization. *Macromolecules*, **30(20)**, 6398-6400.
- [165] **Matyjaszewski, K., Wei, M., Xia, J. and McDermott, N.E.,** 1997. Controlled/"Living" Radical Polymerization of Styrene and Methyl Methacrylate Catalyzed by Iron Complexes, *Macromolecules*, **30(26)**, 8161-8164.
- [166] **Mecerreyes, D., Athoff, B., Boduch, K. A., Trollsos, M. and Hedrick, J. L.,** 1999. Unimolecular Combination of an Atom Transfer Radical Polymerization Initiator and a Lactone Monomer as a Route to New Graft Copolymers, *Macromolecules*, **32(16)**, 5175-5182.
- [167] **Moineau, G., Minet, M., Dubois, Ph., Teyssie, Ph., Senninger, T. and Jerome, R.,** 1999. Controlled Radical Polymerization of (Meth)acrylates by ATRP with NiBr₂(PPh₃)₂ as Catalyst, *Macromolecules*, **32(1)**, 27-35.
- [168] **Hawker, C. J., Hedrick, J. L., Malmström, E. E., Trollsos, M., Mecerreyes, D., Moineau, G., Dubois, Ph. and Jerome, R.,** 1998. Dual Living Free Radical and Ring Opening Polymerizations from a Double-Headed Initiator, *Macromolecules*, **31**, 213.
- [169] **Destarac, M., Matyjaszewski, K. and Boutevin, B.,** 2000. Polychloroalkane initiators in copper-catalyzed atom transfer radical polymerization of (meth)acrylates, *Macromol. Chem. Phys.*, **201(2)**, 265-272. 
- [170] **Destarac, M., Boutevin, B. and Matyjaszewski, K.,** 2000, in K. Matyjaszewski, ed., Controlled/Living Radical Polymerization (*ACS Symposium Series 768*), American Chemical Society, Washington, D.C., Chapt. 17.
- [171] **Haddleton, D. M., Waterson, C., Derrick, P. J., Jasieczek, C. B., Christina, B. and Shooter, A. J.,** 1997. Monohydroxy terminally functionalised poly(methyl methacrylate) from atom transfer radical polymerization, *Chem. Commun.*, **7**, 683-684.
- [172] **Keul, H., Neumann, A., Reining, B. and Höcker, H.,** 2000. Synthesis of telechelics and block copolymers via "living" radical polymerization., *Macromol. Symp.* **161(1)**, 63-72.
- [173] **Coessens, V. and Matyjaszewski, K.,** 1999. Dehalogenation of polymers prepared by atom transfer radical polymerization, *Macromol.Rapid Commun.* **20(2)**, 66.
- [174] **Xu, Y., Pan, C. and Tao, L.,** 2000. Block and star block copolymers by mechanism transformation. II. Synthesis of poly(DOP-b-St) by combination of ATRP and CROP, *J. Polym. Sci., Polym. Chem. Ed.*, **38(3)**, 436-443.

- [175] **Matyjaszewski, K., Beers, K. L., Kern, A. and Gaynor, S.G.,** 1998. Hydrogels by atom transfer radical polymerization. I. Poly(N-vinylpyrrolidinone-g-styrene) via the macromonomer method, *J. Polym. Sci., Part A: Polym. Chem.* **36(5)**, 823-830. 
- [176] **Nakagawa, Y. and Matyjaszewski, K.,** 1998. Synthesis of well-defined allyl end-functionalized polystyrene by atom transfer radical polymerization with an allyl halide initiator, *Polym. J. (Tokyo)* **30(2)**, 138. 
- [177] **Haddleton, D. M., Heming, A. M., Kukulj, D., Duncalf, D. J. and Shooter, A. J.,** 1998. Atom Transfer Polymerization of Methyl Methacrylate. Effect of Acids and Effect with 2-Bromo-2-Methylpropionic Acid Initiation, *Macromolecules*, **31(6)**, 2016-2018.
- [178] **Malz, H., Komber, H., Voigt, D., Hopfe, I. and Pionteck, J.,** 1999. Synthesis of functional polymers by atom transfer radical polymerization, *Macromol. Chem. Phys.*, **200(3)**, 642-651.
- [179] **Kajiwarra, A. and Matyjaszewski, K.,** 1999. EPR and kinetic studies of atom transfer radical polymerization of (meth)acrylates, *Polym. J.*, **31(1)**, 70-75. 
- [180] **Zeng, F., Shen, Y., Zhu, S. and Pelton, R.,** 2000. Synthesis and Characterization of Comb-Branched Polyelectrolytes. 1. Preparation of Cationic Macromonomer of 2-(Dimethylamino)ethyl Methacrylate by Atom Transfer Radical Polymerization, *Macromolecules*, **33(5)**, 1628.
- [181] **Shen, Y., Zhu, S., Zeng, F. and Pelton, R.,** 2000. Synthesis of Methacrylate Macromonomers Using Silica Gel Supported Atom Transfer Radical Polymerization, *Macromol. Chem. Phys.* **201(13)**, 1387-1394.
- [182] **Yurteri, S., Cianga, I. and Yagci, Y.,** 2003. Synthesis and Characterization of α - ω -Telechelic Polymers by Atom Transfer Radical Polymerization and Coupling Processes, *Macromol. Chem. Phys.*, **204**, 1771.
- [183] **Ohno, K., Fujimoto, K., Tsujii, Y. and Fukuda, T.,** 1999. Synthesis of a Well-Defined Anthracene-Labelled Polystyrene by Atom-Transfer Radical Polymerization, *Polymer*, **40(3)**, 759-763.
- [184] **Erdogan, M., Hizal, G., Tunca, U., Hayrabetyan, D. and Pekcan, O.,** 2002. Molecular weight effect on swelling of polymer gels in homopolymer solutions: a fluorescence study, *Polymer*, **43(6)**, 1925.
- [185] **Korn, M.R. and Gagne, M. R.,** 2000. Simultaneous atom transfer and nitroxide mediated controlled free radical polymerization of styrene, *Chem. Commun.* **18**, 1711-1712.
- [186] **Erdogan, M., Hepuzer, Y., Cianga, I., Yagci, Y. and Pekcan, O.,** 2003. Diffusion of pyrene end-capped polystyrene prepared via atom transfer radical polymerization into polystyrene gels in the presence of toluene, *J. Phys. Chem.*, **107(40)**, 8363-8370.

- [187] **Alkan, S., Toppare, L., Hepuzer, Y. and Yagci, Y.,** 1999. Block copolymers of thiophene-capped poly(methyl methacrylate) with pyrrole, *J. Polym.Sci., Part A: Polym. Chem.* **37(22)**, 4218-4225.
- [188] **Mecerreyes, D., Pompose, J.A., Bengoetxea, M. and Grande, H.,** 2000. Novel Pyrrole End-Functional Macromonomers Prepared by Ring-Opening and Atom-Transfer Radical Polymerizations, *Macromolecules*, **33(16)**, 5846.
- [189] **Degee, P., Dubois, P. and Jerome, R.,** 1997. Bulk polymerization of lactides initiated by aluminium isopropoxide. 3. Thermal stability and viscoelastic properties, *Macromol. Chem. Phys.*, **198(6)**, 1985-1995.
- [190] **Johns, Db., Lenz, R.W. and Luecke, A.,** 1984. Lactones, in *Ring-Opening Polymerization*, 1, 464, Eds. Ivin K.J. and Saegusa, T., Elsevier, London.
- [191] **Löfgren, A., Albertsson, A.C., Dubois, P. and Jerome, R.,** 1995. Recent advances in ring-opening polymerization of lactones and related-compounds, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C35(3)**, 379-418.
- [192] **Mecerreyes, D., Jerome, R. and Dubois, P.,** 1999. Novel macromolecular architectures based on aliphatic polyesters: relevance of the "coordination-insertion" ring-opening polymerization, *Adv. Polym. Sci.*, **147**, 1-59.
- [193] **Kricheldorf, H.R. and Kreiser, S.I.,** 1996. Polylactides - synthesis, characterization and medical application, *Macromol. Symp.*, **103**, 85-102.
- [194] **Saegusa, T., Kobayashi, S. and Hayashi, K.,** 1978. Polymerization via zwitterion 171 alternating copolymerization of 2-phenylimino-1,3-dioxolane with beta-propiolactone, *Macromolecules*, **11(2)**, 360-361.
- [195] **Penczek, S.,** 2000. Cationic ring-opening polymerization (crop) major mechanistic phenomena, *J. Polym. Sci. Polym. Chem.*, **38(11)**, 1919-1933.
- [196] **Kubisa, P. and Penczek, S.,** 1999. Cationic activated monomer polymerization of heterocyclic monomers, *Prog. Polym. Sci.*, **24(10)**, 1409-1437.
- [197] **Penczek, S. and Slomkowski, S.,** 1987. Progress In Anionic Ring-Opening Polymerization, in *Recent Advances in Anionic Polymerization*, Chap **19**, 275, Eds. Hogen, E.T. and Smid, J., Elsevier, New York.
- [198] **Jedlinski, Z., Kurcok, P. and Kowalczyk, M.,** 1985. Polymerization of beta-lactones initiated by potassium solutions, *Macromolecules*, **18(12)**, 2679-2683.
- [199] **Lundberg, R.D. and Cox, E.F.,** 1969. Lactones, in *Ring-Opening Polymerization*, Frish, K., Reegen, S., Eds, 2:247 Marcel Dekker, New York.
- [200] **Duda, A., Florjanczyk, Z., Hofman, A., Slomkowski, S. and Penczek, S.,** 1990. Living pseudoanionic polymerization of epsilon-caprolactone - poly(epsilon-caprolactone) free of cyclics and with controlled end groups, *Macromolecules*, **23 (6)**, 1640-1646.

- [201] **Bero, M., Czapla, B., Dobrzynski, P., Janeczek, H. and Kasperczyk.,** 1999. Copolymerization of glycolide and epsilon-caprolactone - 2 - random copolymerization in the presence of tin octoate, *J. Macromol. Chem. Phys.*, **200 (4)**, 911-916.
- [202] **Dubois, P., Ropson, N., Jérôme, R. and Teyssie, P.,** 1996. Macromolecular engineering of polylactones and polylactides.19. Kinetics of ring-opening polymerization of epsilon-caprolactone initiated with functional aluminum alkoxides, *Macromolecules*, **29**, 1965-1975.
- [203] **Kricheldorf, H.R. and Meier, H.J.,** 1993. Polylactones.22. ABA triblock copolymers of L-lactide and poly(ethylene glycol), *Macromol. Chem.* **194 (2)**, 715-725.
- [204] **Kowalski, A., Duda, A. and Penczek, S.,** 1998. Kinetics and mechanism of cyclic esters polymerization initiated with tin(II) octoate, 1. Polymerization of epsilon-caprolactone, *Macromol. Rapid. Commun.* **19 (11)**, 567-572
- [205] **Kowalski, A., Duda, A. and Penczek, S.,** 2000. Kinetics and mechanism of cyclic esters polymerization initiated with tin(II) octoate. 3. Polymerization of l,l-dilactide, *Macromolecules*, **33 (20)**, 7359-7370.
- [206] **Kricheldorf, H.R., Kreiser, S.I. and Stricker, A.,** 2000. Polylactones 48. Sn(Oct)₂-initiated polymerizations of lactide: a mechanistic study, *Macromolecules*, **33 (3)**, 702-709.
- [207] **Quirk, R. and Lee, B.,** 1992. Experimental criteria for living polymerizations, *Polym. Int.*, **27 (4)**, 359-367.
- [208] **Kricheldorf, H.R., Boettcher, C. and Tönnies, K.U.,** 1992. Polylactones.23. Polymerization of racemic and meso D,L-lactide with various organotin catalysts stereochemical aspects, *Polymer*, **33 (13)**, 2817-2824.
- [209] **Kowalski, A., Libiszowski, J., Duda, A. and Penczek, P.,** 2000. Polymerization of l,l-dilactide initiated by tin(II) butoxide, *Macromolecules*, **33 (6)**, 1964-1971.
- [210] **Mclain, S.J. and Drysdale, N.E.,** 1991.*Us Patent*, 5 028 667.
- [211] **Mclain, S.J. and Drysdale, N.E.,** 1992. Living Ring-Opening Polymerization Of Epsilon-Caprolactone By Yttrium And Lanthanide Alkoxides *Abstr. Pap. Am. Chem. S* **203**, 160-Poly Part 3.
- [212] **Domb, A.J., Kost, J. And Wiseman, M.D.,** 1984. Handbook of Biodegradable Polymers 'Polycaprolactone', Perrin, D.E. and English, J.P., Chap.3, 63-77.
- [213] **Pitt, C.G., Gratzl, M.M., Kimmel, G.L., Surles, J. and Schlinder, A.,** 1981. Aliphatic Polyesters II. The Degredation of Poly(D,L,-lactide), Poly(ε-caprolactone) and their copolymers *in vivo*. *Biomaterials*, **2**, 215-219.

- [214] **Schlinder, A., Hibionada, Y.M. and Pitt, C.G.,** 1982. Aliphatic Polyesters III. Molecular Weight and Molecular Weight Distributions in Alcohol-Initiated Polymerizations of ϵ -Caprolactone, *J. Polym. Sci. P. Chem. Ed.*, **20**, 319-326.
- [215] **Pitt, C.G., Chasalow, Y.M., Hibionada, Y.M., Klimas, D.M. and Schlinder, A.,** 1981. Aliphatic Polyesters I. The Degredation of Poly(ϵ -caprolactone) *in vivo*, *J. Appl. Polym. Sci.*, **68**, 1534-1538.
- [216] **Woodward, S.C., Brewer, P.S., Moatmed, F., Schlinder, A. and Pitt, C.G.,** 1985. The Intracellular Degredation of Poly(ϵ -caprolactone), *J. Bio. Mat. Res.*, **19**, 437-444.
- [217] **Ali, S.A., Ahong, S.P., Doherty, P.J. and Williams, D.F.,** 1993. Mechanisms of Polymer Degredation in Implantable Devices, *Biomaterials*, **14**, 648-656.
- [218] **Williams, D.F.,** 1994. Molecular Biointeractions of Biomedical Polymers with Extracellular Exudate and Inflammatory Cells and Their, Effect on Biocompatibility *in vivo*. *Biomaterials*, **15**, 779-785.
- [219] **Bezwada, R.S., Jamiolkowski, D.D., Lee, I.L., Vishvaroop, A., Persivale, J., Trenka-Benthin, S., Erneta, E., Surydevara, A.Y. and Liu, S.,** 1995. Monocryl[®] Suture a New Ultra-Pliable Absorbable Monofilament Suture, *Biomaterials*, **16**, 1141-1148.
- [220] **Hinrichs, W.L., Zweep, H.P., Satoh, S., Feijen, J. And Wildavuur, C.R.,** 1994. Supporting Microporous, Degredable Protheses to Improve the Arterialization of Autologous Vein Grafts, *Biomaterials*, **15**, 83-91.
- [221] **Advincula, R., Xia, C.J. and Inaoka, S.,** 2000. Ladder-type oligomeric para-phenylene) series tethered to poly(alkylene) main chain: The orthogonal approach to functional polymers, *Abst. Pap. Am. Chem. Soc.* **219**, 413.
- [222] **Storey, R.F., Warren, S.C., Allison, C.J., et al.,** 1993. Synthesis of Bioabsorbable Networks From Methacrylate-Endcapped Polyesters, *Polymer*, **34(20)**, 4365-4372.
- [223] **Storey, R.F. and Hickey, T.P.,** 1994. Degradable Polyurethane Networks Based on D,L-Lactide, Glycolide, Epsilon-Caprolactone and Trimethylene Carbonate Homopolyester and Copolyester Triols, *Polymer*, **35(4)**, 830- 838.
- [224] **Riffle, J.S., Steckle, W.P., White, K.A. and Ward, R.S.,** 1985. Polydimethylsiloxane- poly(ϵ -caprolactone) Block Copolymers – Synthesis and Applications, *Abst. Pap. Am. Chem. Soc.*, **189**, 145.
- [225] **Guo, Z.R., Wan, D.C. and Huang, J.L.,** 2001. Synthesis and Characterization of Poly(ϵ -CL)-block-poly(MMA-co-St)-block-poly(ϵ -CL) by Combination of Coordination and Controlled Radical Polymerization, *Macromol. Rapid Commun.*, **22(5)**, 367-371.

- [226] **Kim, C., Lee, S.C., Kwon, I.C., Chung, H. and Jeong, S.Y.,** 2002. Complexation of Poly(2-ethyl-2-oxazoline)-block-poly(ϵ -caprolactone) Micelles With Multifunctional Carboxylic Acids, *Macromolecules*, **35(1)**, 193.
- [227] **Choi, Y.R., Bae, Y.H. and Kim, S.W.,** 1998. Star-shaped Poly(ether-ester) Block Copolymers: Synthesis, Characterization, and Their Physical Properties, *Macromolecules*, **31(25)**, 8766-8774.
- [228] **Joziassse, C.A.P., Grablowitz, H. and Pennings, A.J.,** 2000. Star-Shaped Poly[(trimethylene carbonate)-co-(ϵ -capro-lactone)] and Its Block Copolymers With Lactide/Glycolide: Synthesis, Characterization and Properties, *Macro. Chem. Phys.*, **201(1)**, 107-112.
- [229] **Dubois, P., Barakat, I., Jerome, R. and Teyssie, Ph.,** 1993. Macromolecular Engineering of Polylactones and Polylactides.12.Study Of The Depolymerization Reactions of Poly(ϵ -caprolactone)With Functional Aluminum Alkoxide End-Groups, *Macromolecules*, **26(17)**, 4407-4412.
- [230] **Yurteri, S., Cianga, I., Degirmenci, M. and Yagci, Y.,** 2004. Synthesis and Characterization Of Poly(p-phenylene)-graft-Poly(ϵ -caprolactone) Copolymers By Combined Ring-Opening Polymerization and Cross-Coupling Processes, *Polym. Int.*, **53(9)**, 1219-1225.
- [231] **Carlblom, L.H. and Pappas, S.P.,** 1977. Photoinitiated Polymerization of Methyl Methacrylate and Methyl Acrylate With ^{14}C -labeled Benzoin Methyl Ethers, *J. Polym. Sci. P. Chem. Ed.*, **15(6)**, 1381-1391.
- [232] **Yurteri, S., Cianga, I., Demirel, A.L. and Yagci, Y.,** 2005. New Polyphenylene-g-polystyrene and Polyphenylene-g-polystyrene/poly(ϵ -caprolactone) Copolymers by Combined Controlled Polymerization and Cross-Coupling Processes, *J. Polym. Sci. P. Chem. Ed.*, **43(4)**, 879-896.
- [233] **Cianga, I. and Yagci, Y.,** 2004. New Polyphenylene- Based MacromolecularArchitectures By Using Well-Defined Macromonomers Synthesized Via Controlled Polymerization Methods, *Prog. Polym. Sci.*, **29(5)**, 387-399.
- [234] **Cianga, I., Hepuzer, Y. and Yagci, Y.,** 2002. Poly(p-phenylene) Graft Copolymers With Polytetrahydrofuran/ Polystyrene Side Chains, *Polymer*, **43(8)**, 2141-2149.
- [235] **Yurteri, S., Cianga, I. and Yagci, Y.,** 2005. Synthesis And CharacterizationSynthesis And Characterization Of Poly(ϵ -caprolactone)-b-Polystyrene Macromonomer By Combined Ring-opening And Atom Transfer Radical Polymerizations And Its Use For The Preparation Of Grafted Polyphenylenes By Suzuki Polycondensation, *Designed Mon.& Polym.*, **8(1)**, 61-74.

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2. S. Yurteri, I. Cianga, Y. Yagci “Synthesis and Characterization of α - ω - Functional Telechelics by Atom Transfer Radical Polymerization and Coupling Processes” *Macromol.Chem. Phys.*, 204, 1771 (2003)
3. A.E.M. Muftuoglu, I. Cianga, S. Yurteri, Y. Yagci “Use of N,N-Dimethylaniline End-Functional Polymers in Photoinduced Block Copolymerization” *J.Appl. Polym. Sci.*, 93,387 (2004)
4. S. Yurteri, I. Cianga, M. Degirmenci, Y. Yagci “Synthesis and Characterization of Poly(p-phenylene)-g-Poly(ϵ -caprolactone) Copolymers by Combined Ring- opening Polymerization and Cross-coupling by Processes” *Polym. Int.*, 53, 1219 (2004)
5. S. Yurteri, I. Cianga, A. L. Demirel, Y. Yagci “New Polyphenylene-g-Polystyrene and Polyphenylene-g-Polystyrene/Poly(ϵ -Caprolactone)

Copolymers by Combined Controlled Polymerization and Cross-Coupling Processes” *J. Polym. Sci., Part A: Polym.Chem.*43,879 (2005)

6. S. Yurteri, I. Cianga, Y. Yagci “Synthesis and Characterization of Poly(ϵ -Caprolactone)-b-Polystyrene Macromonomer by Combined Ring-opening and Atom Transfer Radical Polymerizations and its Use for the Preparation of Grafted Polyphenylenes by Suzuki Polycondensation” *Designed Mon.& Polym.*, 8, 61 (2005)
7. A.L. Demirel, S. Yurteri, I. Cianga, Y. Yagci “Layered Morphology of Poly(phenylene)s in Thin Films Induced by Substitution of Well-defined Poly(ϵ -caprolactone) Side Chains” *Macromolecules*, 38, 6402 (2005)

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