ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

POLY(PHENYLENEVINYLENE)S AS SENSITIZERS FOR VISIBLE LIGHT INDUCED CATIONIC POLYMERIZATION

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİ(FENİLEN VİNİLEN) TÜREVLERİNİN GÖRÜNÜR BÖLGEDE KATYONİK POLİMERİZASYON İÇİN FOTOBAŞLATICI OLARAK KULLANIMI

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OCAK 2015

Semih ERDUR, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **509121076**, successfully defended the **thesis** entitled "**(POLY(PHENYLENEVINYLENE)S AS SENSITIZERS FOR VISIBLE LIGHT INDUCED CATIONIC POLYMERIZATION)**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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Thank you all…

January 2015 Semih ERDUR
Chemist

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ABBREVIATIONS

^{1}H-NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATRP : Atom Transfer Radical Polymerization
C_{60} : Buckminsterfullerenes
CHO : Cyclohexeneoxide
CL : ε-Caprolactone
CRT : Cathode-Ray-Tubes
CTC : Charge Transfer Complexes
DSC : Differential Scanning Calorimetry
EL : Electroluminescence
GPC : Gel Permeation Chromatography
HOMO : Highest Occupied Molecular Orbital
HR : Heck Reaction
IBVE : IsoButyl Vinyl Ether
ITO : Indium Tin Oxide
LED : Light Emitting Diode
LUMO : Lowest Occupied Molecular Orbital
MA : Methyl Acrylate
MEH-PPV : Poly[2-methoxy-5-(2’-ethylhexyloxyl)-1,4-phenylene vinylene]
NLO : Nonlinear Optical
NVC : N-Vinylcarbazole
OLED : Organic Light Emitting Diode
PCL : Poly (ε-Caprolactone)
PFET : Polymer Field Effect Transistor
PI : Photoinitiator
PL : Photoluminescence
PLED : Polymer Light Emitting Diode
PMMA : Poly (methyl methacrylate)
PPV : Poly(phenylene vinylene)
PSt : Polystyrene
ROP : Ring-opening Polymerization
Sn(Oct)$_2$: Stannous Octoate
TAS : Triaryl Sulphonium Salts
TGA : Thermogravimetric Analyzer

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POLY(PHENYLENE VINYLENE)S AS SENSITIZERS FOR VISIBLE LIGHT INDUCED CATIONIC POLYMERIZATION

SUMMARY

Conjugated polymers have been widely studied as materials due to their interesting optical and nonlinear optical properties and electronic conductivity that lead to a wide range of practical applications such as information storage, optical signal processing, substitutes for batteries, solar energy conversion, and optical signal processing. Moreover, electroluminescence from conjugated polymers is a rapidly increasing a great deal of research has gone into research interest since the first report of polymeric lightemitting diodes (PLEDs) based on poly(phenylene vinylene) (PPVs). Current interest in among a variety of conjugated polymers, In particular, PPV and its derivatives have attracted much attention for the most promising class of high performance polymers due to their relatively high photoluminescence (PL) and electroluminescence (EL) quantum efficiencies as well as good colour tunability through molecular structure designs. They also show high chemical and excellent mechanical properties, thermal stability that allows the fabrication of electronic devices such as flexible LEDs. PPV itself has a rigid structure and is inherently insoluble, thus making it impossible to process these materials into thin films required for the most applications. As a result, considerable effort has been directed toward the preparation of well-defined conjugated polymers with improved solubility, processability and stability. Incorporation of conformationally mobile, relatively long and flexible side chains onto the polymer backbone has been important for synthesizing fusible and soluble rigid-rod conjugated polymers. Taking into consideration the substantial interest not only in the synthesis of new types of polymers, but also in the modification of commodity polymers to improve their properties to meet the requirements for high-tech applications, with a soft coil polystyrene (PSt) or poly(ε-caprolactone) (PCL) has been used in which nanostructured photoactive conjugated oligo(phenylene vinylene) segments are attached as side chains to the backbone. It is possible to form a new polymer with novel and interesting properties. Utilization of several conjugated aromatic compounds for the sensitization of onium salts has prompted us to apply PPVs as photosensitizers for cationic polymerization. Therefore, in order to overcome solubility problems of bare PPVs associated with the rigid structure, PPVs with polystyrene and poly(ε-caprolactone) grafts (PPV-*g*-PSt and PPV-*g*-PCL, respectively) were synthesized. The first step in the synthesis of the desired PPVs was to obtain precursor macromonomers. In the preparation of macromonomers, controlled polymerization methods were delibaretly employed so as to obtain polymers with desired functionalities at the chain ends, and combine with proper molecular weights and polydispersities Dibromo-benzene functional polystyrene (DBB-PSt) was synthesized by Atom Transfer Radical Polymerization (ATRP) of styrene by using 1,4-dibromo-2-(bromomethyl)benzene as initiator in the presence of CuBr/bpy as

catalytic system. The corresponding poly(ε-caprolactone) derivative (DBB-PCL) was prepared by Ring Opening Polymerization (ROP) of ε-caprolactone by using [2,5-dibromo-(4-hydroxymethyl) phenyl)]methanol as bifunctional initiator, in the presence of stannous octoate. In the next step, these polymers were coupled with (4-formylphenyl)boronic acid by Suzuki coupling to give aldehyde functional macromonomers. Finally, the obtained polymers were coupled with *p*-xylylenebis(triphenylphosphonium bromide) by the Wittig reaction in the presence of potassium *tert*-botoxide to yield the desired conjugated polymers. The resulting main chain conjugated graft copolymers were soluble as were the starting macromonomers and PPVs showed blue or green fluorescence in solution. Even tough photopolymerization can be initiated radically, cationically and anionically, much effort has been devoted to free radical and cationic systems mainly due to the availability of a wide range of photoinitiators and the great reactivity of monomers. The majority of industrial applications of photoinitiated polymerizations for various techniques deal with free-radical systems. However, there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations which may affect the properties of the final product. Therefore, photinitiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming these limitations. Some important examples of these initiators are iodonium and sulfonium salts. These onium salts give an irreversible photochemical reaction in response to UV excitation due to their thermal stability, solubility in monomers and efficiency in generating reactive species. However, these onium salts only absorb in the region of 220–300 nm. This means, in visible region, they are either poorly responsive or completely insuffıcent. Thus, their use in applications requiring long wavelength light emitting sources is limited. This drawback can be evaded by using an activator that broadens the spectral sensitivity of the onium salt photoinitiators. These activators are photosensitizers and they can initiate polymerization in the near-UV or visible wavelengths of light. In this work, we report the use of PPVs derivatives for electron transfer photosensitization of onium salts. For this purpose, PPV-*g*-PSt and/or PPV-*g*-PCL were used as photosensitizers. The excited state emission characteristics of the compounds were investigated by means of fluorescence and phosphorescence spectroscopic measurements. The cationic polymerization of typical monomers, such as cyclohexene oxide (CHO), isobutyl vinyl ether (IBVE) and *N*-vinylcarbazole (NVC) with the described initiating system was also tested at room temperature at appropriate wavelengths in the presence of oxidizing salts such as diphenyliodonium hexafluorophosphate (DPI), and *N*-ethoxy-2-methylpyridinium (EMP). The initiation mechanism, as correlated with optical absorption and fluorescence spectroscopic measurements, free energy changes (ΔG) and proton scavenging studies, involves formation of exciplex by the absorption of light in the first step. Subsequently, an electron transfer from the excited PPV-*g*-PSt or PPV-*g*-PCL to oxidizing salt occurs to yield radical cations of the PPV backbone. Thus, formed radical cations abstract hydrogen from the surrounding monomer or the solvent to release a Bronsted acid, which initiates the polymerization. Triphenylsulphonium hexafluoroarsenate (TPS) was found to be inefficient in the photoinduced electron transfer process due to the unfavorable thermodynamic conditions.

POLİ(FENİLEN VİNİLEN) TÜREVLERİNİN GÖRÜNÜR BÖLGEDE KATYONİK POLİMERİZASYON İÇİN FOTOBAŞLATICI OLARAK KULLANIMI

ÖZET

Konjuge polimerlere olan mevcut ilgi, bilgi depolama ve optik sinyal üretimi, batarya yerine kullanım ve güneş enerjisi dönüşüm malzemeleri gibi birçok farklı uygulamalara öncülük eden ilginç optik ve elektriksel iletkenlik özelliklerine bağlıdır. Ayrıca, konjuge polimerlerden elektrolüminesans, poli(*p*-fenilen vinilen) (PPV) esaslı ilk polimerik ışık-yayan diodların (PLEDs) bildirilmesinden bu yana hızla gelişen bir alandır. Çeşitli konjuge polimerler arasında özellikle, PPV ve türevleri iyi film oluşturma özellikleri ile yüksek fotolüminesans (PL) ve elektrolüminesans (EL) kuantum verimlerinin yanı sıra, moleküler yapı tasarımları ile ayarlanabilir renk özelliği göstermelerinden dolayı ileri teknoloji performanslı polimerlerinin gelecek vaad ettiği için çok fazla ilgi uyandırmaktadır. Ayrıca iyi mekanik özellik ve üstün kimyasal ve ısısal dayanıklılık göstermeleri de esnek LED'ler gibi elektronik cihazların üretimine kolaylık sağlar.

PPV'in kendisi sert bir yapıya sahiptir ve bu nedenle çözünmez özellik gösterir. Bu da malzemelerin birçok uygulama alanı için gerekli olan ince filmlere işlenebilirliğini imkânsız kılar. Sonuç olarak, iyileştirilmiş, çözünebilirlik, işlenebilirlik ve dayanıklılık özelliklerine sahip iyi tanımlanmış konjuge polimerlerin hazırlanmasına önemli bir çaba yönlendirilmiştir.

Polimer ana zincirine hareketli, uzun ve esnek yan zincirlerin eklenmesi eriyebilir ve çözünebilir sert yapılı konjuge polimerlerin sentezinde önem kazanmıştır. Sadece yeni polimerlerin sentezlenmesi değil, aynı zamanda var olan ve bilinen polimerlerin modifikasyonları da dikkate alınarak, polistiren (PSt) ve poli(ε-kaprolakton) (PCL), ana zincirlerine oligo(fenilen vinilen) segmanların yan zincir olarak bağlanması ile kullanılmıştır.

PSt veya PCL yapıya katılmasıyla tamamen farklı ve ilginç özelliklere sahip yeni bir polimer oluşturulması mümkündür. Onyum tuzlarının uyarlaştırılması için kullanılan çeşitli konjuge aromatic bileşikler, benzer amaçla katyonik polimerizasyon için PPV nin kullanılabileceğini ortaya koymuştur. Sert ve çözünmeyen PPV nin çözünürlük problemini ortadan kaldırmak için yan zincir olarak PSt veya PCL gibi yumuşak yapıların birleştirilmesiyle böylece bu sorunun üstesinden gelindi.

İlk olarak istenilen PPV nin sentezlenmesi için öncü makromonomerlerin elde edilmesi gerekmektedir. Bu makaromonemerlerin hazırlanmasında, kontrollü polimerizasyon yöntemleri ve Suzuki kenetlenme reaksiyonu için uygun fonksiyonel gruplara sahip etkin başlatıcılar hazırlanarak zincir-ortası veya zincir-sonu dibromobenzen grupları içeren iyi-tanımlı, PSt veya PCL esaslı polimerler ATRP (Atom Transfer Radical Polymerization) veya halka açılma polimerizasyonu (ROP) gibi kontrollü polimerizasyon yöntemleri ile sentezlenmiştir.

1,4-Dibromo-2-(bromometil) benzen, 1,3-dibromo-5- (bromometil) benzen, ve 1,4-dibromo-2,5-di(bromometil)benzen CuBr /2,2'-bipridin katalizör sistemi ile stirenin (St) ATRP reaksiyonunda başlatıcı olarak kullanılmıştır.
2,5-Dibromo-1,4-(dihidroksimetil)benzen katalizör kalay oktoat (Sn(Oct)$_2$) varlığında ε-kaprolaktonun (CL) ROP reaksiyonunu başlatmıştır. Bu polimerler sonraki aşamalarda da kullanılacağından, uygun verimlerle düşük molekül ağırlıklı ve düşük polidispersiteli polimerlerin sentez edilmesine çalışılmıştır. Öncü polimerler Suzuki kenetlenme reaksiyonu için gerekli fonksiyonel gruplar korunmuştur. Son olarak, potasyum *tert*-butoksit varlığında Wittig reaksiyonu ile elde edilen polimerler, *p*-ksililenebis (trifenilfosfonyum bromür) ile etkileştirilerek istenilen konjugue polimerler sentezlendi. Böylece, ana zincire aşılanarak elden edilen PPV türevleri çözülebilir özelliğe sahiptir ve mavi yada yeşil floresans özelliği göstermektedir. Son zamanlarda, fotobaşlatılmış polimerizasyon, pek çok ekonomik ve ekolojik beklentileri karşıladığı için gerek endüstri gerekse akademik çalışmalarda gittikçe artan bir öneme sahip olmaktadır. Fotobaşlatılmış polimerizasyon, sahip olduğu mükemmel avantajları dolayısı ile kaplama, yapıştırıcı, kontakt lens, mürekkep, baskı levhaları, diş dolgu malzemeleri optik frekans yönlendiricileri ve mikroelektronik gibi sayısız uygulamaların temelini oluşturmaktadır. Fotopolimerizasyon, ısısal polimerizasyona göre bir çok üstün özellik gösterir. Oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamada polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır. Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilse de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından serbest radikal ve katyonik sistemlere daha fazla ilgi duyulmaktadır. Genellikle endüstriyel uygulamalarda serbest radikal fotopolimerizasyon sistemleri kullanılmaktadır. Ancak, bu tip polimerizasyonların oksijenin yavaşlatma etkisi ve son ürünün özelliklerini etkileyebilen kürleşme sonrasındaki kısıtlamalar gibi bazı olumsuzlukları bulunmaktadır. Bu nedenle, fotobaşlatılmış katyonik polimerizasyon özellikle bu dezavantajların giderilmesi açısından gelecekte daha fazla yer alacağı düşünülmektedir. Bilinen pek çok katyonik fotobaşlatıcı mevcuttur. İyodunyum ve sülfonyum tuzları en çok bilinen ve kullanılan örnekleri oluşturmaktadır. Bu onyum tipi fotobaşlatıcılar, ısısal kararlılıkları, katyonik olarak polimerleşebilen pek çok monomer içindeki çözünürlükleri ve fotoliz sonucunda reaktif türler oluşturma kabiliyetleri bakımından önemli bir role sahiptirler. Brønsted asitlerinin yanı sıra radikal türlerinin de meydana getiriliyor olmasından dolayı bu tuzlar serbest radikal fotobaşlatıcısı olarak ve eşzamanlı serbest radikal ve katyonik polimerizasyonlarında da kullanılabilmektedir. Ancak, onyum tuzları ışığı sadece 220-300 nm arasında absorpladığı için istenilen uzun dalga boylarında kullanımı sınırlıdır. Bu olumsuzluk, aktivatorler yardımıyla ortadan kaldırılabilir ve fotobaşlatılmış katyonik polimerizasyonların spektral hassasiyetini UV ve görünür bölgeye taşınabilir. Bu aktivatorler fotouyarıcı olarak bilinir.

Bu çalışmada, onyum tuzlarının elektron transfer fotouyarılmasında PPV türevlerinin kullanımını ayrıntılı bir şekilde ele alınmıştır. Bu amaçla, iki farklı PPV türevi olan PPV-*g*-PSt ve/veya PPV-*g*-PCL fotouyarlaştırıcı olarak kullanılmıştır. Bu bileşiklerin uyarılmış hal yayınım özellikleri floresans ve fosforesans spektroskopik ölçümleri aracılığıyla incelenmiştir. Siklohekzen oksit (CHO), isobütil vinil eter (IBVE), ve *N*-vinilkarbazol (NVC) monomerlerinin katyonik polimerizasyonu oda sıcaklığında uygun dalgaboylarında çeşitli onyum tuzları örneğin; difeniliyodonyum hekzaflorofosfat ($Ph_2I^+PF_6^-$) ve *N*-etoksi-2-metilpiridinyum varlığında başlatılmıştır.

Optik absorpsiyon ve floresans spektroskopik ölçümleri, serbest enerji değişimleri (ΔG) ve proton yakalama çalışmaları ile ilişkendirilerek öngörülen mekanizma, ilk aşamada ışığın absorplanmasıyla eksipleks oluşumunu içermektedir. Sonraki adımda, uyarılmış moleküllerden iyodonyum iyonuna elektron transfer edilmesiyle PPV türevlerinin radikal katyonları oluşmaktadır. Bu yüzden bu proses sonucunda meydana gelen güçlü Brønsted asidi çeşitli monomerlerin katyonik polimerizasyonunu başlatmaktadır. Trifenilsülfonyum tuzlarının elverişsiz termodinamik koşullarından dolayı elektron transfer prosesini başlatmada etkisiz olduğu belirlenmiştir.

1. INTRODUCTION

Photopolymerization is a typical process that transforms a monomer to a polymer by the help of photon energy. For this procedure to be applied, a photolabile compound, known as the photoinitiator, decomposing upon irradiation to give radicals or cations depending on its structural nature, is used. The corresponding polymerization is then initiated by these species formed. Both photoinduced polymerization types were studied in detail and their mechanisms were investigated. Photoinitiated radical polymerization has significant benefits as it can be applied to a wide range of monomer formulations and many photoinitiators with different absorption characteristics are readily available. Specifically, low energy consumption becomes a major demand lately which conceives intense research for the development of new photoinitiators absorbing light in the near UV and visible range of the magnetic spectrum. The corresponding cationic mode, on the other hand, is applicable to oxirane and vinyl ether type monomers, which do not undergo polymerization by radical routes. In addition, it is not affected by the oxygen inhibition present in the air facilitating industrial applications without additional processes. However, the polymerization suffers from the availability of limited number of photoinitiators especially in the low energy region of the spectrum. The well-known and most widely used examples of cationic photoinitiators, are diphenyliodonium and triphenylsulfonium salts with UV sensitivity. Although at relatively lower efficiency, *N*-alkoxy pyridinium and phosphonium salts are also introduced as efficient alternative photoinitiators in the UV range. For the utilization of these photoiniators in the long wavelength demanding applications, three modes of indirect activation are proposed. These include a) oxidation of free radicals by oxidants (also called as free radical promoted cationic polymerization) b) formation of charge transfer complexes and c) the use of photosensitizers in conjunction with onium salts. Among these, photosensitizers/onium salt combinations offers unique initiating systems involving an electron transfer from the excited state photosensitizer to the onium salts to yield

Bronsted acid, which initiates cationic polymerization of appropriate monomers. The suggested mechanism is shown in Figure (1.1).

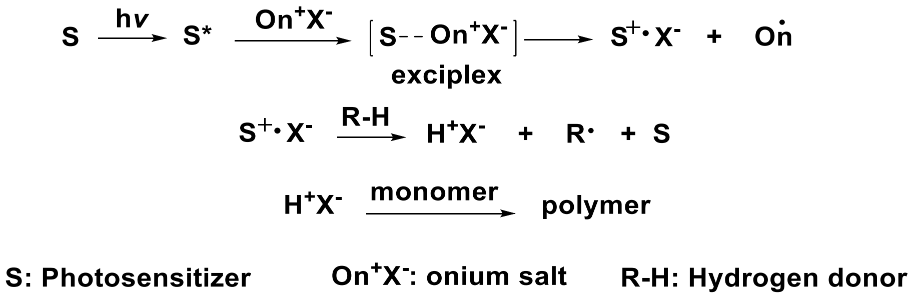


Figure 1.1 : Photosensitized electron transfer mechanism of cationic polymerization.

In this mechanism, sensitizers, which are generally conjugated aromatic compounds, absorb the incident photon energy and triggered to their excited states. The excited state sensitizers form exciplexes with ground state onium salts to fragment into the radical cation of the sensitizer and the radical form of the onium salt. The positively charged sensitizer is reduced by a surrounding monomer or a solvent to give Bronsted acid, which in turn initiates polymerization. Since the photosensitizers absorb light in higher wavelengths compare to the onium salts, this method offers utilization of polymerizations at higher wavelengths. Anthracene, perylene, pyrene, and phenothiazine type polynuclear aromatic compounds are known to be efficient photosensitizers fulfilling these requirements. In earlier studies, we reported that structurally related thioxanthone and thiophene derivatives with extended conjugation can also act as photosensitizers at long wavelengths even in the visible range for the photoinitiated free radical and cationic polymerizations using onium salts. In a recent work, fullerene end-capped polystyrene (PS-C_{60}) was reported to be an alternative photosensitizer for cationic polymerization acting in a similar manner to polynuclear aromatic compounds. Due to its excellent photophysical properties and favorable thermodynamic conditions, PS-C_{60} displayed high initiation efficiency when used in conjunction with onium salts. In related works from Lalevee’s laboratory, several long wavelength initiating systems were reported. Various dyes, silanes and polythiophenes were shown to be efficient to induce reduction of onium salts even at visible range using LED lamps offering environmentally friendly processes.

Substantial π-electron delocalization along the backbones of conjugated polymers offersinteresting optical and nonlinear optical properties. These physical properties afford their applicability in a variety of fields such as solar energy conversion, substituents for batteries, and data storage. The most common classes of such polymers are polyphenylenes, poly(phenylene vinylene)s (PPV) and polythiophenes. However, their utilization for such technologies is limited due to their poor processability and solubility characteristics. In order to overcome such limitations, several side-chain modification approaches were proposed. Recently, we have synthesized polystyrene (PSt) and poly(ε-caprolactone) (PCL) side chain functionalized PPV by the combination of controlled polymerization and coupling processes. Such graft copolymers exhibited excellent solubility properties while preserving their existing photophysical properties.

In the present study, we report the use of these side-chain modified PPVs as polymeric photosensitizers in conjunction with onium salts to initiate the cationic polymerization of oxiranes such cyclohexene oxide (CHO) and vinly monomers such as isobutyl vinylether (IBVE) and N-vinyl carbazol (NVC). As will be shown below, these PPV derivatives are capable of efficiently initiating cationic polymerization in the near UV and visible range of the electromagnetic spectrum. Besides the solubility and absorption characteristics, the polymeric nature of the photoinitiators offers additional advantage to overwhelm migration problems associated with the structurally similar low molar mass polynuclear aromatic compounds.

2. THEORETICAL PART

2.1 Conjugated Polymers

Conjugated polymers have attracted great interest [10] due to their wide range of potential applications including corrosion inhibition [16] aerospace industries light emitting diodes [11] batteries [12] electro chromic devices [13], sensors [14] electromagnetic shielding [15], solar cell devices and electronics industries because of their applicability in the fabrication of electronics and electro-optic devices arising from characteristic electronic and optical properties [17]. Substantial π-electron delocalization along the backbones of conjugated polymers offers interesting optical and nonlinear optical properties [18-20]. These physical properties afford their applicability in a variety of fields such as solar energy conversion, substituents for batteries, and data storage. They are insulators and they are colorless, i.e., they possess no mobile charges and the lowest electronic excitations are in the UV region. There exists a peculiar class of polymers with quite different properties; these are polymers with conjugated double bonds in the main chain. They are semiconductors or conductors and interact with light. Inherently conducting polymers have been an area of extensive research over the past decades and this culminated with the Nobel Prize in chemistry awarded to MacDiarmid, Heeger and Shirakawa in 2000 for their discovery that "doped" polyacetylene can conduct electricity changed the way that polymers were viewed and led to major advances in plastic electronics [21-23].

Among these was the discovery of electroluminescent polymers and their application in light-emitting devices. These devices are now becoming commercially available, representing the final step in the advance of organic electronics from a laboratory curiosity to a part of everyday life. Conjugated polymers possess excellent properties such as non-linear optical behaviour, electronic conductivity, photoluminescence, electroluminescence, as well as thermochromism, electrochromism, and exceptional mechanical properties [10, 24-28]. Typical conjugated polymers include polyacetylene (PA), poly(p-phenylene) (PPP), polythiophene (PT), poly(p-phenylene vinylene)

(PPV), polypyrole (PPy), polyfluorene (PF), polycarbazole (PCz), poly(ethylene dioxythiophene) (PEDOT) and poly(p-phenylene ethynylene) (PPE) as shown in (Figure 2.1).

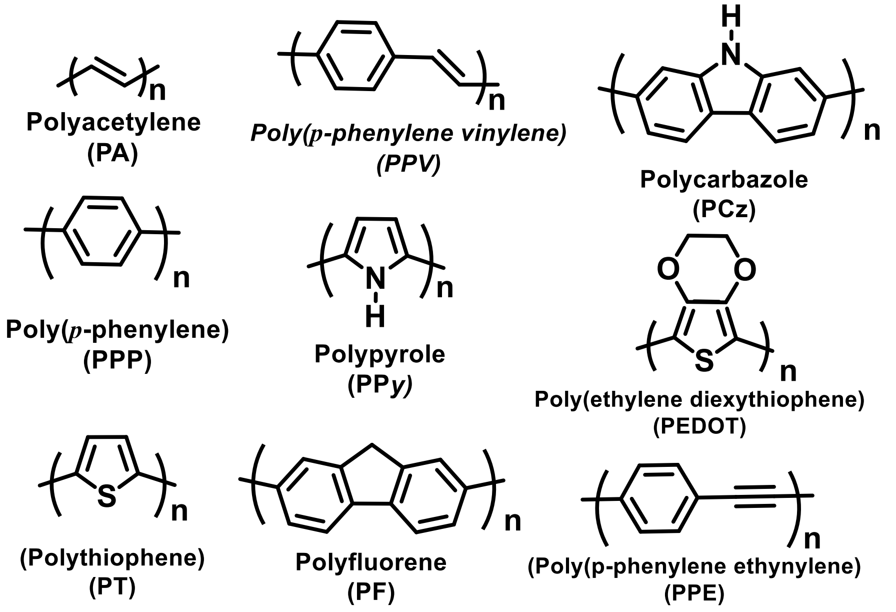


Figure 2.1 : Structures of typical conjugated polymers.

Conjugated polymers are organic macromolecules, which consist alternating single and double bonds in their polymer backbone. They are defined as extended conjugated systems containing delocalized π-electrons arising from their alternating structure of single and double bonds along polymer chains [10]. The peerless optical and electric properties of conjugated polymers are attributed to delocalized π-electrons and the overlap of p-orbitals. For instance, strong absorption of light in the visible region is one of the special features of molecules containing conjugated repeating units, which is due to the lower energy required by the π-electrons to promote them to the excited state, since they are less tightly bound to the carbon nuclei. The degeneration of the molecular orbital of double bonds gives a HOMO band and a LUMO band, as an analogue to the valence band and the conduction band in inorganic semiconductors. The energy difference between these two bands is called the band gap. HOMO and LUMO energy levels of conjugated polymers as well as their band gaps are adjustable by copolymerizing with different units. Conjugated polymers are interesting materials due to both their semiconducting properties and highly tunable molecular ordering that can proceed in a hierarchical way on multiple length scales ranging from nanometers to macroscopic dimensions, leading to a vast variety of nano-, meso-, and micro-structures.

Conductors (metals) are materials that possess partially filled bands, and this characteristic is the key factor leading to the conductive nature of this class of materials. Semiconductors, on the other hand, have filled (valence bands) and unfilled (conduction bands) bands that are separated by a range of forbidden energies (known as the ‘band gap’ [10].

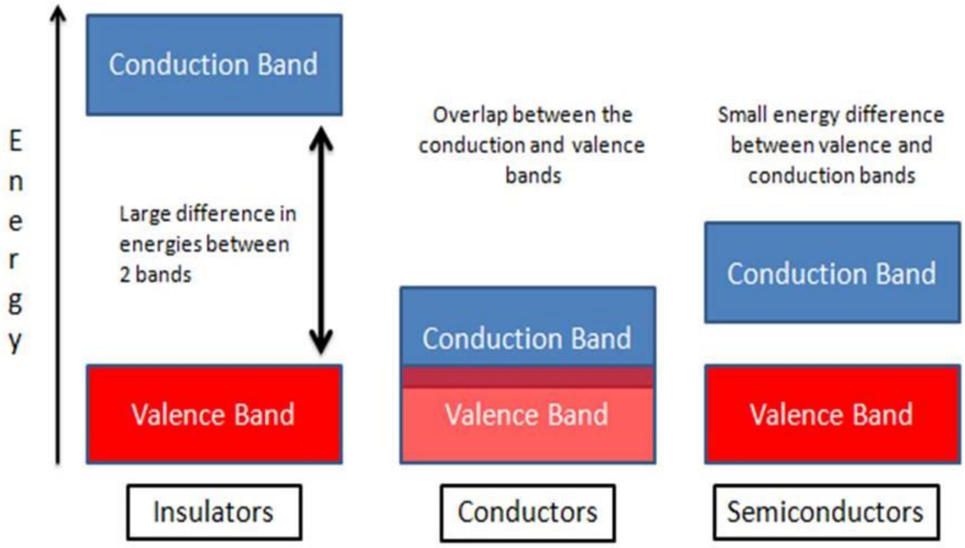


Figure 2.2 : Band structures of insulator, semiconductor and conductor.

As shown in the diagram above, (Figure 2.2) the key difference between semiconductors and conductors is that conductors have a natural overlap between their valence electrons and the conduction band, while semiconductors have a noticeable gap between the two. The result is that the electrons of conductors are able to carry a current under any condition. Meanwhile, the conductive ability of semiconductors requires energy to be put into the semiconductor band, increasing the number of available conducting electrons. This energy usually comes in the form of heat, which is why semiconductors are able to conduct more effectively as they rise in temperature.

The highest occupied band is called the valence band, and the lowest unoccupied band is the conduction band. The energy difference between them is called the band gap. Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be electrically conducting, as neither empty nor full bands can carry electricity [29].

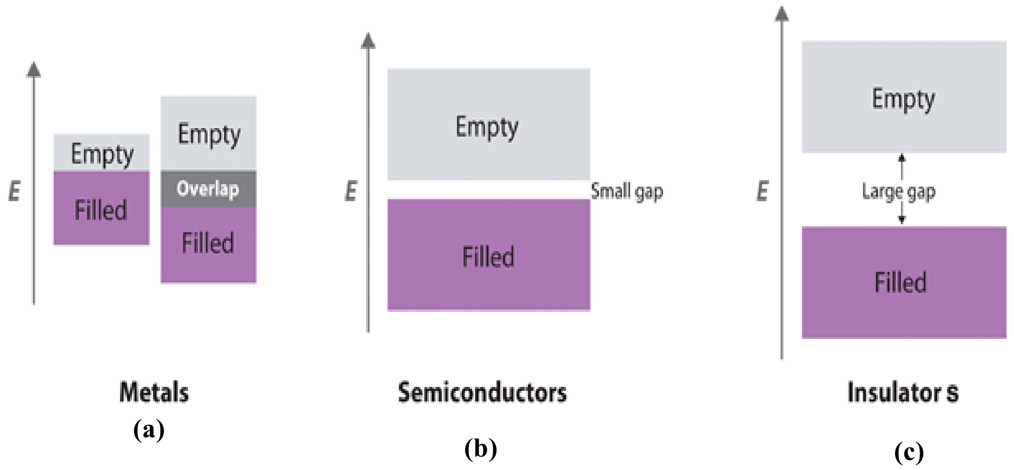


Figure 2.3 : The energy difference between the band gap of insulator, semiconductor and metal.

As can be shown in (Figure 2.3) owing to the presence of partially filled energy bands, metals have high conductivities (Figure 2.3 (a)). The energy bands of insulators and semiconductors, however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap (Figure 2.3 (b)). In contrast, conjugated polymers have narrower band gaps (Figure 2.3 (c)) and doping can change their band structures by either taking electrons from the valence band (p-doping) or adding electrons to the conduction band (n-doping) [1]. The charge carrier delocalization along the polymer backbone increases the effective conjugation length of the polymer and extends into a three dimensional system through inter-chain. Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity [2].

2.1.1 Routes for synthesis of conjugated polymers

There are several synthetic strategies available for the formation of a single bond between two unsaturated carbons. In addition to electrochemical or chemical oxidative polymerizations [30,31], transition- metal-catalyzed cross-coupling reactions provide a particularly powerful synthetic strategy for Csp^2-Csp^2 and Csp-Csp^2 bond formation. Several conjugated polymers are usually prepared by chemical or electrochemical processes which provide films with different morphologies in particular and modification.

The most common procedures used for the preparation of conjugated polymers are chemical oxidative coupling polymerization electrochemical polymerization, organometallic coupling processes and photochemical polymerization.

2.1.1.1 Electrochemical polymerization

Organic conjugated polymers (conducting polymers) have emerged as potential candidates for electrochemical sensors Due to their straightforward preparation methods, unique properties, and stability in air, conducting polymers have been applied to energy storage, electrochemical devices, memory devices, chemical sensors, and electrocatalysts. Electrochemical preparation of conjugated polymers was firstly defined by Diaz in 1981 [32]. The polymerization proceeds via coupling of two radical cations, formed by oxidation of the monomer, to yield a dihydrodimer dication which leads to a dimer after loss of two protons and rearomatization (Figure 2.4) [24].

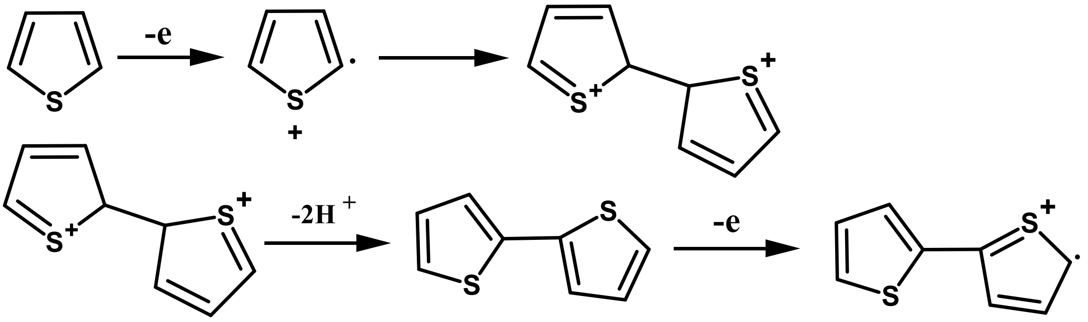


Figure 2.4 : Electrochemical polymerization of thiophene.

In this coupling mechanism, the formation of the dihydro dimer is the key propulsive force. The dimer has lower oxidation potential than the monomer and, as a result it is easily oxidized to give rise to further couplings. Electrochemical polymerization, can be described that the electrode in the supporting electrolyte solution with monomer-soluble radical oxidation by applying an external potential involves the formation of the cation .The polymerization reaction in the electrochemical polymerization process is a radical addition reactions. But also condensation reactions is occurred partially.

Electrochemical polymerization includes short reaction times, small amounts of monomers, and gives polymers in their oxidized state in the form of electrode supported, stable films, which possess favorable opto-electronic properties.

2.1.1.2 Chemical oxidative coupling polymerization

Oxidative coupling as a synthetic technique has received considerable attention in recent years, especially in the field of natural products. The oxidative coupling chemical polymerization can be carried out with different oxidizing agents. For examples, Barton and Kirby [3] have coupled N-(3-hydroxy-4-methoxyphenyl)-N-methyl-4-hydroxyphenethylamine to give narwedine using manganese dioxide, Hassell and Lewis [4] used lead dioxide to couple oxidatively geodin hydrate in a partial synthesis of geodoxin, and Davidson and Scott [5] used manganese dioxide in the synthesis of picrolichenic acid. Among other oxidizing agents, alkaline ferricyanide has been used by Wanzlick and Scott [6]. 2,4,6-Tri-t-butylphenoxy has been used by Cahnmann and Matsuura [7] and chromium trioxide was employed by Kenner, et al., in coupling various phenols [8].

The most commonly used oxidants for the synthesis of conjugated polymers are Lewis acid catalysts such as $AlCl_3$, $RuCl_{3,}$ $FeCl_3$, and $MoCl_{3.}$ A more convenient method developed by sugimoto et al. uses ferric chloride as the oxidizing agent and chloroform as the solvent under anhydrous conditions. Subsequent reduction with ammonia results in a neutral polymer in good yields. This simple coupling reaction is widely employed for the synthesis of polythiophenes from thiophene with alkyl, alkoxy, and alkyl sulfonic acid substituents and bithiophenes with one or two alkyl substituents. These bithiophene monomers can also be polymerized using milder oxidants. Sugimoto et al explored transition metal halides such as iron (III), molybdenenum (V) ,ruthenium(III) chlorides as oxidants for the polymerization of 3-hexylthiophene.For example, poly(9,9-dialkylfluorene)s (PAFs) and poly(3-alkylthiophene)s (PATs) [33,34] was synthesized by Yoshino and co-workers via this method. In this method, the monomer is dissolved in chloroform or other appropriate organic solvents and oxidatively polymerized with $FeCl_3$ or $AlCl_3$. Ferric chloride oxidizes the 3-alkylthiophene monomer to produce radical cations in the 2 and 5- positions of the thiophene which then couple to form a polymer. The cycle of three consecutive steps (e.g., loss of electron, coupling of radical cations, and deprotonation) is repeated to give regiorandom-PATs with comparatively high molecular weights and broad polydispersities. Polymers obtained by the oxidative polymerization exhibit a regiorandom structure (Figure 2.5).

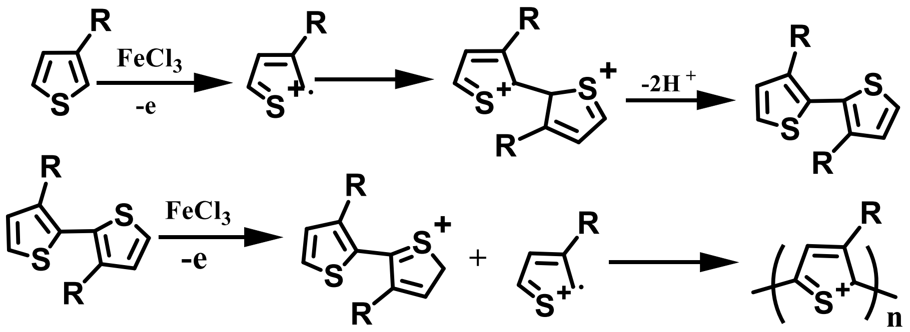


Figure 2.5 : Chemical oxidative coupling polymerization mechanism.

2.1.1.3 Organometallic coupling

Cross- coupling of an aromatic organometallic compound with an aromatic organohalide using nickel and palladium catalysts is well-known method for the synthesis of oligoheterocycles. Especially, Nickel, palladium, zinc, boron and tin-catalyzed cross-coupling of an organometallic compound with organohalides is a well-known method. While palladium is far more popular than nickel in cross coupling reactions such as Suzuki coupling, nickel is more often used in the intermolecular coupling of two different unsaturated functional groups (such as an alkyne and an aldehyde) in the presence of a reducing agent. Suzuki, Yamamoto, Kumada and Heck coupling reactions are often used to prepare conjugated polymers.

Suzuki coupling

The coupling of organoboron compounds with aryl and alkenyl halides or triflates is called the Suzuki reaction or Suzuki–Miyaura coupling and was discovered in the early 1980s.

Recent catalyst and method developments have broadened the possible applications enormously, so that the scope of the reaction is not restricted to aryls, but also includes alkyls, alkenyls, and alkynyls. The reaction relies on a palladium catalyst such as tetrakis(triphenylphosphine)palladium(0) to effect part of the transformation [35-38]. The palladium catalyst is 4-coordinate, and usually involves phosphine ligands. Potassium trifluoroborates and organoboranes or boronate esters may be used in place of boronic acids. Some pseudohalides such as triflates may also be used as coupling partners. The versatility of the reaction originates from the mild reaction conditions and availability of the reagents. Besides , it is not influenced by the presence of water, is highly tolerant to a wide range of functional groups and proceeds regio- and stereoselectively. In partıcular, Non-toxicity and easy removal of the inorganic by product makes the reaction attractive for laboratories and industrial processes [39]. The mechanism of the Suzuki reaction viewed from the perspective of the palladium catalyst, is shown in Figure (2.6).

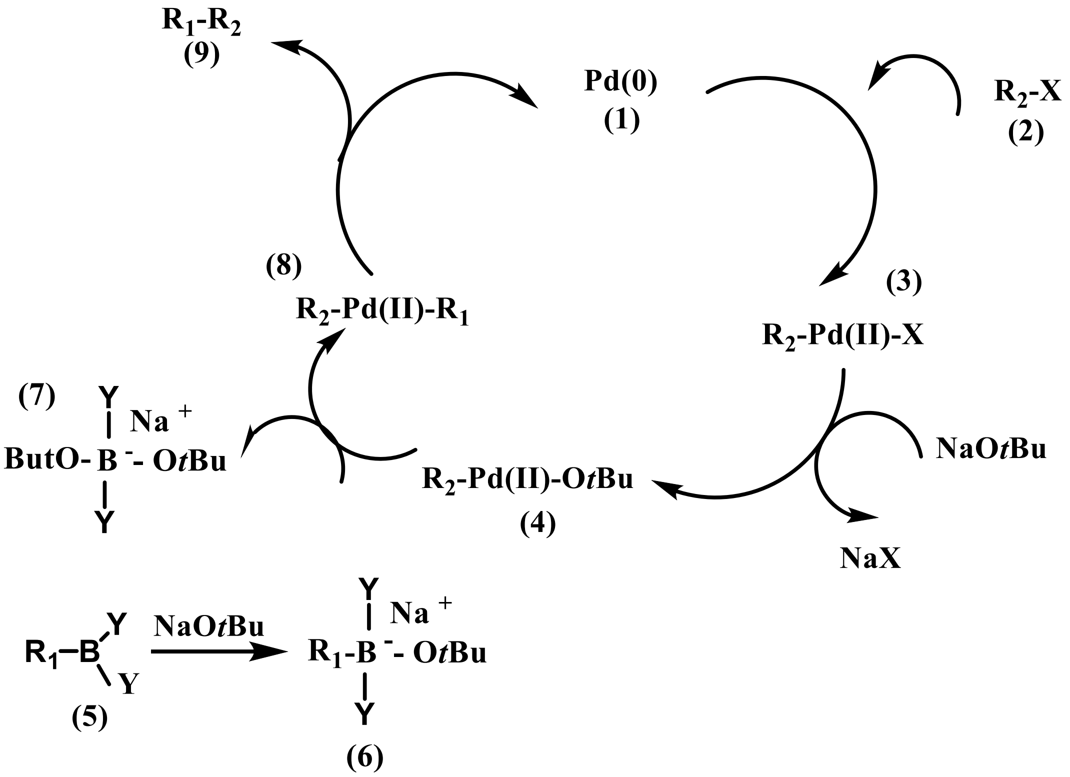


Figure 2.6 : The mechanism of Suzuki coupling reaction.

The first step is the oxidative addition of palladium to the halide **(2)** to form the organopalladium species **(3)**. Reaction with base gives intermediate **(4)** which via transmetallation with the boronate complex **(6)** forms the organopalladium species **(8)**. Reductive elimination of the desired product **(9)** restores the original palladium catalyst **(1)**.

Yamamoto coupling

Yamamoto coupling, which was developed by using the polycondensation of dihaloaromatic compounds, is a convenient and efficient approach for the synthesis of conjugated polymers [40]. The polymerization is considered by oxidative addition, disproportionation and reductive elimination steps by using nickel (0) complexes (Figure 2.7) [41].

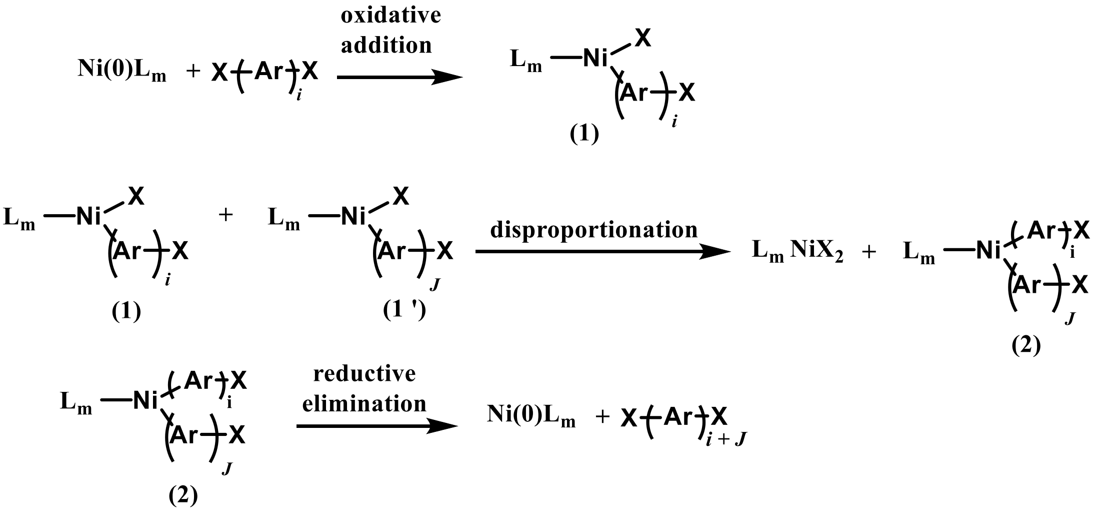


Figure 2.7 : The mechanism of Yamamato coupling reaction.

The first step is oxidative addition of C-X to Ni(0)L_m. The second step is disproportionation. In the final step, diorganonickel (II) complexes NiR_2Lm undergo reductive coupling (or reductive elimination) reactions to give R-R. The coordination of molecules, such as aromatic compounds, leading to the backdonation from the central metal facilitates the reductive elimination of R-R. It is possible to isolate the complexes **(1)** and **(2)** as well as a complex of the type L_m(XNi-Ar-Ni(X)L_m when the Ni-C bond is highly stabilized [42].

Furthermore, unsaturated organic groups were shown to undergo much easier coupling reaction on the metal center. The rates for reductive elimination folowed the following order : vinyl-vinyl > phenyl-phenyl >alkynyl-alkynyl > alkyl-alkyl. The activation barriers and the reaction energies for unsymmetrical R-R′ couplings were found to be close to the averages of the corresponding values of the symmetrical R-R and R′- R′ coupling reactions ; for example: vinyl-vinyl > vinyl > alkyl > alkyl-alkyl [43].

Kumada coupling

The Kumada cross-coupling reaction is the organic reaction of an organohalide with an organomagnesium compound, also known as a Grignard reagent, to give the coupled product using a palladium or nickel catalyst. The palladium catalyzed mechanism begins with oxidative addition of the organohalide to the Pd (0) to form a Pd (II) complex. Transmetalation with the Grignard reagent then follows, where the R group of the Grignard reagent replaces the halide anion on the palladium complex and makes a magnesium (II) halide salt. Reductive elimination then gives the final coupled product, regenerates the catalyst, and the catalytic cycle can begin again (Figure 2.8**)** [44].

$$\mathbf{RX + R'Mgx \xrightarrow[Pd(PPh_3)_4]{Ni(PPh_3)_4\ or} R\text{-}R'}$$

R= aryl,vinyl
R'= aryl,vinyl,alkyl
X= I <Br <Cl

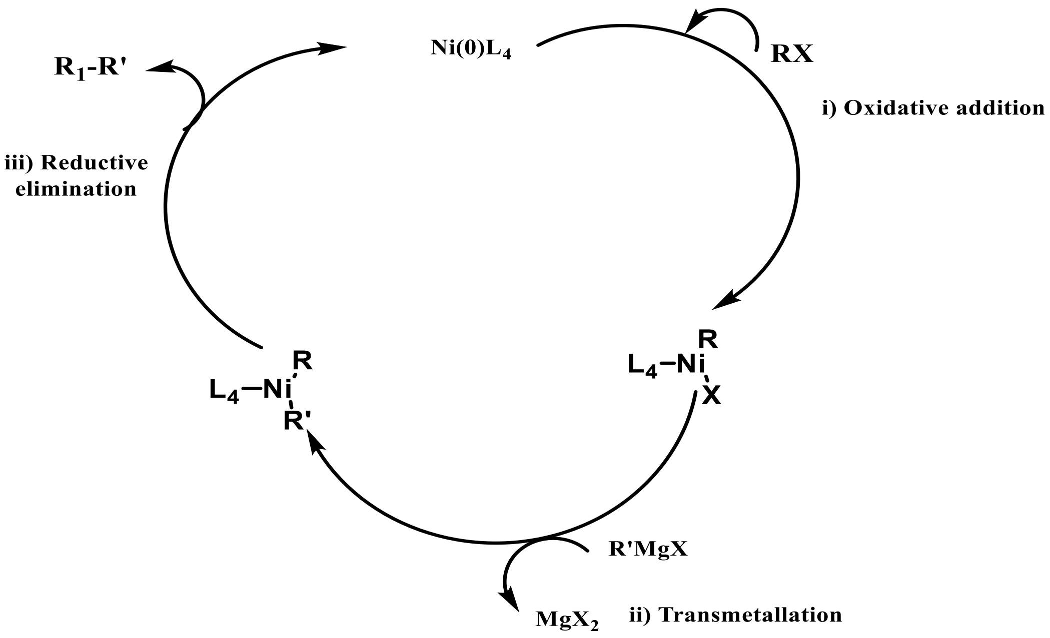


Figure 2.8 : The mechanism of Kumada cross- coupling catalytic cycle.

Heck coupling

The Heck reaction is a cross-coupling reaction of an organohalide with an alkene to make a substituted alkene using palladium as a catalyst and a base. The arylation and vinylation of alkenes with aryl or vinyl halides was discovered independently by Heck and Mizoroki et al. [45]. Nearly 35 years ago and it is nowadays known universally as the Heck reaction (HR) .The reaction begins by oxidative addition of the aryl halide to the palladium, which is followed by coordination and migratory insertion of the olefin to the palladium. Bond rotation then places the two groups trans to each other to relieve the steric strain and subsequent β-hydride elimination results in a trans final product. Base mediated reductive elimination regenerates the palladium (0) catalyst. Reaction steps involve oxidative addition, insertion and β-hydride elimination (Figure 2.9). The forming product is an alkene.

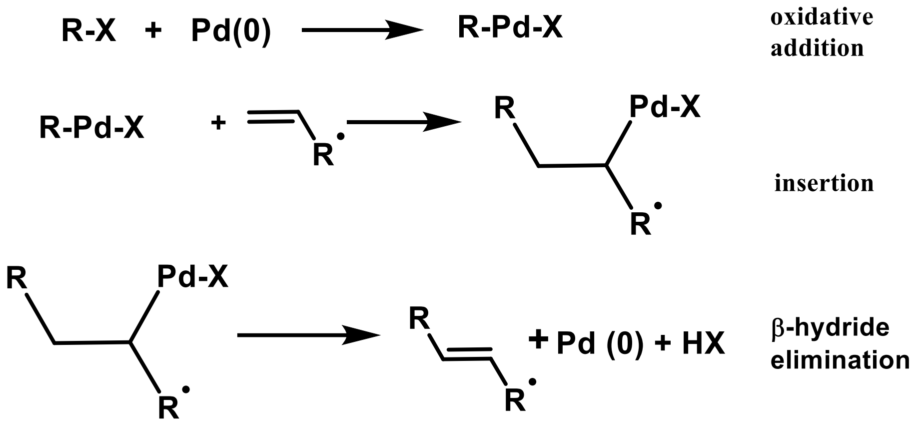


Figure 2.9 : Heck reaction steps involve oxidative addition, insertion and β-hydride elimination.

With alkenes bearing mesomerically electron withdrawing groups, the rate of insertion increases. Sterical hindrance of alkene is also important at insertion step. β-hydride elimination is also syn, but in the case of acyclic alkenes, due to the free rotation, a stable trans alkene is obtained. Generally, polar solvents are used for the reaction. By intramolecular Heck reactions, ring systems are obtained with good efficiencies and free of limitations such as sterical hindrances, and also syn stereochemistry of both insertion and elimination steps are kept. One of the benefits of the Heck Reaction is its outstanding *trans* selectivity. The catalytic cylcle for the Heck reaction involves a series of transformations around the palladium catalyst. The palladium (0) compound required in this cycle is generally prepared in situ from a palladium (II) precursor [46,47].

2.1.2 Polythiophenes

Polythiophene (PT) and its derivatives are among some of the most widely studied conjugated polymers. This is due to their outstanding thermal stability (42% weight loss at 900°C), electrical conductivity (3.4×10^{-4} to 1.0×10^{-1} S/cm when doped), and environmental stability.Polythiophene was first synthesized in the early 1980s via metal-catalyzed polycondensation polymerization of 2,5-dibromothiophene or the oxidative polymerization of thiophene [48,49].

Polythiophenes are of great interest because of their comparatively small band gaps, environmental stability, and good processibility. One major disadvantage of these compounds is their low solubility in most organic solvents, which may be attributed to strong intermolecular π-π interactions. Also, there are also some other special features such as fast nonlinear optical (NLO) response, excellent crystallinity, and better mechanical properties, which polythiophenes generally does not afford. These features could be achieved by structural modification approaches such as attachment of pendant side chains to polythiophene backbone, annulations of thiophene ring, introduction of conjugated spacers, synthesis of regioregular polythiophene derivatives, synthesis of thiophene based copolymers and thiophene based metallopolymers [24].

Polythiophenes (PTs) (including oligothiophenes) are one of the most studied and important classes of linear conjugated polymers. Versatile synthetic approaches to PTs, both chemical and electrochemical, easy functionalization and unique electronic properties, which can be widely tuned, focus a tremendous interest to this class of polymers. Due to electron-rich character of the thiophene ring, PTs can be easily and reversibly oxidized by chemical or electrochemical mean to form p-doped, usually highly conducting materials. The first electronic transition of undoped PT (which strongly depends on the structure) lies between 300 and 500 nm (e ~ 10,000 M^{-1} cm^{-1}),upon doping undergoes dramatic bathochromic shift transforming into so called “conducting” band, which tails from the visible to deep IR region.

Structural modification of polythiophenes has a great importance, since they possess so many unique properties for possible wide a growing number of applications. There are two important reasons for functionalization of polythiophenes: **i)** improving electrical properties in order to obtain low band gap polythiophene derivatives with good conductivity and **ii)** improving physical properties in order to obtain processable polythiophene derivatives with long term stability [50].

During the past two decades, tremendous efforts were put into searching for low band gap polythiophene derivatives due to their practical advantages over other higher band gap materials. Easy doping with possible intrinsic metallic conductivity, improved photoconductivities for solar cell application, large nonlinear optical coefficients, and possible transparent materials in doped states are the reasons for the significance of low band-gap conducting polymers.

Polymers based on dithienothiophenes have lower band gaps compared to polythiophene analogues, due to their additional fused ring. These polymers were first synthesized electrochemically [51,52], and later it was found that they are very attractive polymers with high doping levels, high columbic efficiencies and excellent cycling abilities for battery applications [53]. Various photochemical strategies have also been employed to synthesize polydithienothiophenes [54-57].

2.1.3 Polypyrrole

What distinguishes conducting polymers is the conjugated structure of the backbone; the polymer chain has an alternating single and double bond (Figure 2.10). shows the conjugation in the molecular structure of polypyrrole. The single (sigma) bond has electrons localized between the two atoms, but the double (π) bond has the electrons in lobes above and below the sigma bond as seen in (Figure 2.11). Polypyrrole (PPy), is synthesised from the pyrrole monomer, which consists of a 5-membered ring, containing a nitrogen (N) heteroatom. As with other organic molecules, pyrrole polymerisation occurs upon oxidation of the monomer, which forms a conjugated polymer chain with overlapping π-orbitals and a positive charge along the polymer backbone [58]. PPy was first synthesised chemically in 1916 by the oxidation of the pyrrole monomer using hydrogen peroxide, which yielded an amorphous black powder known as ‘pyrrole black’. It was not until many years later that the first electrochemical synthesis of polypyrrole was reported by Dall’Ollio et al. in 1968. Dall’Ollio et al. used an aqueous solution of pyrrole and sulphuric acid to electrosynthesise a layer of PPy on a platinum electrode [59]. Since then, a wide variety of substrates and solutions have been used to deposit polypyrrole electrochemically.

There have been a lot of investigations into polypyrrole as it has a large surface area owing to its fibrous structure and it is a high capacity electrode material. Its ease of preparation, inherent electrical conductivity and high stability in both aqueous systems and in air make PPy a promising interfacial material. As a result, it is one of the most intensively used and studied polymers and accordingly it is an ideal candidate for a number of advanced technologies such as sensors. An additional feature of PPy is that it forms a biologically compatible polymer matrix [60], which has led to its use in a broad number of biomedical fields including biosensors [61,62], tissue engineering [63,64] and implantable biodevices [65]. Another interesting and prominent property of PPy is its ability to switch its redox behaviour. This has resulted in the design of ion-selective electrodes, electrochromic displays, solar cells, drug delivery systems and actuators [66].

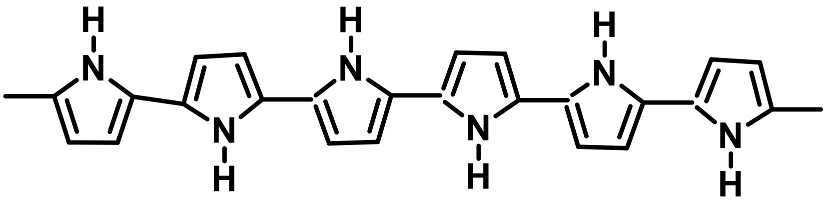


Figure 2.10 : Chemical structure of polypyrrole. The alternating single and double bond makes this polymer a semiconductor.

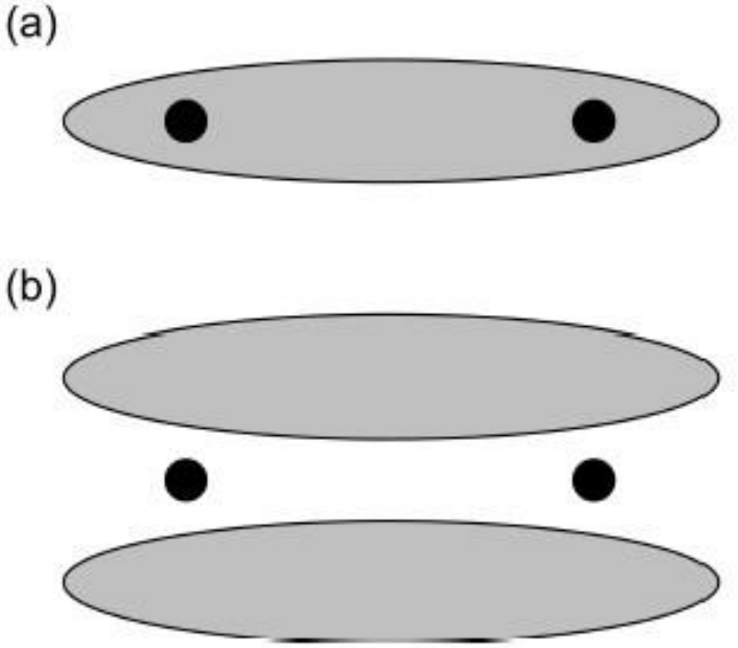


Figure 2.11 : (a) Sigma bonds have most of the electron density between the two nuclei, (b) π bonds have electron density above and below the nuclei. Dots represent the nuclei, and the gray ellipses are the electron clouds.

Since the electronic properties of polypyrrole vary widely with synthesis conditions, it is to be expected that the electrochemical properties do as well. In general, polypyrrole acts as a porous electrode, with no electron transfer between the electrolyte and the polymer.

2.1.4 Poly (phenylene vinylene)s (PPVs)

Conjugated polymers are dependent upon π-conjugation for their properties and are thus different from most commercial polymers by having a backbone of alternating single bonds with double or triple bonds [67]. Conjugated polymers that emit light when an electric field is imposed on are known as “electroluminescent” polymers and have emerged a substantial academic and industrial interest as potential materials for electro-optical and opto-electronic applications [11-68].

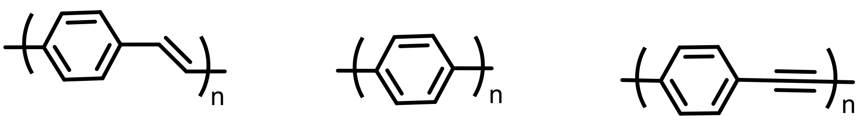
Organic materials with delocalised π electrons have absorptions in the visible region of the solar spectrum. To fabricate a solar cell using a conjugated organic material, a donor and acceptor must be chosen, the donor must be a good p-type or hole conducting material whereas the acceptor must be a good n-type or electron conducting material. Generally, conjugated polymers with alkoxy or alkyl substituents Phenoxy, carbazole copolymers are good p-type materials. The commonly used acceptor materials are derivatives of buckminsterfullerenes (C_{60}). Alternatively n-type conjugated polymers such as PPVs with electron withdrawing moieties appended can be used as a replacement to these allotropes of carbon [69-71].

Conjugated polymers such as poly (arylenevinylene)s, polythiophenes and poly (p-phenylene) exhibit interesting electrical, nonlinear optical and electrooptical properties which make them good candidates for applications in rechargeable batteries, supercapacitors, field-effect transistors, sensors electrochromic display devices and light-emitting diodes (LEDs) and also high photoluminescence quantum yields, generating increasing interest in the excitonic properties of these materials [72]. At present, the best known and most intensively studied example of such a system is poly (p-phenylene vinylene).

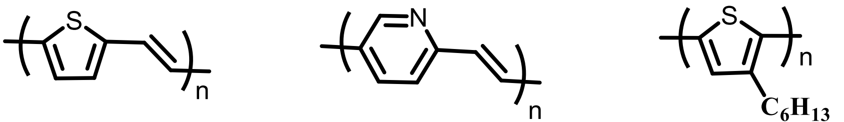
Poly (p-phenylene vinylene)s (PPVs) are also widely used in the manufacture of optical and electrical devices because of their electroluminescent activity and nonlinear optical responses [73]. By modifying the structure of PPV, various luminescent derivatives can be created that emit colors from the UV to the IR region. For example, introducing electron-donating groups into the polymer unit leads to a red shift in the absorption maxima, while electron-withdrawing groups induce a blue shift. These spectral shifts also modify the nonlinear optical response significantly.

The search leads to discovery of electroluminescence in aromatic conjugated polymer. which was first reported in poly (p-phenylenevinylene). PPV. Since that, researchers have focused their research and effort towards the development of organic semiconductor with electroluminescence properties.

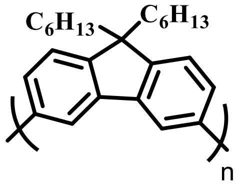
Some examples for the types that belong to the family of π-conjugated polymers are poly (p-phenylene vinylene) (PPV), poly (p-phenylene) (PP), poly (p-phenylene ethynylene) (PPE), poly(p-theinyl vinylene), poly(p-pyridyl vinylene) (PPyV), poly(3-hexyl thiophene) and poly(9,9-dihexyl fluorene). The basic structures of these polymers are shown in Figure (2.12). Since the first reports of electroluminescence from conjugated polymers by Holmes, Friend and coworkers, among the vast kinds of electroluminescent polymers, the most widely studied group is PPVs. PPV and its derivatives are very attractive materials for optoelectronic devices such as polymer light- emitting diodes (PLEDs), photovoltaics and polymer field effect transistors (PFETs) due to their unique charge transport and luminescence properties.



Poly(*p*-phenylene vinylene) Poly(*p*-phenylene) Poly(*p*-phenylene ethynylene)



Poly(*p*-thienyl vinylene) Poly(*p*-pyridyl vinylene) Poly(3-hexylthiophene)



Poly(9,9-dihexylfluorene)

Figure 2.12 : Some types of π-conjugated polymers.

2.1.4.1 Properties of PPVs

Mechanical properties

The PPV and its derivatives has a rigid structure and is inherently insoluble, interactable and infusible. This hinders its processability into thin films that is required for most of the applications. Consequently, tremendous efforts have been made for the design and synthesis of well-defined conjugated polymers with improved solubility, processability and stability. These initial problems have been addressed by introducing conformationally mobile, relatively long and flexible side chains, such as alkyl or/and alkoxy groups to PPVs [74-76] and PPs [77,78] and PPEs [79-82].

Poly(phenylene vinylene), PPV, has a nondegenerate ground state with eight carbons in the repeat unit, leading the π band to split into eight sub-bands, and calculated by others from a tight-binding Hamiltonian, and borrowed from .The four lowest energy bands are filled and the four highest energy bands are empty. The bands labeled with D are delocalized along the chain and are broadened. The two bands labeled L are localized on the ring and their wave functions are at the para linkages and do not participate in hopping.

PPV was used as an emitting layer that emits green-yellow light which posseses very interesting electroluminescence properties. The main structure of PPV comprises of phenylene and vinylene units. It is a conducting polymer because it is able to conduct electricity through conjugation of it electron along the polymer backbone, when an electric current is applied through the material. The electrons transition between the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) level gives rise to the conduction wave function. PPV was reported to have band gap energy of about 2.50 eV, which is in the semiconducting region.

Poly[2-methoxy-5-(2'-ethylhexyloxyl)-1,4-phenylene vinylene] (MEH-PPV) Figure (2.13) represents the basic and the mostly investigated PPV derivative bearing alkoxy side groups and serves as a model providing solubility in common organic solvents [74] and processability for use in different applications [83].

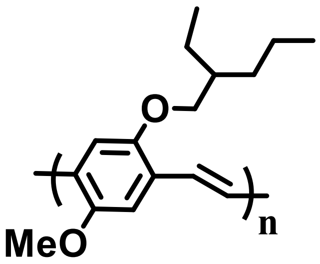


Figure 2.13 : The structure of Poly[2-methoxy-5-(2'-ethylhexyloxyl)-1,4-phenylene vinylene] (MEH-PPV).

Thermal properties

PPV exhibits a higher stability when compared to some other related π-conjugated polymers. The initial degradation temperature for PPV is at around 500^0C [84] and in the range of 500-600^{o}C, degradation products including toluene and xylene moieties are detected by in situ mass spectrometry. A slight increase, compared to neat PPV derivatives, is observed in the case of block copolymers of PPV and poly (methylmethacrylate) (PMMA) [85]. PPV can be converted into graphite at temperatures above 800^0C [86,87]. Pyrolysis at 3000^{o}C, strongly affects the electrical conductivity of PPV.

Poly (paraphenylene vinylene) (PPV) can be easily prepared from a workable precursor which allows preparation of films or stretched samples, has good chemical stability and shows remarkable optical non linearity. In the doped state it shows high electrical conductivity reaching values of σ =103 Ω^{-1} cm^{-1} (H_2SO_4 doping) and σ=102 Ω^{-1} cm^{-1} (AsF_5 doping) for stretch oriented samples. When doped with sulfur trioxide, conductivities of 105 Scm^{-1} can be obtained which is comparable to neutral graphite. A conductivity of 0,26.103 Scm^{-1} is reported when PPV and other related polymers are pyrolyzed at 1700˚C [88]. Degradation temperatures of some π-conjugated polymers are summarized in Table 2.1 as given below.

Table 2.1： Degradation temperatures of some π-conjugated polymers.

Polymer	T_g (^{o}C) (as onset of degradation)	Reference
Poly(acetylene)	200	84
Poly(*p*-xylene)	420	84
Poly(*p*-phenylene)	450	84
Poly(*p*-phenylene vinylene)	500	84

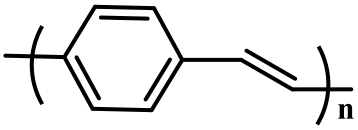
Electrical properties

Poly (p-phenylene vinylene) (PPV) and its derivatives are amongst the most widely studied class of conjugated polymers since the discovery of their electroluminescent properties in 1990. These polymers are studied for applications in numerous photonic devices such as organic solar cells, organic light emitting diodes (OLEDs), but also in field-effect transistors and electrochemical cells. PPV should exhibit a fully π-conjugated structure.

Conjugated polymers have band gaps in the range of 1 to 4 eV, allowing stable optical excitations and mobile charge carriers. The degree of derealization is likely to depend on the nature of the conjugated system [89]. Aromatic rings tend to localize the excitation because the alternative electronic configuration, the quinoid one, is higher in energy. These materials are often strongly fluorescent and emit in the range from near infrared to the ultraviolet. Particular research interest has focussed on PPV, and soluble derivatives thereof, due to the combination of emission in the visible wavelength region and high luminescence quantum yields. It is probable to detect the traps and identify their nature by techniques such as photoluminescence (PL) and electroluminescence (EL) spectroscopy, current voltage and capacitance voltage measurements, capacitance transient spectroscopy and admittance spectroscopy [90].

Optical properties

The generation of a LED device using conjugated polymers goes back to the 1990s. For the first time, it was observed at the Cambridge University that PPV emits yellow-green light when sandwiched between two electrodes. Studies on the electrical conductivity properties were followed by the research on investigation of optical properties. Besides, conjugated polymers attracted great interest for Organic Light Emitting Diode (OLED) applications as they show interesting optical features after the pioneer work of Friend et.al. obtaining green-yellow light from poly(p-phenylene-vinylene) (PPV). PPV was used as an emitting layer that emits green-yellow light which posseses very interesting electroluminescence properties. The main structure of PPV comprises of phenylene and vinylene units, as shown in (Figure2.14).



Poly (*p*-phenylene vinylene)

Figure 2.14 : The main structure of PPV.

PPV is a bright yellow fluorescent polymer that shows emission maxima at 520 nm and 551 nm, in the yellow-green region of the visible spectrum [68]. In EL devices, as well as being used as the light emitting component, PPVs can also be used as the hole-transporting materials [91] due to their good hole-transporting capability. For example, introducing electron-donating groups into the polymer unit leads to a red shift in the absorption maxima, while electron-withdrawing groups induce a blue shift. These spectral shifts also modify the nonlinear optical response significantly. Blue-shifted luminescence can also be achieved by increasing the band gap of the main polymer chain. Because of these properties, PPV can serve as the active element in light-emitting devices (LEDs). In PPV, an increase in static pressure causes a red shift in PL spectra and meanwhile the intensity of the main peak decreases [92]. Due to interaction of the polymeric chains, the structure turns out to be more planar so the length of conjugation becomes longer.

Doping and dopants

Organic materials with delocalised π electrons have absorptions in the visible region of the solar spectrum. To fabricate a solar cell using a conjugated organic material, a donor and acceptor must be chosen, the donor must be a good p-type or hole conducting material whereas the acceptor must be a good n-type or electron conducting material. Generally, conjugated polymers with alkoxy or alkyl substituents Phenoxy, carbazole copolymers are good p-type materials.

The commonly used acceptor materials are derivatives of buckminsterfullerenes (C60). Alternatively, n-type conjugated polymers such as PPVs with electron withdrawing moieties appended can be used as a replacement to these allotropes of carbon. Doping can be done by oxidation (p-doping) or reduction (n-doping) reactions in the backbone of the polymer. Structural and electronic modifications are created in the backbone and the electrical conductivity is improved by doping. Two main doping methods are reactive doping and dye doping. Arsenic pentafluoride can also be used as the dopant for PPV in reactive doping. A Friedel-crafts chain extension and cross-linking takes place and electrical conductivity is by hopping mechanism [93]. Dye doping is achieved by the addition of a fluorescent dye to polymer .The solution method is not used to dope PPV as it is insoluble. Instead, vapor transportation method is used in which the dye molecules are introduced in the polymers in the gas phase, in vacuo [94]. PPV is the only polymer of this type that can been processed into an exceptionally ordered crystalline thin layer film. PPV and its derivatives are electrically conducting upon doping.

2.1.4.2 Applications of PPVs

Light-emitting diodes (electroluminescent devices)

Poly(arylenevinylene)s, polythiophenes and poly (p-phenylene) s exhibit inter- esting electrical, nonlinear optical and electrooptical properties which make them good candidates for applications in rechargeable batteries, supercapacitors, field-effect transistors, sensors, electrochromic display devices and light-emitting diodes (LEDs) [95]. Since the discovery of polymer-based electroluminescent (EL) devices, tremendous effort has been focused on the design and synthesis of new soluble electro-active polymers to gain control of color and efficiency of light emission. Among a variety of polymer systems, p-phenylene-vinylene-based polymers are the most studied, possibly due to the fact that poly (*p*-phenylene vinylene) (PPV) was the first to demonstrate electroluminescence.

The first organic electroluminescent devices were discovered around the time the first light-emitting diodes (LEDs) were introduced into the commercial market in 1962. Like today, early devices were hampered by fabrication and packaging problems and short lifetimes. The fact that electroluminescence (EL) was first observed in conjugated polymers in 1990 by Burroughes et al. reveals the relative youth of this field. Many polymers are now known to display electroluminescence. But poly (p-phenylene vinylene) has proven to be a favorite platform within the research community [68].

PPV can be utilized as a single emissive layer between metallic electrodes, as shown in (Figure 2.15). In this structure, the indium tin oxide (ITO) layer functions as a transparent electrode, allowing the light generated within the diode to leave the device. The top electrode is conveniently formed by thermal evaporation of a metal. LED operation is achieved when the diode is biased sufficiently to achieve injection of positive and negative charge carriers from opposite electrodes. Capture of oppositely charged carriers within the region of the polymer layer can then result in photon emission [96]. For instance, The LED structure consists of a a metal contact (Ca) on the front surface of a PPV film on a glass substrate, partially, coated with a layer of indium/tin-oxide (ITO), the hole-injecting contact.

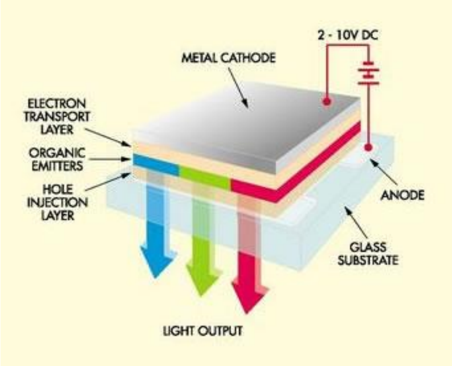


Figure 2.15 : Basic structure of an organic light-emitting diode (OLED).

Diodes of this type can be readily fabricated by the solution-processing of the semiconducting polymer onto the ITO-coated glass, even though the film thickness is no more than typically 100 nm. Spin-coating from solution has been demonstrated as being an effective means of producing a highly uniform layer thickness, with a layer of no more than a few A spread over several cm^2. Electrodes are chosen to facilitate charge injection; ITO has a relatively high work function and is therefore suitable for use as a hole-injecting electrode, and low work-function metals such as Al, Mg, or Ca are suitable for injection of electrons.

Structurally, a typical OLED is composed of an emissive layer, a conductive layer, a substrate, an anode and cathode terminals. The layers are made of special organic molecules that conduct electricity. Their levels of conductivity range from those of insulators to those of conductors, and so they are called organic semiconductors. The first, most basic OLEDs consisted of a single organic layer, for example the first light-emitting polymer device synthesized by Burroughs et al. involved a single layer of poly (*p*-phenylene vinylene).

The photoluminescence (PL) and electroluminescence (EL) spectra of PPV indicated that the emitting species are the same upon excitation by light or electric current.This novel improvement provided the possibility of combining the good mechanical and processing properties of the polymers with semiconductivity. Easy oxidation and reduction and forming polarons without affecting the σ bonds and thus the physical strength of the polymer is an important feature of electroluminescent polymers. The advantages concerning the use of electroluminescent polymers as a component in LEDs are the synthetic access and structure variations and thus color tunability, anisotropic light emission, light weight, large area displays, environmental factors (less toxicity compared to inorganic materials), and flexibility (a variety of unusual shapes of displays can be obtained) [97-99].

Electroluminescent polymers are generally aromatic π-conjugated polymers and that restricts their applications. Regarding this, the concepts, for which the efforts are targeted, include precursor polymers, solubilizing groups, polymers with conjugated and non-conjugated segments in the main chain or in the side chain. Electrical, optical and mechanical properties of such polymers may be affected by impurities, defects, structural disorders, effective length of conjugation and low-molecular weight [100]. Smart synthetic approaches and well-defined structural designs and architectures are the scopes of the research area. The basic requirements for the choice of electroluminescent polymers to be used in a device are good film-forming properties, transparent films, good thermo-mechanical stability and excellent heat ight and environmental stability; and as the emitting component, color tunability and emission in the visible region. The basic architecture for a light emitting device is shown in (Figure 2.16).

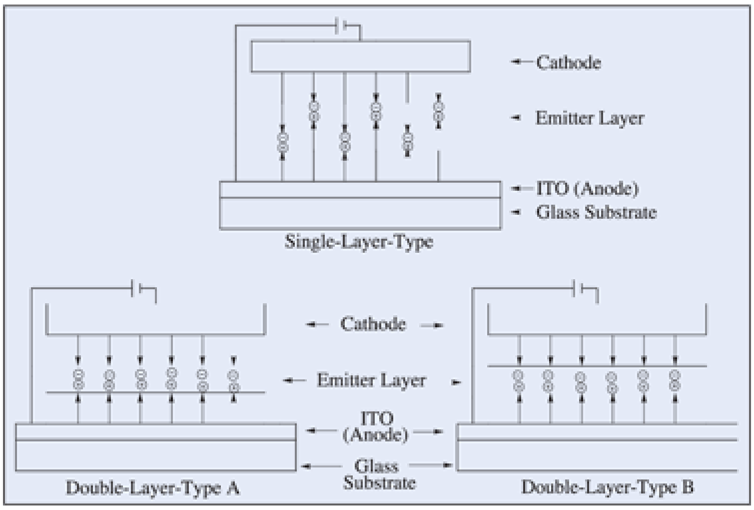


Figure 2.16 : The basic architecture for a single layer LED device.

To initiate light emission, a voltage is applied across the OLED such that the anode is positive with respect to the cathode. This causes a current of electrons to flow through the device from cathode to anode. Thus, the cathode gives electrons to the emissive layer and the anode withdraws electrons from the conductive layer. In other words, the anode gives electron holes to the conductive layer.

The optoelectronic properties of organic materials match well with the requirements necessary for electroluminescent (EL) devices. One of the clearly distinct advantages of OLEDs is the practically unlimited number of molecules that can be made for any particular application one can conceive. This enormous breadth of possible OLED development far outreaches that of both LCDs and LEDs. Many other organic materials also possess high luminescent efficiencies, making them ideal candidates for active displays. Another considerable advantage that OLEDs possess is the economy of their fabrication. The processing of OLEDs is not only less expensive than LCDs but also less wasteful in terms of materials. Polymeric materials can be deposited over large areas easily and upon a variety of substrates. OLEDs can even be processed on mechanically flexible substrates; consequently offering a vast new range of applications. The conservative fabrication of OLEDs is the main driving force toward the production of viable devices based upon this technology.

The mechanical instability of these organic materials presents some drawbacks for the development of OLED-based devices. For example, the low glass transition temperature of these molecules forces the fabrication of the electrodes to be done under "soft" conditions.

Instability is also a factor when an organic EL device is operated for an extended period of time. İt is shown that most organic EL devices reported as far have a short operational lifetime, ranging from a few hours to several hundred hours. This stability has been attributed to the deterioration of the organic as well as the electrode layers. OLED technology can also used in commercial applications such as small screens for mobile phones and portable digital audio players (MP3 players), car radios, digital cameras, and high-resolution microdisplays for head-mounted displays. Such portable applications favor the high light output of OLEDs for readability in sunlight, and their low power drain. Prototypes have been made of flexible and reliable displays which utilize OLED's unique properties. Altough the display market is still dominated by Cathode-Ray-Tubes (CRT) and Liquid-Crystal-Displays (LCD), the impact of organic light emitting diodes (OLEDs) is getting stronger, while the first mass products are starting to hit the market. More examples of PPV related devices and their efficiencies are present in the literatüre [101-105].

Photovoltaic devices

Photovoltaics are best known as a method for generating electric power by using solar cells to convert energy from the sun into a flow of electrons. The photovoltaic effect refers to photons of light exciting electrons into a higher state of energy, allowing them to act as charge carriers for an electric current. The photovoltaic effect was first observed by Alexandre-Edmond Becquerel in 1839. The term photovoltaic denotes the unbiased operating mode of a photodiode in which current through the device is entirely due to the transduced light energy. Virtually all photovoltaic devices are some type of photodiode [106].

The first development of photovoltaic cells was in 1950s as p-n junctions of inorganic materials. Since then, various cells as homojunctions, heterojunctions or other architectures using inorganic materials have been fabricated. Solar radiation is converted to direct-current electrical power by photovoltaic devices.

There are two types of photovoltaic devices [107]. One is the “regenerative” type. The electrons are transported to the anode. The external circuit and the holes are transported to the cathode and are oxidized by external circuit electrons. In this type, light is converted in to electrical power without any chemical change left behind. The other type is known as “photosynthetic type”. There two redox systems; one with the holes at surface of the electrode and the other with the electrons that enter the counter electrode.

In photovoltaic devices, when the light is absorbed, electric charges that are flowing to the electrodes are separated and a difference of electrical potential is built up. Photo induced charge generation and charge transport are two factors that affect the efficiency of the devices. The region between photoactive layer and the electrode is the transition region and a resistance against a charge carrier may occur. A better charge crossing leads to an increase in the efficiency. To interrupt reactions between photoactive layer and the electrode, an electrically insulating transition layer can be introduced, but thickness of this should be kept as ≤ 5 nm not to hinder the charge carrier crossing [108]. While PPV-based devices show high open circuit voltages, poly (thiophene)-based devices show a lower open-circuit voltage although the thiophene units exhibit good donor properties. Thus it is appropriate to combine both structures into one polymer. By such a combination, 1,2 % of power conversion efficiency can be achived. Photovoltaic devices are highly sensitive to oxygen and humidity in the atmosphere [109]. This affects their service times. By the use of encapsulation, the service time of a solar cell can be improved from a few hours up to several months (5 months).

Nanofibers

Nanofibers are defined as fibers with diameters less than 100 nanometers. In the textile industry, this definition is often extended to include fibers as large as 1000 nm diameter. Nanofibers of PPV can be produced from an alcoholic solution of a PPV precursor polymer by electrospinning. The solution is streamed by an electrically charged needle so the droplets are stretched. Voltages of nearly 10 kV are applied and the PPV precursor polymer is converted into PPV fibers after annealing for 2h at 180°C. The morphology of the fibers can be controlled by using poly (vinyl alcohol) (PVA)/ PPV precursor polymers and is characterized by scanning electron microscopy and fluorescence microscopy [110,111].

When compared to bulk material, nano fibers may show a blue shift, a stronger fluorescence intensity and a higher surface voltage .Nanofibers of yellowish-green to blue fluorescence can be produced and may find applications in optical and electronic devices [112].

Nanotubes

Carbon nanotubes exhibit good electrical and thermal conductivity, excellent mechanical strength and low work function. Thus, they are of interest as electron guns and in flat panel displays. Nanotubes of PPV show noticeably distinctive fluorescence decay times when compared to bulk [113] .Graphitic carbonized PPV nanotubes have been prepared. Furthermore, nanotubes with gold nanoparticles were used in field of emitting devices [114].

Sensors

A broad range of applications in research have also been found for this technology: as bio-sensors, as selective filters, as amperometric sensors, as potentiometric sensors, for use in the preparation of pH solutions, in reference electrodes, "and for DNA detection and recognition. Additionally, a variety of sensors outside the laboratory environment have found use for these polymers: in sensors for the food industry, " in chemical-sensors, " as gas sensors, and in applications where a set of sensors that are sensitive to different targeted gases can be collected and used as an electronic nose. Especially, for medical, biological or some environmental applications, the detection of pH changes by sensors is of particular importance. A PPV-based pH sensitive photoconductor has been reported [115]. Changes in pH are determined by changes in photocurrent. For example, Vapors of some organic compounds (e.g. acetone, ethyl acetate, diethyl ether, acetic acid, methanol, ethanol, hexane and toluene) can also be detected by devices of PPV- based block copolymers with phenylene oxide units [116].

2.1.4.3 Synthesis of poly (phenylene vinylene)s

The routes used for the preparation of PPVs can be classified as the polymerizations via quinodimethane intermediates, polycondensations, transition-metal catalyzed polycouplings and metathesis polymerizations. Synthesis with representative structures will be discussed including advantages and disadvantages of each method.

2.1.4.4 Polymerizations via quinodimethane intermediates

Wessling-Zimmerman route

Wessling-Zimmerman is the first developed method for the preparation of PPVs and involves three steps [117]. This route involving the polymerization of several bis-sulfonium salts yielded high molecular weight, water-soluble polyelectrolytes, which generated PPV after treatment with base or exposure to elevated temperatures.

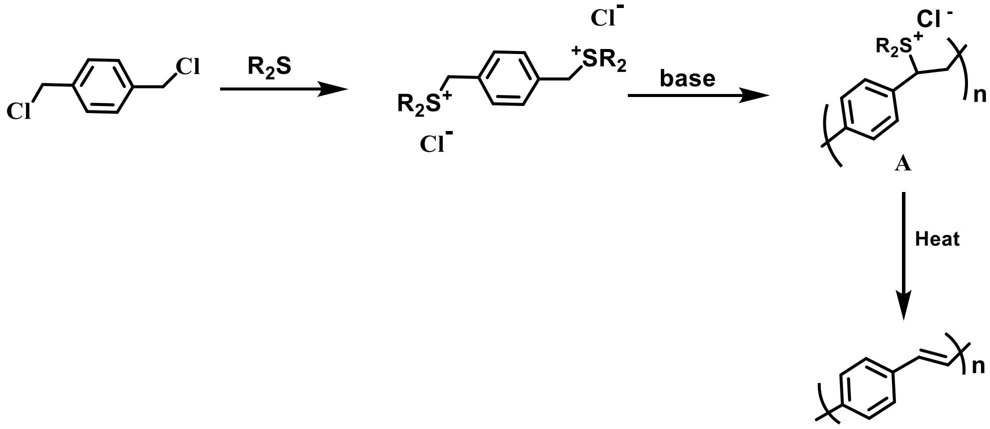


Figure 2.17 : PPV synthesized by the sulphonium salt precursor route.

The complete mechanism for this polymerization is still unresolved. However, the reaction scheme proposed by Wessling involving ylid formation and elimination to form either a diradical or a I-7-xylylcne intermediate, which polymerizes to yield polyelectrolyte **A**, is widely accepted (Figure 2.17).

The polymerization pathway, either radicalic or anionic, has been the subject of a debate, but as the presence of oxygen lowers the molecular weight of PPV drastically, it is believed that radical mechanism is more dominant [118,119].

Vanderzande precursor route

The Wesling route has been modified by Vanderzande and co-workers by using different sulfur-based leaving groups, a sulfinyl or sulfonyl precursor polymer is formed [120-122]. (Figure 2.18) shows the synthetic pathway:

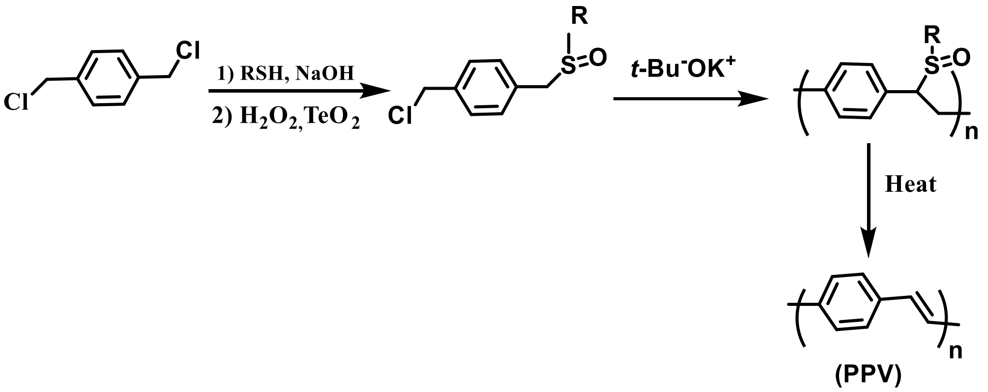


Figure 2.18 : PPV synthesized by Vanderzande precursor route.

Polymers with high molecular weights are obtained and the mechanism is radicalic. Although the monomer synthesis is more complicated, which is a disadvantage for the route, the final PPV shows less defects [123,124]. PPV precursor polymers bearing ester and carboxyl groups have also been synthesized via the sulfonium route. After conversion into PPVs, carboxyl functionalities can be changed to nitro, amino or aldehyde groups [125].

The Gilch Reaction

The Gilch route has been one of the most frequently used method for the synthesis of PPVs [126]. The reaction involves the direct conversion of a dihalomethyl derivative in to PPV in the presence of an excess strong base such as potassium-tert-butyl alcoholate (Figure 2.19). If the base is not in excess, the halo-precursor monomer can be isolated and then converted to the final polymer via treatment by base or thermally in vacuum.

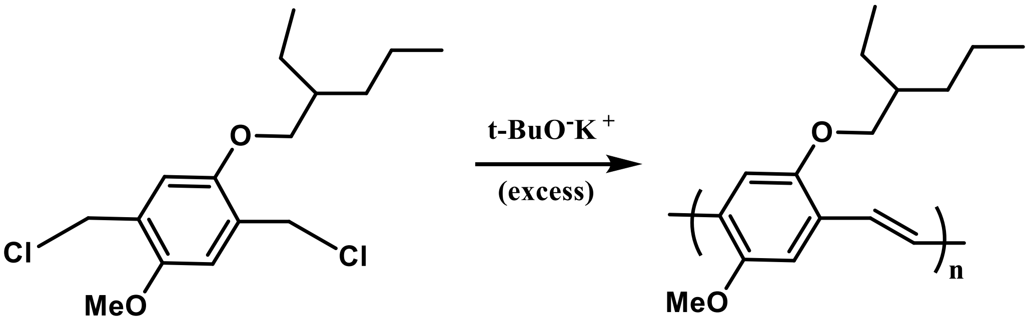


Figure 2.19 : PPV synthesized by Gilch Reaction.

Hörhold method

PPVs bearing subtituents, such as cyano and/or aryl, on vinylene bond can be synthesized by Hörhold-Method [127]. First a geminal-dichloride is prepared and then the final polymer is obtained by the self-condensation of this geminal-dichloride in the presence of base (Figure 2.20).

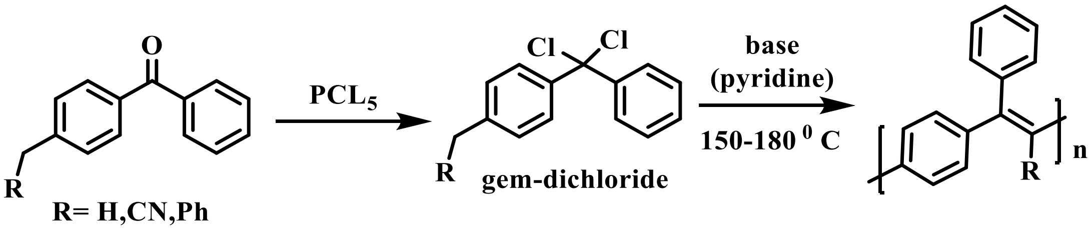


Figure 2.20 : PPV synthesized by Hörhold method.

Polycondensation routes

The Wittig and Wittig-Horner polycondensations

The Wittig reaction [128] is a very common and frequently used reaction in organic chemistry. Typically, an alkyl- or aryl-phosphoniurn ylid reacts with an aldehyde or a ketone to an alkene as shown in (Figure 2.21).

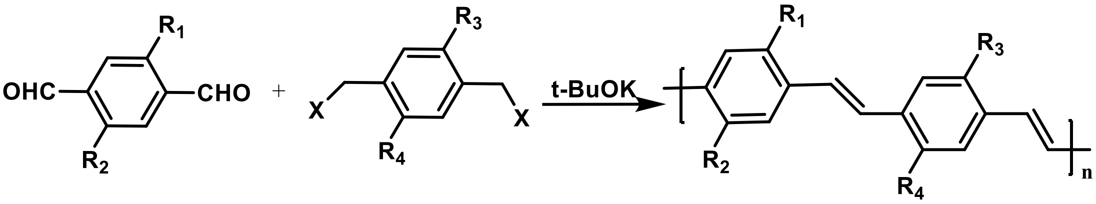


Figure 2.21 : PPV synthesized via the Wittig and Wittig-Horner polycondensations.

These methods have two advantages over quinodimethane routes:

1) It is possible to prepare alternating copolymer structures.

2) Polymers do not possess defects (such as ethane or ethyne moieties as in Gilch route.

Even tough the molecular weights of the gained polymers are lower when compared to Gilch route, they exhibit better optical properties due to lack of defects. On the other hand, “cis” and “trans” conformations of the vinylene bonds are possible.

Horner condensation yields higher molecular weight polymers with all the vinylene bonds in trans- conformation. In wittig condensation percentage of the double bonds in cis-conformation is higher and this affects the optical properties of the polymer [129-131].

Knoevenagel condensation

In Knoevenagel condensation, dialdehydes are condensed with bisnitriles and thus PPVs with alternating structures can be synthesized.

The method also allows the preparation of PPVs with substituted vinylene bonds in the backbone. PPVs bearing cyano groups on the double bonds with a high electroluminescence activity have been prepared [132,133]. The synthesis can be described as shown in Figure (2.22).

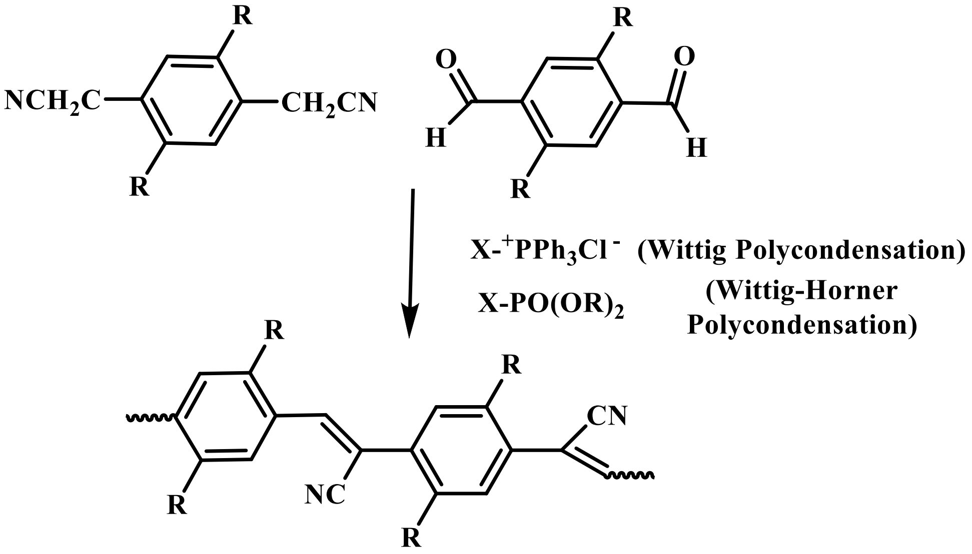


Figure 2.22 : Synthesis of PPVs bearing cyano groups by Knoevenagel condensation.

Both of the monomers can also be readily obtained from the bischloromethyl compound, which itself is a monomer for Gilch reaction, as given below Figure (2.23).

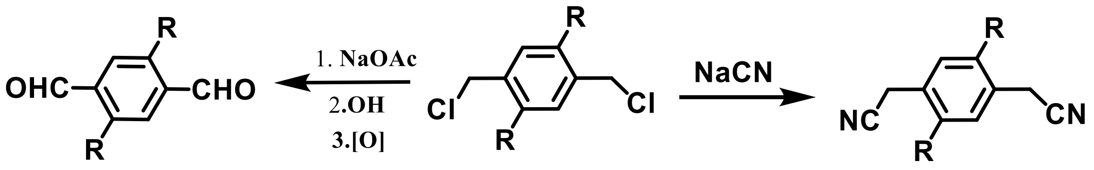


Figure 2.23 : Preparatiof of dialdehydes and bisnitriles from the bischloromethyl compound.

Transition metal-catalyzed methods

Transition metal-catalyzed cross-coupling processes offer a direct route for synthesis of PPVs as homopolymers or alternating copolymers. The monomers should be substituted in order to have soluble polymers; if not, immediately insoluble polymer is obtained.

The Heck Reaction

The Heck reaction probably is one of the most exploited monomer and polymer forming transition metal catalyzed carbon-carbon coupling reaction. With the Heck reaction, organic halides and vinylic compounds are, Pd-catalyzed and under the elimination of HX (X = Cl, Br, I), coupled to generate a carbon-carbon bond. Even the molecular weights of the polymers are lower when compared to Gilch route, they possess relatively less defects. Conceivable synthesis of alkorotic polymers by the Heck reaction as shown in reaction Figure (2.24).

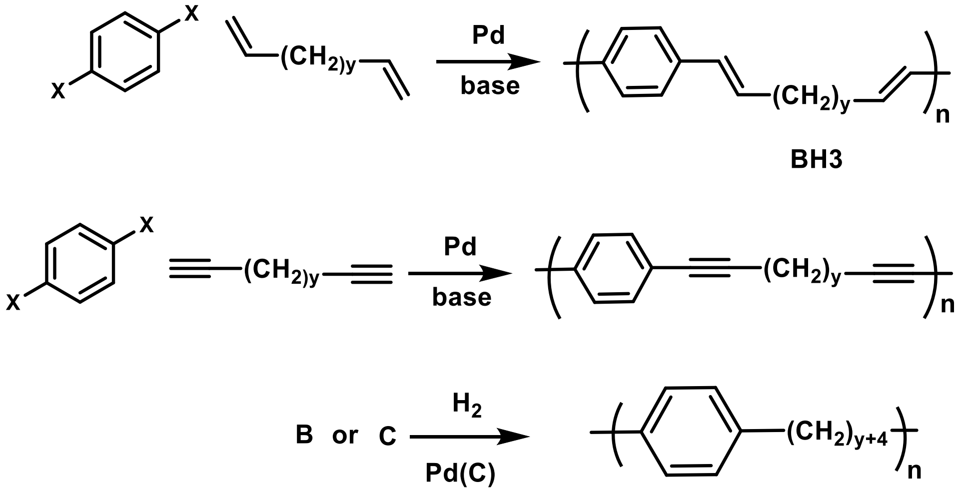


Figure 2.24 : Conceivable synthesis of alkorotic polymers by the Heck reaction.

Greiner and Heitz employed this useful organic chemistry tool to the synthesis of monomers and polymers, such as poly (*p*-phenylene vinylene) (PPV) as shown in reaction (reaction 2.15) derivatives of PPV and other poly(arene vinylene)s from dibromoarenes and ethylene.

Self polymerization is also possible with monomers having both functionalities, such as substituted vinyl bromobenzenes [134].

Stille coupling

The Stille cross-coupling reaction is the organic reaction of an organohalide with an organostannane compound to give the coupled product using a palladium catalyst. The mechanism begins with oxidative addition of the organohalide to the Pd (0) to form a Pd (II) complex.

The Stille coupling of haloarenes with trans-1,2-bis(tributylstannyl)ethylene has also been used occasionally in the synthesis of substituted PPVs or copolymers, however, the yields and molecular weights are generally low [135-137].

Metathesis Polymerization

Transition metal-catalyzed metathesis of divinylbenzenes has been used to prepare substituted PPVs but the obtained materials were just oligomers [138,139]. The second metathesis polymerization type is ring opening metathesis polymerization (ROMP) which has been introduced by Grubbs [140]. Precursor polymers of PPVs were obtained by conversion of substituted bicyclo [2.2.2] octa- 2,5-dienes in the presence of molybdenum-based metathesis catalyst. The precursor polymer is aromatized by using trioctylamine at 200°C or at 280°C under inert conditions.

Ring opening metathesis polymerization is a living polymerization, thus allows control over molecular weight of the polymers. On the other hand, it is difficult to prepare the desired monomers and it is not a direct route for preparation of PPVs.

2.1.4.5 Structure-property relationships in PPVs

As electroluminescent polymers are the active components in fabrication of various devices, some properties such as emission colors with high efficiency and intensity, good electrical and optical stability must be addressed while designing a synthesis. Meeting all these criteria is a big challenge for the synthetic chemists as the structure of the polymer has an important influence on the final properties of the materials and thus the device performance.

The conjugation length and effects of the substituents are two main structural factors which influence the emission color and efficiency of PPVs. Aggregation in solid state also affects the emission spectra by a red-shift and photoluminescence efficiency by enhancing the radiative decays.

Substituent effects on emission color of PPVs

Besides improving the solubility and the subsequent processability, the side chains attached to the backbone of conjugated polymers give rise to considerably changes in their optical, electronic and transport properties [141-144].

By choosing the appropriate substituents, the emission color of PPVs can be tuned from blue-green to red and even into near infrared. As indicated earlier, unsubstituted PPV is a bright yellow polymer that shows emission maxima at 520 nm and 551 nm in the yellow-green region of the visible spectrum [68].

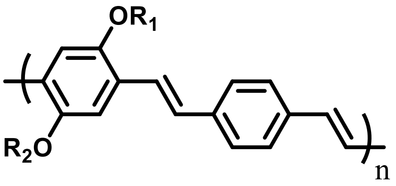
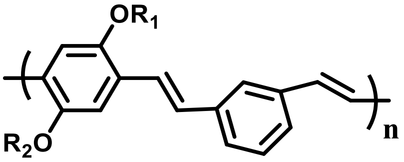
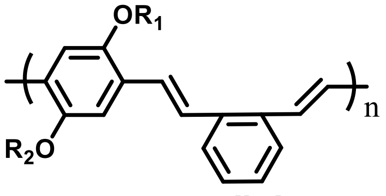
When alkoxy groups are linked to the phenylene ring, a red shift in the emission is monitored. The position and the size of the subtituents are also essential for the luminescence efficiency because of chain packing. Bulky side chains decrease the non-radiative decays due to interchain interactions, so PL and EL efficiency increases [75]. Interchain interactions may lead to aggregate formation which leads to a redshift in solid-state emission [145,146].

Extremely large substituents reduces the conductivity and hence the EL efficiency. Steric effects cause a blue shift in the emission as the polymer backbone is twisted (out of plane) to decrease the steric interactions of substituents and hence effective conjugation is reduced. Alkyl, aryl or sillyl side groups do not cause a red-shift in the emission and all are green emitting polymers [147,148]. If the substituents on the vinylene moiety are bulky, they cause remarkable blue-shift on the emission maxima, if not, they seem to have no influence [149].

Effect of conjugation degree on emission color of PPVs

The conjugation length of chromophores within a conjugated polymer affects the emission color. The ortho, metha or para-positions of the phenylene units influence the conjugation. Typical phenylene units are presented in Table 2.2. All para-polymer shows an emission maximum of 550 nm, whereas for the polymer with meta-phenylene units λ max is 490 nm as the conjugation is broken to some extent. In the case of ortho-phenylene units, a blue shift is observed (λmax =500 nm) but this is more due to the twisting of the polymer backbone because of steric interactions, not to the disturbtion of the conjugation [150].

Table 2.2 : Effect of o-, m- and p-positions of phenylene units on emission color of PPVs.

Phenylene Units	Emission
	all-para λ_{max} *= 550 nm*
	metha- λ_{max} *= 490 nm*
	ortho- λ_{max} *= 500 nm*
R_1 ,R_2 = Alkyl	

Introduction of non-conjugated units into the polymer chain also affects the conjugation length and emission color. In partıcular, Low levels of non-conjugated units enhances the EL-efficiency due to exciton confinement, but high levels affects charge transport and decreases the efficiency [151,152].

Effect of phenyl group on the emission of PPVs

When a phenylene group is replaced by an “oligophenylene” unit (such as pentaphenylene) a blue-shift in the emission is observed. Replacement by a heterocycle causes red-shifts. It is more complicated in the case of fused aromatic polycyclics. When the phenylene unit is replaced by 1,4-naphthalane or 9,10-antharacene a remarkable red shift is observed, but in the case of 2,6- naphthalane and 3,6-phenanthrene slight blue-shifts are observed compared to PPV.

As a result, the band gap of π-π* transition is related to the structure of the polymer and the light emitted (the color) depends on the band gap. Therefore any modification with any specific purpose in the polymer structure will affect the band gap and hence the emission color.

2.2 Photopolymerization

In the last few decades, photoinitiated polymerization has assumed coming to life concern as it congregates the basis of numerous applications radiation curing, imaging, microelectronics, medicine or optics (with various and very different applications, e.g., in coatings, varnishes, paints, inks, adhesives, graphic arts, printing plates, stereolithography, dental fillings, photoresists, fabrication of three dimensional objects, laser direct imaging, computer-to-plate technology, holographic optical elements or tooth are also available [155-162]. Photopolymerization has several advantages compared to thermal polymerization such as low energy requirement, spatial control, and fulfillment of green chemistry demands since polymerization processes may operate without solvent and also, photopolymerization process has continued to expand the growth of plastic market share. Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail. However, most of the applications are based on the free radical mode due to the less purity demand, applicability to a wide range of formulations based on methacrylates unsaturated polyesters, and acrylated polyurethanes and the availability of photoinitiators having spectral sensitivity in a broad wavelength range.

Photopolymerization or photoinitiated polymerization is a process of formation of crosslinked higher molecular weight materials (polymers) from monomer or oligomer molecules under exposure of laser light, usually of wavelengths in the ultraviolet spectrum.

Polymerization reactions are divided into two groups known as step reactions (also called condensation reactions) and chain reactions (also known as addition reactions). Step reactions require bifunctional or polyfunctional monomers, while chain reactions require the presence of an initiator.

İt is interestingly shown that the reactive species involved in the polymerization reaction by laser flash photolysis, time-resolved fluorescence and phosphorescence, and electron spin resonance spectroscopy as well as monitoring the polymerization itself by different methods including real time IR spectroscopy, in-line NIR reflection spectroscopy, differential scanning calorimetry, in situ dielectric analysis, and recently developed optical pyrometry [163].

Photoinitiated polymerization is usually applied to a chain process that is initiated by light and both the initiating species and the growing chain ends are radicals or cations and, in some cases, anions or weak bases (Figure 2.25). However, the corresponding photoinitiated polycondensation process in which a macromolecule is obtained by a step-growth addition of low molecular weight materials is in its infancy.

Photopolymerization is one of the most attractive and simple polymerization methods in the polymer community. Use of solar energy as a power source for reactions has made it possible to reduce the fabrication processes cost with low environmental pollutions. Photopolymerization meets various industrial applications such as coatings, adhesives, inks and printing technologies, dental fillings [160], and fabrication of three dimensional objects. However, as in all polymerization echniques, photoinduced process requires the use of sufficient photoinitiators possessing suitable spectral characteristics matching with the emitting resource. Many photoinitiating systems acting at UV and visible region have been developed. Especially in coating industries, as many coatings are accomplished in the presence of air, designing new initiating systems that prevent oxygen quenching as well as other drawbacks such as relatively strong odor and migration from cured films are of importance.

Photopolymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated from photosensitive compounds, namely photoinitiators and/or photosensitizers, by ultra violet-visible (UV-Vis) light irradiation [164]. The wavelength or range of wavelengths of the initiating source is defined by the reactive system involving the monomer(s), the initiator(s), and any photosensitizers, pigments or dyes which may be present. An active center is produced when the initiator absorbs light and undergoes some type of decomposition, hydrogen abstraction, or electron transfer reaction.

Photocurable formulations are mostly free of additional organic solvents: the monomer which serves as reactive diluent, is converted to solid environmentally safe resin without any air pollution. UV curing is often very fast process, taking place as, pointed out above, without heating. If the polymerization mixture absorbs light and the efficiency of radical formation is high, photocuring can be performed with no light source but sunlight. These features make photopolymerization an ecologically friendly and economically technology that has high potential for further development.

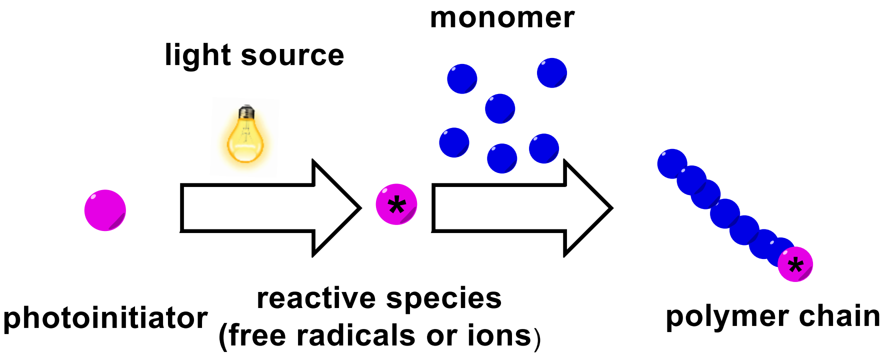


Figure 2.25 : General presentation of photoinitiated polymerization.

2.2.1 Photoinitiated cationic polymerization

Despite the fact that the most worldwide industrial applications are based upon the photo-initiated free radical polymerization, there are some drawbacks associated with this type of polymerization, such as the inhibition effect of oxygen and post-cure limitations, which may affect the properties of the final product. A certain number of advantages of the photoinitiated cationic polymerization over the photoinitiated free radical polymerization have been reported [165-167].

Cationic photopolymerization overcomes volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems related to high viscosity. What's more, once initiated, cationically polymerizable monomers such as vinyl ethers and epoxides undergo dark-polymerization in which they slowly polymerize without radiation [164]. In recent years, the use of onium salt initiated cationic photopolymerization has reached commercial significance as a wide variety of uses have emerged and the benefits of this technology have been realized. The advantages afforded by photopolymerization processes have led to their rapid growth in applications in different fields such as films, inks and coatings on a variety of substrates, including paper, metal and wood. In addition, a variety of high-tech and electronic applications of this technology, such as coatings for optical fibers and the fabrication of printed circuit boards have emerged. There are two possible pathways for the initiation of photoinduced cationic polymerization; direct photolysis and indirect photolysis.

2.2.1.1 Direct photolysis

In direct photolysis, initiating species are generated upon irradiation of a photosensitive compound, namely photoinitiator (PI), at appropriate wavelengths. PI absorbs incident light and undergoes decomposition leading to production of initiating species and subsequent reaction of the radical cation and/or protonic acid (react with cationic polymerizable monomers (M), and yield polymer) with solvent or monomer lead to the formation of Bronsted acid, H^+ ,which is responsible for further initiation as given below in (Figure 2.26). Most photoinitiators, used in cationic photopolymerization mainly absorbs light between 225 to 350 nm. For practical applications, however, they are expected to absorb light at quite longer wavelengths. Several attempts have been described to overcome this problem.

$$\mathbf{PI} \xrightarrow{h\nu} \mathbf{H^+ + R^{\cdot +} + \text{other products}}$$

$$\mathbf{R^{\cdot +} + M \longrightarrow \text{polymer}}$$

$$\mathbf{H^+ + M \longrightarrow \text{polymer}}$$

Figure 2.26 : Photoinitiated cationic polymerization by direct photolysis.

Photoinduced cationic polymerization can be initiated by a number of agents including Lewis and Brønsted acids, carbonium ions and onium salts. A key feature of cationic polymerization is the use of acids possessing anions of very low nucleophilicity, which do not terminate the polymerization process. Consequently, most cationic photoinitiators are depend upon salts of non-nucleophilic anions such as BF_4^-, PF_6^-, AsF_6^- and SbF_6^-. Generally, molecular weights and percentage conversion increase in the order of $BF_4^- < PF_6^- < AsF_6^- < SbF_6^-$. The counter anions have to be nonnucleophilic in order to prevent the termination of a growing chain.

Cationic photoinitiators are generally divided into two classes, ionic and non-ionic photoinitiators. These classes consist of structurally related compounds which undergo similar photochemical reactions.

1) Ionic cationic photoinitiators: Onium salts and organometallic salts

2) Non-ionic cationic photoinitiators: Organosilanes, latent sulphonic acids and miscellaneous non-ionic compounds

Among these photoinitiators, however, onium salts will be discussed as the present thesis involves the use of them in the experimental section.

Onium salts

Onium salts are the most well-known photoinitiators used in the research of photoinduced polymerization. They contain chromophopric groups as the light sensitive body with heteroatoms as cationic centers in the structure. As counterions, mostly inorganic metal complex anions are used [168]. The cation of an onium salt is the light absorbing portion of the compound and its structure determines the wavelength sensitivity and quantum yield of the initiator. In addition, the character of the cation also has an influence on the excited state chemistry and whether or not the onium salt can undergo photosensitization with a photosensitizer. The character of the anion can be widely varied to tune the strength of the acid that is generated [169,170].

During the past decade, onium salts with highly nucleophilic counterions such as Cl^-, Br^- and I^- have also been used in conjuction with Lewis acids. Different types of onium salts are shown in (Figure 2.27).

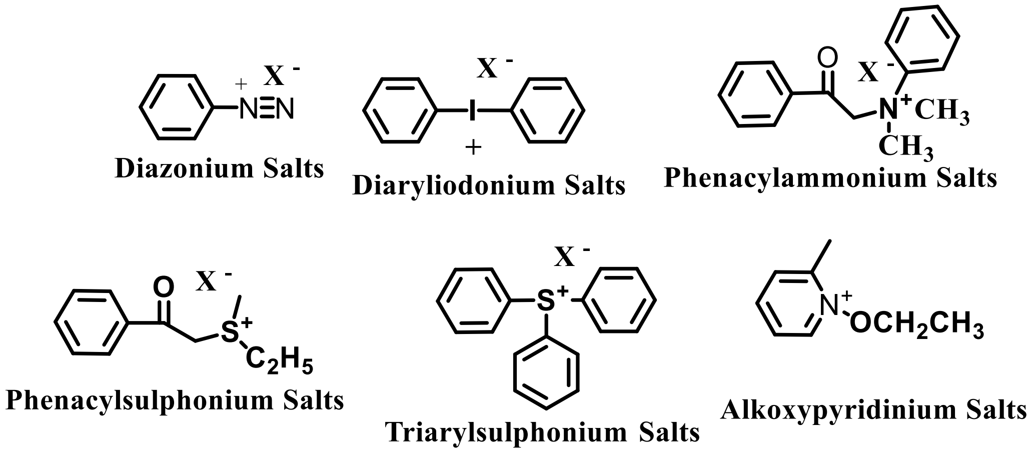


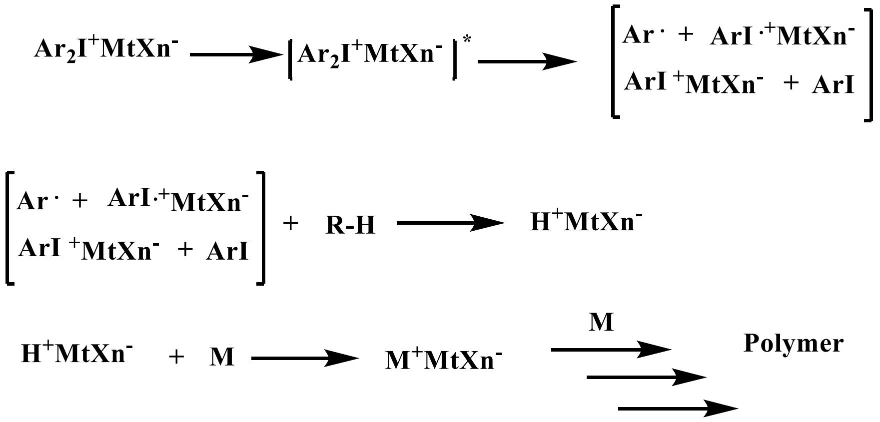
Figure 2.27 : Types of onium salt photoinitiators.

Diaryliodonium salts

Diaryliodonium salts are the most frequently used halonium salts as they are easy to obtain and quite reactive the nucleophillic halogen counterion must be replaced by a non-nucleophillic anion in order to prevent the termination of cationic polymerization [171-173]. As they generally have low spectral sensitivity, an electrophillic substitution reaction can be applied on the aromatic rings to possess electron donating species which can move absorption bands to lower energies. Alternatively, some special additives can be used to carry out polymerization at longer wavelengths.

Photolysis of diaryliodonium salts take place either through homolytic or heterolytic cleavage of the halogen-aryl bond to form species which react with a hydrogen donor compound to yield a Brønsted acid that initiates polymerization (Figure 2.28).

Notably, the electron donating substituents on the aromatic structures not only shifts absorption bands to longer wavelengths, but also favors photolysis of diaryliodonium salts to afford higher polymerization rates. Iodine has an extraordinary hypervalent structure, which imparts good stability to diaryliodonium salts. Chloronium and bromonium analogs of iodonium salts were synthesized; however, they were thermally unstable and had a difficult synthetic route [51]. Quantum efficiencies of diaryliodonium salts vary from 0.7 – 0.9. Aromatic rings are responsible for absorption range in UV–Vis region. Diaryliodonium salts absorbs between 230 – 300 nm in general.



R-H : solvent or monomer
MtXn- : PF_6- ,SbF_6-,Asf_6-,etc.

Figure 2.28 : Photolysis mechanism of diaryliodonium salts.

Triarylsulphonium salts

Triaryl sulphonium salts (TAS) are generally produced by the method of Pitt [174]: a Friedel–Crafts condensation of aromatic hydrocarbons with sulphur dichloride, followed by chlorination and further condensation. Various alkylaryl sulphonium salts may be synthesized by an alkylation of mercaptobenzene [175].

$$Ar_3S^+MtXn^- \xrightarrow{h\nu} \left[Ar_2S^{\cdot +}MtXn\right]^* + Ar^{\cdot}$$

$$Ar_2S^{\cdot +}MtXn^- + R\text{-}H \longrightarrow Ar_2HS^{\cdot +}MtXn^- + R^{\cdot}$$

$$Ar_2HS^{\cdot +}MtXn^- \longrightarrow Ar_2S + H^+MtXn^-$$

$$Ar_3S^+MtXn^- \xrightarrow{h\nu} Ar_2S + Ar^+MtXn^-$$

$$Ar^+MtXn^- + R\text{-}H \longrightarrow Ar\text{-}R + H^+MtXn^-$$

R-H : solvent or monomer

MtXn- : PF_6- ,SbF_6-,Asf_6-,etc.

Figure 2.29 : Photolysis mechanism of triarylsulphonium salts.

The photolysis mechanism is similar with the diaryliodonium salts. When irradiated in appropriate wavelengths, TAS's undergo either a homolytic or a heterolytic cleavage followed by a proton release after some additional steps which are summarized in Figure 2.29.

N-Alkoxy pyridinium salts

N-Alkoxy Pyridinium salts are obtained with relatively high yields by a reaction of pyridine *N*-oxides with a triethyloxonium salt in methylene chloride or chloroform. Quinolinium salts can also be prepared from the corresponding *N*-oxides [177]. In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions. The spectral response of these salts is in 260-310 nm range [176]. When irradiated in suitable wavelengths, these salts readily initiate polymerization of appropriate monomers according to the following mechanism as exemplified for the case of *N*-ethoxy–2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) in (Figure2.30)

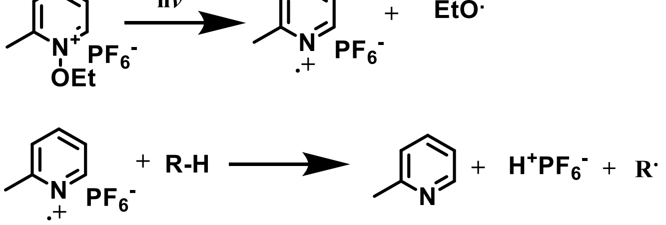


Figure 2.30 : Photolysis mechanism of *N*-ethoxy–2-methyl pyridinium hexafluoro phosphate (EMP^+ PF_6^-).

Especially, some reactive monomers like isobutylvinylether and N-vinylcarbazol are observed to polymerize even in dark when used in conjuction with N-ethoxy-4 cyanopyridinium (EPP) and N-ethoxyisoquinolinium (EIQ) salts.

2.2.1.2 Indirect photolysis

Without absorption of the incident photon energy, photochemical processes cannot occur. Especially, for practical applications, onium salts should absorb light perceivable at wavelengths longer than 400 nm where commercially available medium and high- pressure mercury lamps emit much of their radiation and these medium- and high-pressure mercury lamps that are frequently used as light sources provide emissions at 313 and 366 nm. Seeing that this requirement is not fulfilled for certain readily available onium salts several systems were developed to extend the applicability of the onium salt photoinitiators. If daylight is to be used for curing a coating formula, light absorption at wavelengths longer than 400 nm is highly desired. Moreover, some special additives can be used in conjunction with photoinitiators to carry out polymerization at longer wavelengths. Notably, in general, the additives are the light absorbing species here. Provided the systems therefore obtained do initiate cationic polymerizations, the initiation can be explained through one of the following mechanisms.

Sensitization by Classical Energy Transfer

This mechanism involves the electronic excitation of the ground state of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state. Energy may be transferred from the excited sensitizer (S*) to the onium salt (I) by either resonance excitation or exchange energy transfer. Depending on the two components involved, the energy transfer may proceed either in the excited singlet or in the triplet state.

In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I*) are formed. The further reactions may also differ from those, taking place when the onium salt is excited by direct absorption of light. This conclusion has been drawn on the bases of product analyses [178]. An obvious explanation for this difference is the spin multiplicity: in the below discussed sensitized excitations triplet states of the onium salts are populated. In contrast to this, through direct irradiation of the onium salt, electrons are excited primary to the singlet state. A sufficient energy transfer requires the excitation energy of the sensitizer E*(S) to be at least as large as the excitation energy of the photoinitiator E*(I). The photopolymerization with most onium salts can be sensitized by commonly used photosensitizers, such as acetophenone or naphthalene. However, in many cases this reaction does not proceed via energy transfer, since most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt.

Table 2.3 : Halfwave Oxidation Potentials $E^{ox}_{1/2}$ (vs Standard Calomel Electrode (SCE)) and Triplet or Singlet Energies E^{*} Of Commonly Used Photoinitiators

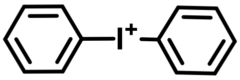
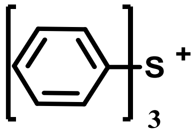
Photosensitizers	$E^{1/2}{}_{ox}$(V)	E*(kJ mol $^{-1}$)
Acetophenone	2.9	308(E_T)
Benzophenone	2.7	290(E_T)
Thioxanthone	1.7	277(E_T)
Anthracene	1.1	319(E_S)
Perylene	0.9	277(E_S)
Phenothiazine	0.6	239(E_T)
m-Triflouromethyl acetophenone	2.7	305(E_T)
Xantone	-	311(E_T)

Energy transfer sensitization did not turn out to be technically useful, although being a possible pathway in starting the decomposition of onium salts. The reason is that the high triplet energies required allow only the use of sensitizers absorbing at wavelengths below 350 nm. Other multicomponent initiating systems (vide infra) show a more practical spectral response.

Diphenyliodonium cations were excited to their first excited triplet state by energy transfer from m-trifluoromethyl acetophenone [179]. As can be seen from Tables (2.3), the energy transfer is energetically allowed. Electron transfer in the exciplex can be excluded, since the oxidation potential of m-trifluoromethyl acetophenone is relatively low. The oxidation potential of unsubstituted acetophenone is about 0.2 V higher than that of m-trifluoromethyl acetophenone.the former was found to sensitize the photoreactions of diphenyliodonium salts via electron transfer in the exciplex state.

In Table 2.4, the triplet excitation energies and reduction potential of selected onium salts are presented .

Table 2.4 : Reduction Potential and Triplet Excitation Energies of Selected Onium Ions.

Onium Cation	$E^{red}{}_{1/2}$(V) (vs SCE)	E*(kJ mol $^{-1}$)
	-0.2	268
	-1.1	314

2.2.2 Photoinitiated free radical promoted cationic polymerization

Many radicals can be oxidized by onium salts leading to generation of cations which are considered as initiating species for cationic polymerization. Two types of free radical induced initiation are available: oxidation of radicals and addition fragmentation reactions.

Among these reactions, oxidation of radicals is the most flexible route, since free radical photoinitiators with a wide range of absorption characteristics are available. Many photochemically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization according to the following reactions as given below in Figure (2.31) [180,181].

$$\mathbf{PI} \xrightarrow{\mathbf{h\nu}} \mathbf{R}^{\cdot}$$

$$\mathbf{R}^{\cdot} \xrightarrow{\mathbf{On}^{\cdot}} \mathbf{R}^{+} + \mathbf{On}^{\cdot}$$

$$\mathbf{R}^{+} + \mathbf{M} \longrightarrow \mathbf{Polymer}$$

Figure 2.31 : The mechanism of cationic polymerization.

The cations thus generated are used as initiating species for cationic polymerization. This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of sensitized cationic polymerization. Free radicals may be produced not only by photochemically but also thermally or by irradiating the system with high-energy rays. The photochemical generation of radicals can be applied even at low temperatures. Being photolyzed with high quantum yields, benzoin derivatives are so far the most effective photoinitiators for the free radical promoted cationic polymerization [182].

The use of addition fragmentation reactions in photoinduced cationic polymerization is another distinguished approach and it has been subject of recent investigations [183-191]. Addition fragmentation reactions are indeed a very versatile method to adjust the spectral response of the polymerization mixture with the aid of free radical photoinitiators, since they are not based on easily oxidizable radicals. The allylic salts have so far been applied for addition fragmentation type initiations.

The first step consists in the photogeneration of free radicals. Virtually any photolabile compound undergoing homolytic bond cleavage may be used as a radical source. The radicals add to the double bond of the allylonium salt thus producing a radical in β-position to the heteroatom of the onium salt cation. Accordingly, the molecule undergoes fragmentation yielding initiating cations as shown in Figure (2.32).

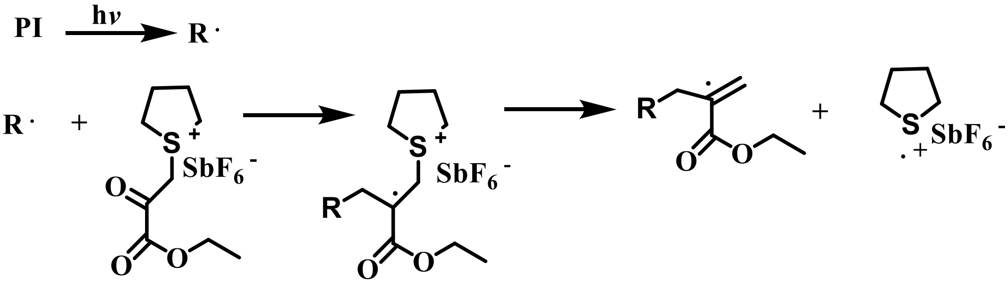


Figure 2.32 : Mechanism of photoinitiated free radical promoted cationic polymerization [183].

Sensitization via Exciplexes

The use of photosensitizers is critical to the success of cationic photopolymerizations in many applications in which photopolymerizations are employed as it accelerates the rates of reactions and requires less energy as they provide polymerizations in longer wavelengths [192-198]. Electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene and phenothiazine, are suitable as photosensitizers as they give redox reactions with onium salts through exciplex to finally yield the initiating species for photo-induced cationic polymerizations [199]. The mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt is illustrated by reactions as given in Figure (2.33(a-g)).

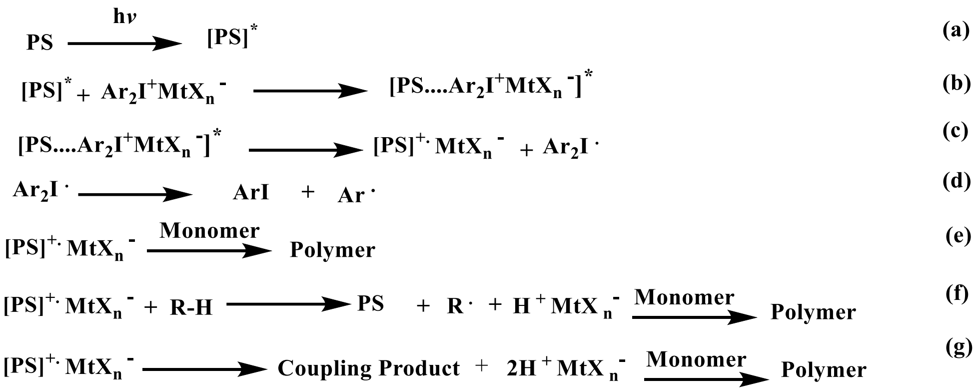


Figure 2.33 : The mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt.

First, photosensitizer absorbs the light to give the corresponding excited species [PS]* (a). An excited state complex (exciplex) is formed as an intermediate between onium salt and excited photosensitizer (b). In the following step, one-electron is transferred from the sensitizer to the onium salt (c). Unstable diaryliodine radical decomposes rapidly and makes the process irreversible by preventing back electron transfer (d). The radical cations formed by reaction (c) would be capable of initiating cationic polymerization (e) since direct initiation by the species formed from polynuclear aromatic compounds is a well -known process and, due to the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented. Principally, polymerization could also be initiated by the Brønsted acids formed via hydrogen abstraction (f) or coupling reactions (g).

According to the Rehm-Weller equation [200] as shown in (equation 2.1) electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. Based on the oxidation potential ($E_{1/2}^{ox}$) and active excitation energy (E^*) of the photosensitizer (PS) and the reduction potential ($E_{1/2}^{red}$) of the initiator (PI), the free energy change (ΔG) for the photoinduced electron transfer process is estimated. The calculation of ΔG is applied in order to predict whether or not an oxidation would take place.

$$\Delta G = f_c \left(E_{1/2}^{\,ox}(\mathrm{S}) - E_{1/2}^{\,red}(\mathrm{ox})\right) - E^*(\mathrm{PS}) \qquad \textbf{(2.1)}$$

Despite the many potential applications, photosensitizers also have several serious drawbacks that limit their use. For example, they are generally expensive, toxic, and poorly soluble in most reactive monomers and polymer systems. Moreover, they are easily lost from thin film coatings during polymerization and have high vapor pressure at room temperatures. Therefore, there is a progressing need for long-wavelength-active photosensitizers in order to overcome these limitations. One way to obtain non-toxic polymers through sensitization is to copolymerize compounds, which can behave either as a photosensitizer or as a monomer with different monomers. Another way is to polymerize these monomeric photosensitizers and afterwards subject them to sensitize the polymerization of convenient monomers. In both ways non-toxic and odorless polymers can be obtained after polymerization [201-204].

Ground state charge-transfer complexes (CTCs)

Although it is not considered to be a general method for the indirect initiation, certain salts can undergo decomposition upon irradiation in their appropriate charge transfer complexes (CTC). For example, pyridinium salts are capable of forming ground state CTCs with electron-rich donors such as methyl- and methoxysubstituted benzene [205]. Notably, these complexes absorb at relatively high wavelengths, where the components are virtually transparent. For example, the complex formed between *N*-ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2,4-trimethoxybenzene possesses an absorption maximum at 420 nm.

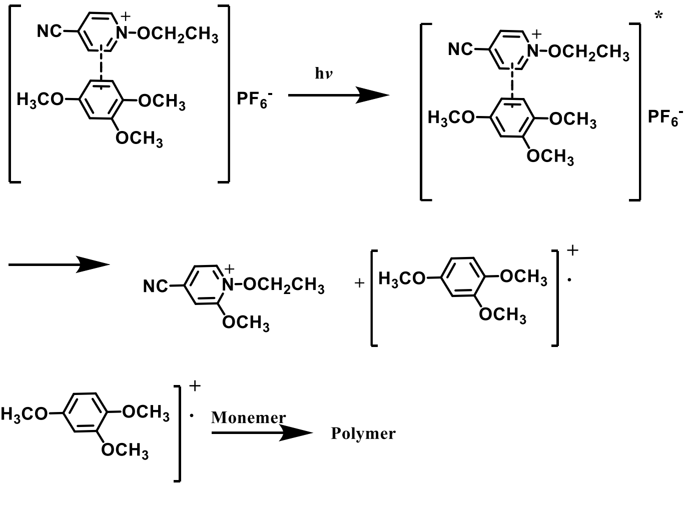
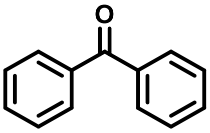
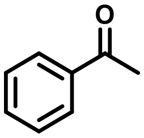
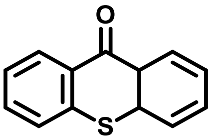
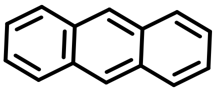
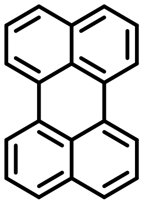
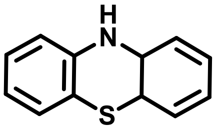


Figure 2.34 : The mechanism of charge-transfer complexes (CTCs) as photoinitiator.

The following mechanism has shown the action of a CTC as photoinitiator (Figure 2.34). Since polymerization also takes place even in the presence of a proton scavenger like 2,6-di-tert-butylpyridine an initiation through Brønsted acid formation can totally be excluded.

The oxidation potentials and absorption characteristics of sensitizers used most frequently in conjunction with onium salts are summarized in Table 2.5.

Table 2.5 : Structures, oxidation potentials, triplet or singlet excitation energies and absorption characteristics of some common photosensitizers.

Photosensitizers	$E^{1/2}_{ox}$(PS) (V)	E^*(PS) (kj.mol^{-1})	λ_{max} (nm) (ε_{max} (mol^{-1} .cm $^{-1}$))
 **Benzophenone**	2.7	290 (E_T)	252 (17600) 333 (148) 342 (140)
 **Acetophenone**	2.9	308(E_T)	242 (17600) 279 (17600) 318 (17600)
 **Thioxanthone**	1.7	277(E_T)	219 (12600) 255 (1050) 298 (60)
 **Anthracene**	1.1	319(E_S)	252 (15200) 356 (44200) 378 (3510)
 **Perylene**	0.9	277(E_S)	252 (53000) 435 (39500)
 **Phenothiazine**	0.6	239(E_T)	254 (61000) 318 (4680)

2.3 Aim of This Work

In this study, A novel visible light sensitive photoinitiating system for the cationic polymerization of oxiranes such as cyclohexene oxide (CHO) and vinly monomers such as isobutyl vinylether (IBVE) and N-vinyl carbazole (NVC) in the presence of proposed poly- (phenylenevinylene) (PPV) derivatives as photosensitizers for visible light induced cationic polymerization have been explored. Poly (phenylenevinylene) (PPV) derivatives have been used as photosensitizers for oxidizing salts such as diphenyliodonium hexafluorophosphate (DPI), N-ethoxy-2-methylpyridinium (EMP) photoinitiators. Highly conjugated compounds with good absorption bands in long wavelength UV and visible region are selected to activate cationic polymerization. These versatile intermediates; such as exciplex, facilitate photoinitiated cationic polymerization of commercially critical monomers such as cyclic ethers and vinyl epoxides. Polymerizations were carried out using long wavelength UV light in the presence of diphenyliodonium hexafluorophosphate ($Ph_2I^+PF^-_6$). The initiation mechanism, based on the optical absorption measurements, free energy changes (ΔG), and proton scavenging studies, involves formation of exciplex by the absorption of light in the first step. Subsequently, an electron transfer from the excited PPV-g-PSt or PPV-g-PCL to oxidizing salt occurs to yield radical cations of the PPV backbone. In addition, we also demonstrate that it was possible to initiate photopolymerization under solar irradiation in the presence of these photosensitizers.

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 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.

Cyclohexene oxide (CHO, 98%, Aldrich):

It was distilled over CaH_2 under reduced pressure before use.

n-Butyl vinyl ether (BVE, >97%, Fluka):

It was distilled over CaH_2 under reduced pressure before use.

N-Vinylcarbazole (NVC, 98%, Aldrich):

It was crystallized from ethanol before use.

3.1.2 Solvents

Diethyl ether (J.T. Baker):

It was dried with $CaCl_2$ and distilled over sodium wire.

Dichloromethane and chloroform (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) :

For use in chemical reactions, it was dried over potassium hydroxide, distilled over sodium wire, and finally distilled over sodium/benzophenone. For chromatography as eluent it was used as received (HPLC Grade).

Methanol (Technical) :

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

Carbontetrachloride (J.T. Baker):

It was used as received.

Dimethylacetamid (Aldrich):

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

3.1.3 Other chemicals

2,5-Dibromotoluene (Aldrich)

It was used as received.

3,5-Dibromotoluene (Aldrich)

It was used as received.

Sodium borohydride ($NaBH_4$) (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.

Triethylamine (TEA) (J.T. Baker)

It was distilled over calcium hydride before use.

p-Xylene (Aldrich)

It was used as received.

2,5-Dibromo-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, (NBS, 99%, Acros)

It was used directly.

Triphenylphosphine (PPh_3) (Fluka, Acros)

It was used as received.

Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (Aldrich)

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

Tin octoate ($Sn(Oct)_2$) (Sigma)

It was used as initiator in ring opening polymerization of ε-caprolactone as received.

3-Aminophenylboronic acid hemisulfate (Acros)

It was used as received.

4-Formylphenylboronic acid (Aldrich)

It was used as received.

4-Aminophenol (Aldrich)

It was used as recceived.

2-Pyrrole carboxaldehyde (Fluka)

It was used as received.

1-Naphthyl carboxaldehyde (Fluka)

It was used as received.

Potassium-tert-butoxide (Aldrich)

It was used as received.

1,4-Bis(bromomethyl)benzene (Aldrich)

It was used as received.

p-Toluene sulfonic acid (Fluka)

It was used as received.

Iron (III) chloride, anhydrous (Fluka)

It was used as received.

Diphenyliodonium hexaflourophosphate (DPI, 98%, Alfa Aesar)

It was used as received.

Triphenylsulfonium hexaflourophosphate (TPS, 98%, Alfa Aesar)

It was used as received.

***N*-Ethoxy-2- methylpyridinium hexafluorophosphate (EMP)**

It was prepared according to the procedure described by Reichardt [176].

3.2 Equipment

3.2.1 Gel permeation chromatography (GPC)

Gel-permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system consisting of a pump, a Viscotek UV detector, and

Viscotek a differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. The effective molecular weight ranges were 456 −42 800, 1050−107 000, and 10 200−2 890000, respectively. THF was used as an eluent at a flow rate of 1.0 mL min $^{-1}$ at 30 °C. Both detectors were calibrated with polystyrene standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01software.

3.2.2 UV-visible spectrophotometer

UV spectra were recorded on a Shimadzu UV-1601 spectrometer.

3.2.3 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.4 Nuclear magnetic resonance spectroscopy (NMR)

^{1} H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard.

3.2.5 Fluorescence spectrophotometer

Fluorescence and phosphorescence measurements were performed on a Jobin Yvon-Horiba Fluoromax-P spectrophotometer.

3.2.6 Light source

A Ker-Vis blue photoreactor equipped with 6 lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm was used in all polymerization experiments. The light intensity was 45 mW.cm^{-2} as measured by Delta Ohm model HD-9021 radiometer.

3.2.7 Thermal gravimetric analysis (TGA)

Thermal Gravimetric Analysis was done on Perkin Elmer Diamond TG/DTA with a heating rate of 5°Cmin^{-1} under nitrogen flow 20.0 (mL/min).

3.3 Preparation Methods

3.3.1 Synthesis of dibromobenzene functional polystyrene (DBB- PSt)

CuBr (0.21 g, 1.5 mmol), bipyridine (bpy), (0.70 g, 4.5 mmol), 1,4-dibromo-2-(bromomethyl)benzene, and styrene (10 mL, 87.5 mmol) were introduced to a round-bottom flask equipped with a magnetic stirrer under an inert atmosphere. The flask was kept in an oil bath at 110 °C for 55 min. The reaction mixture was poured into 10-fold excess methanol. The precipitate was collected after filtration and dried in vacuum for overnight. Conversion: 35%.

$M_{n,theo}$: 2360. $DP_{n\ (H\text{-}NMR)} = 19.5$; , $M_{n,NMR} = 2270$; $M_{n,GPC} = 2400$, $M_w/M_n = 1.30$.

The preparation of 1,4-dibromo-2-(bromomethyl)benzene, was reported in a previous study. Mp(DSC): 94−95 °C. ^{1}H NMR ($CDCl_3$), (δ, ppm): 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, CH_2Br).

3.3.2 Synthesis of dibromobenzene functional poly(ε-caprolactone) (DBB-PCL)

ε-Caprolactone (CL) (6 mL, 51 mmol), (2,5- dibromo-1,4-(dihydroxymethyl)benzene (0.64 g (2.04 mmol),), and $Sn(Oct)_2$ ($[OH]/[Sn(Oct)_2]$) 200/1 molar ratio) were introduced into a Schlenk tube which was previously flamed under vacuum to remove the moisture and filled with nitrogen. The reaction mixture was kept at 110 °C. After 24 h the mixture was diluted with CH_2Cl_2 and poured into 10-fold excess of cold methanol. The precipitate was filtered and properly dried. . $DP_{n\ (H\text{-}NMR)} = 26$; $M_{n,NMR} = 3260$; $M_{n,GPC} = 3640$. M_w/M_n: 1.32.

The preparation of 2,5-dibromo-1,4-(dihydroxymethyl)benzene was described elsewhere.

Mp(DSC): 217−218 °C. ^{1}H NMR (acetone- d_6), (δ, ppm): 7.74 (s, 2H, Ar), 4.65 (s, 4H, CH_2), 3.29 (s, 2H, OH)

3.3.3 Synthesis of aldehyde-functional polymers by suzuki coupling reaction (DBA-PSt and DBA-PCL)

DBB-PCL (0.75 g, 0.21 mmol) or DBB-PSt (0.68 g, 0.21 mmol), 4-formylphenylboronic acid (0.16 g,1.04 mmol), and $Pd(PPh_3)_4$ (0.01 g (0.008 mmol) were introduced into a round-bottom flask containing $NaHCO_3$ (1M, 10 mL) and THF

(15 mL) under dry nitrogen The reaction mixture wasrefluxed in dark for 4 days under inert atmosphere. Thus, formedaldehyde functionalized polymers were precipitated into cold methanol, filtrated off, and dried. The polymers were passed through silica column using THF as eluent and reprecipitated in methanol for further purification.
For DBA-PSt, $M_{n,NMR}$ = 2420 and $M_{n,GPC}$ = 2480. M_w/M_n: 1.34
For DBA-PCL, $M_{n,NMR}$ = 3310 and $M_{n,GPC}$ = 3720. M_w/M_n: 1.36

3.3.4 Synthesis of p-xylylenebis(triphenylphosphonium bromide)

1,4-Bis(bromomethylbenzene) (5.2 g, 0.02 mol) or 1,4-dibromo-2,5-bis(bromomethyl)-benzene and PPh_3 (9.8 g, 0.042 mol) were dissolved in DMF (40 mL) in a round-bottom flask with a stirrer. The mixture was refluxed for 4 h. The white precipitate was filtered off and washed with diethyl ether to remove the unreacted materials. ^{1}H NMR ($CDCl_3$), (δ, ppm): 7.76−7.4 (m, 30H, PPh_3), 6.83 (s, 4H, Ar), 5.37−5.2 (d, 4H, CH_2).

3.3.5 General procedure for the synthesis of PPV with PSt or PCL side chains by the wittig reaction

Aldehyde functional polymers (0.2 mmol) and p-xylylenebis(triphenylphosphonium bromide) (0.2 mmol) was dissolved in dry THF (3 mL). t-BuOK solution (0.14 g, 1.2 mmol in 1 mL THF) was added dropwise under nitrogen to this reaction mixture, and the resulting solution was stirred for 24 h at room temperature. THF (1 mL) was further added to the solution to decrease the viscosity of the media. This process was further repeated twice and the reaction solution was precipitated into methanol after 48 h. Thus, obtained polymers were passed through a column of silica using THF as eluent and reprecipitated into methanol.
For PPV-g-PS, $M_{n,GPC}$ = 10600. M_w/M_n: 2.55.
For PPV-g-PCL, $M_{n,GPC}$ = 23300. M_w/M_n: 1.61

3.3.6 Photopolymerization

A typical photopolymerization procedure is as follows. A Pyrex tube was heated in vacuo with a heat gun and flushed with dry nitrogen. Then PPV derivative, CH_2Cl_2, the monomer and the oxidant were introduced to the tube. The resulting mixture was further bubbled with dry nitrogen and the tube was properly sealed. The stirring solution was irradiated with a light source emitting light at λ= 400−500 nm for 1 h and precipitated into methanol. The obtained polymers were dried under reduced pressure. Conversions for all samples were calculated gravimetrically.

3.3.7 Photo-DSC studies of polymerization

Photodifferential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified PerkinElmer Diammond DSC equipped with a Polilight PL400 Forensic Plus light source between 320 and 500 nm. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 20 mW cm^{-2} by a UV radiometer covering broad UV range. The measurements were carried out in an isothermal mode at 25 °C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of epoxy groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the epoxy groups (C) or the extent of the reaction was determined according to eq (3.1):

$$C=\Delta H_t/\Delta H_0^{theory} \qquad \textbf{(3.1)}$$

where ΔH_t is the reaction heat evolved at time t, and ΔH0theory is the theoretical heat for complete conversion. $\Delta H_0^{\text{theory}} = 81.40$ kJ mol^{-1} for an epoxy bond of cylcohexene oxide. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eq (3.2):

$$R_p = dC/dt = (dH/dt) / \Delta H_0{}^{theory} \qquad \textbf{(3.2)}$$

3.3.8 Fluorescence quenching studies

The fluorescence quenching studies were performed with solutions containing a constant concentration of PPV-*g*-PSt or PPV-*g*-PCL (3×10^{-6} mol·L^{-1}) and varying amounts of $Ph_2^+PF_6^{-}$. Dichloromethane was used as solvent. The variation of the fluorescence emission intensity was investigated by the increasing concentration of $Ph_2^+PF_6^-$.

4. RESULTS AND DISCUSSION

Utilization of several conjugated aromatic compound for the sensitization of onium salts has prompted us to apply PPVs as photosensitizers for cationic polymerization. In order to overcome solubility problems of bare PPVs associated with the rigid structure, PPVs with polystyrene and poly (ε-caprolactone) grafts (PPV-*g*-PSt and PPV-*g*-PCL, respectively) were synthesized. The first step in the synthesis of the desired PPVs was to obtain precursor macromonomers. In the preparation of macromonomers, controlled polymerization methods were deliberately employed so as to obtain polymers with desired functionalities at the chain ends, and combine with proper molecular weights and polydispersities Dibromo-benzene functional polystyrene (DBB-PSt) was synthesized by Atom Transfer Radical Polymerization (ATRP) of styrene by using 1,4-dibromo-2-(bromomethyl)benzene as initiator in the presence of CuBr/bpy as catalytic system. The corresponding poly (ε-caprolactone) derivative (DBB-PCL) was prepared by Ring Opening Polymerization (ROP) of ε-caprolactone by using [2,5-dibromo-(4-hydroxymethyl) phenyl)]methanol as bifunctional initiator, in the presence of stannous octoate.

In the next step, these polymers were coupled with (4-formylphenyl)boronic acid by Suzuki coupling to give aldehyde functional macromonomers. Finally, the obtained polymers were coupled with *p*-xylylenebis(triphenylphosphonium bromide) by the wittig reaction in the presence of potassium *tert*-botoxide to yield the desired conjugated polymers. The molecular weight characteristics of the intermediates at various stages and final polymers are given in Table 4.1. As can be seen, the modification of benzyl bromide functionality to aldehyde functionality did not cause significant change in the molecular weight and polydispersity. The final PPV graft copolymers exhibited higher molecular weight and polydispersity as a consequence of the step-growth polymerization nature.

Table 4.1 : Molecular Weight Characteristics of the Precursor Polymers and PPV Graft Copolymers.

Type of Polymer	$M_{n,NMR}$[a] (g·mol^{-1})	$M_{n,GPC}$[b] (g·mol^{-1})	M_w/M_n[b]
DBB-PSt	2270	2400	1.30
DBB-PCL	3260	3640	1.32
DBA-PSt	2420	2480	1.34
DBA-PCL	3310	3720	1.36
PPV-*g*-PSt	-	10600	2.55
PPV-*g*-PCL	-	23300	1.60

[a] Calculated by ^{1}H-NMR data.
[d] Determined byGPC according to polystyrene standards.

The ^{1}H-NMR spectrum PPV-*g*-PSt and PPV-*g*-PCL are given below. The structure was proved by ^{1}H-NMR spectrum, given in (Figure 4.1) and (Figure 4.2).

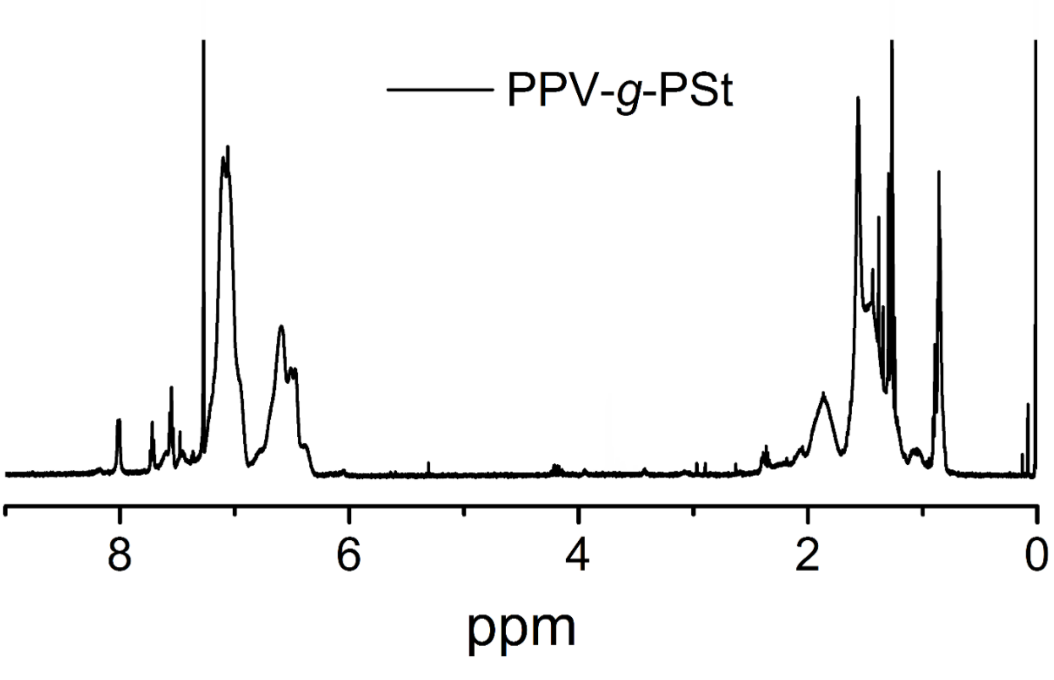


Figure 4.1 : ^{1}H-NMR spectrum of PPV-*g*-PSt.

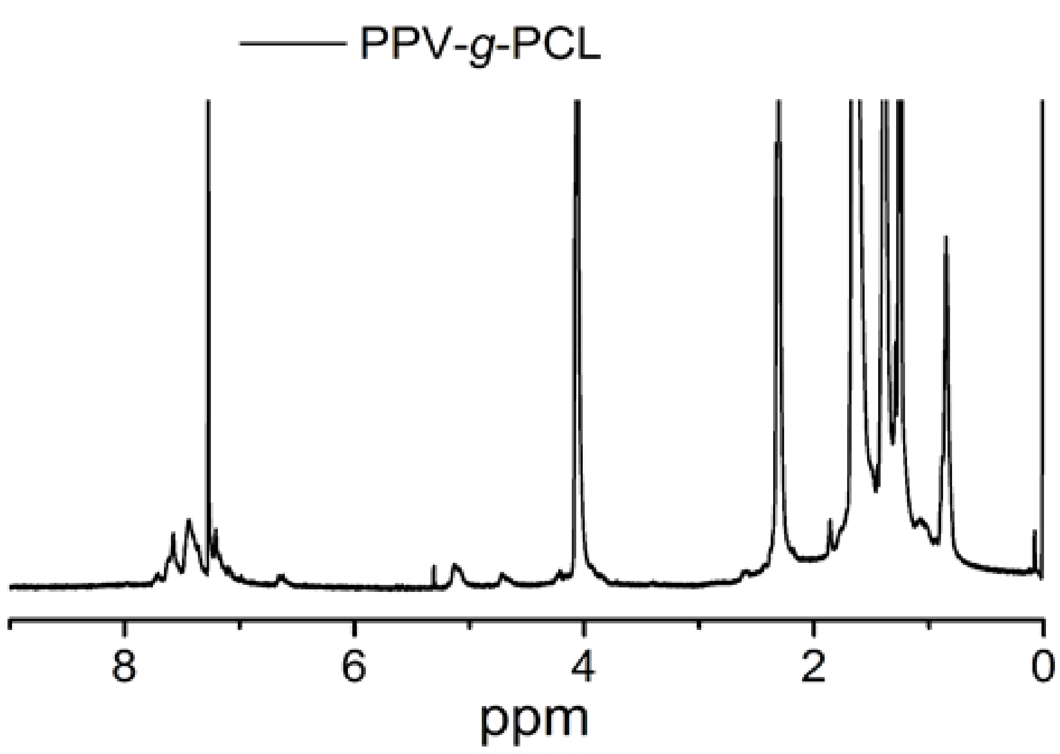


Figure 4.2 : ^{1}H-NMR spectrum of PPV-*g*-PCL.

As the conjugated sequences contain aldehyde groups at both ends, the functionalized polymers are candidates for synthesis of conjugated polymers with macromolecular side chains (PPVs or Schiff base type polymers). We applied the wittig method in combination with p-xylylenebis(triphenylphosphonium bromide) or 2,5-dibromo-p-xylylenebis (triphenylphosphonium bromide) and PPVs having as lateral substituents the respective PCL or PSt chains were synthesized.The general reactions involving the preparation of macromonomers and final PPVs are presented in (Figure 4.3).

(Figure 4.4) shows the UV-vis spectra of the PPVs and the onium salts (diphenyliodonium hexafluorophosphate (DPI), *N*-ethoxy-2-methylpyridinium hexafluorophosphate (EMP) and triphenylsulfonium hexaflourophosphate (TPS) used in this study. As can be seen, the onium salts do not display spectral sensitivity in the region where the photopolymerization takes place.

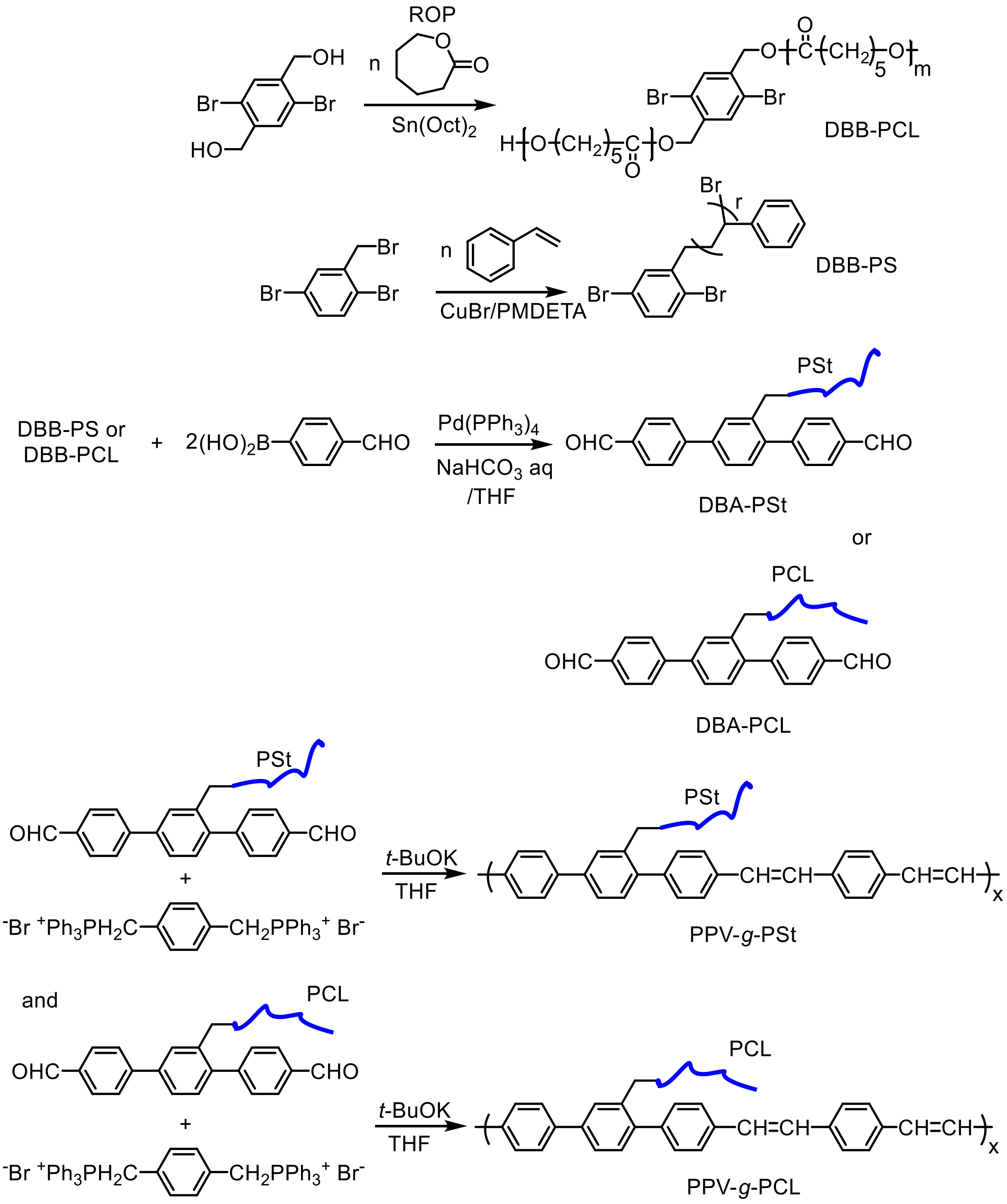


Figure 4.3 : Syntheses of PPV-g-PSt and PPV-g-PCL.

PPVs on the other hand have a tail absorption in this region, facilitating the possibility of their use for the sensitization of the onium salts in visible light induced photopolymerization experiments.

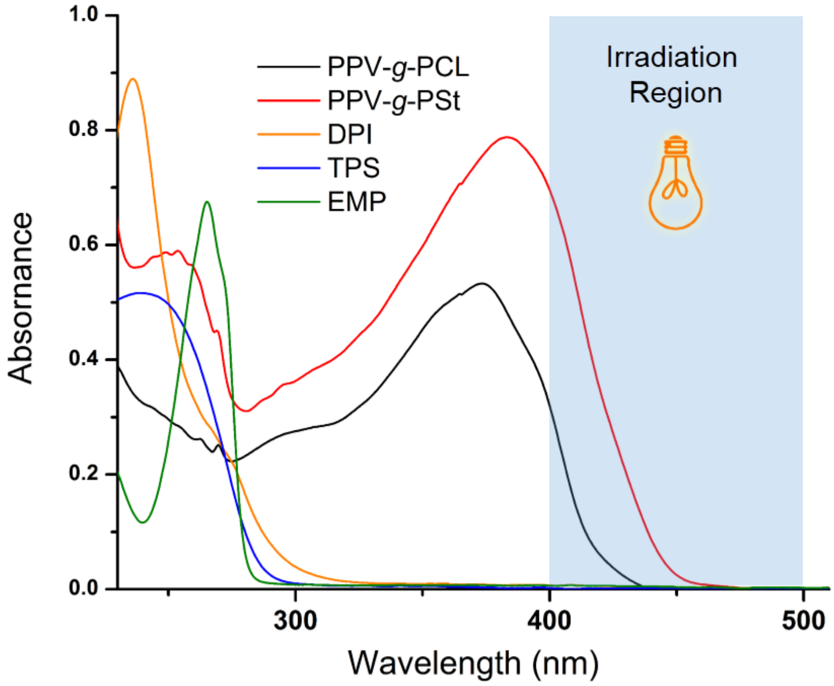


Figure 4.4 : UV-vis absorption spectra of poly(phenylene vinylene) derivatives and oxidants. Concentration in all cases was 1 x 10^{-4} mol L^{-1}.

The excited state emission characteristics of PPVs were investigated by means of fluorescence measurements to confirm their potential use as photosensitizers. (Figure 4.5) shows the excitation and emission spectra of PPV-*g*-PSt in CH_2Cl_2 at room temperature. The absorption and the fluorescence spectra of PPV-*g*-PSt exhibit mirror image behavior.

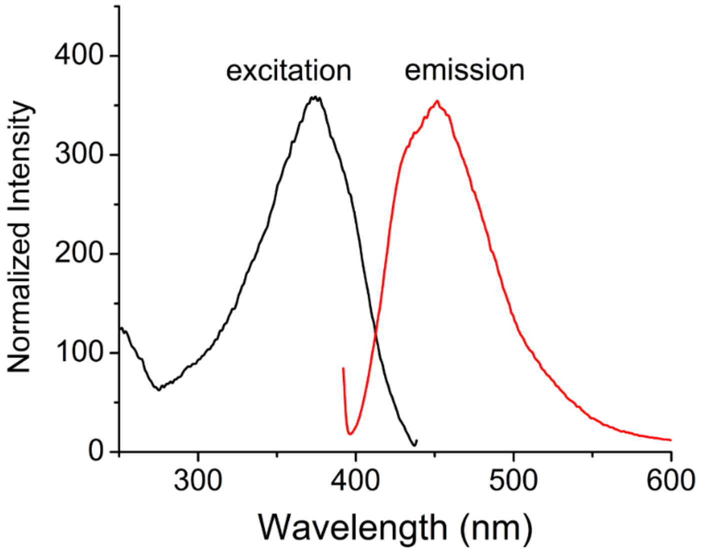


Figure 4.5 : Excitation and emission sprectra of PPV-*g*-PSt in CH_2Cl_2 [3 × 10^{-6} M].

In the presence of DPI, the fluorescence of the PPV-*g*-PSt is significantly quenched (Figure 4.6a). The linear pattern in the Stern-Volmer plot depicted in (Figure 4.6b) demonstrates the decrease of the fluorescence intensity with increasing DPI concentrartion. This linear function confirms the reaction of excited state PPV-*g*-PSt with ground state DPI. It can also be noted that the fluorescence emission maxima is shifted to the higher wavelengths. The observed shift may be due to the possible excimer formation at the relatively high concentration of PPV-*g*-PSt.

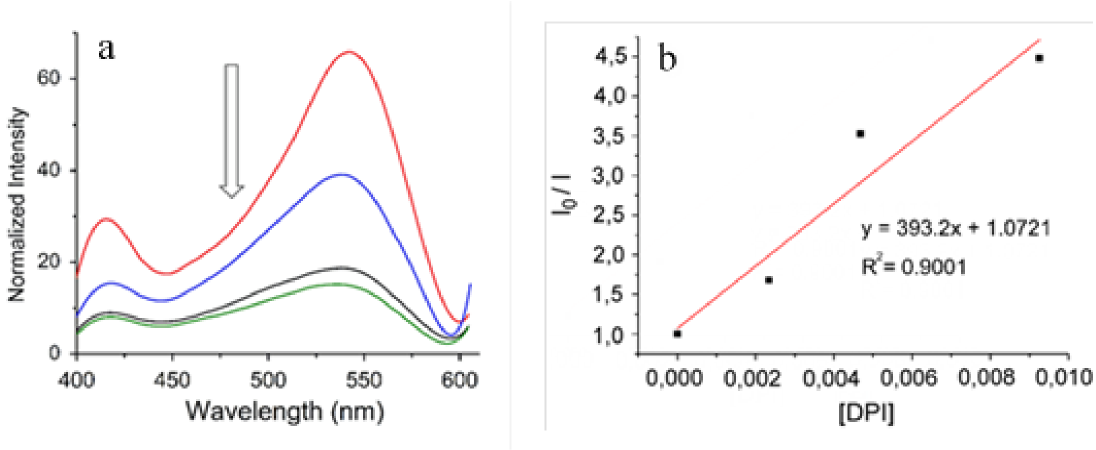


Figure 4.6 : Quenching of emission of PPV-g-PSt (a) Stern-Volmer plot for the fluorescence quenching of PPV-g-PSt by DPI in CH_2Cl_2, [PPV-g-PSt] = [9×10^{-6}], (b) (I_0= fluorescence intensity of PPV-g-PSt; I = fluorescence intensity in the presence of DPI).

In a typical photopolymerization experiment, PPVs were dissolved in dichloromethane and given onium salt and the monomer were subsequently added in dry atmosphere. Sealed reaction tubes irradiated through a visible light source nominally emitting at λ = 400-500 nm. The results are collected given in Table 4.2. It illustrates the expected rate and molecular weight dependencies on the type and concentration of both PPV and of onium salt. As can be seen, the efficiency of PPV-*g*-PSt is higher compare to that of PPV-*g*-PCL, which might be attributed to its higher absorbency in the visible region (See Figure 4.4) arising from the π-π stacking interactions of the PSt side chains with the PPV main chain. The reason for this, The concentration of PPV-*g*-PSt is 3 times higher for fluorescence quenching experiments. At this higher concentration, the shift of the fluorescence emission might be due to the excimer formation between the aromatic rings of the polymer backbone. This phenomenon is often observed with polynuclear aromatic compounds.

Table 4.2 : Visible Light Induced Cationic Polymerization[a] of Cyclohexene Oxide Using Poly(phenylenevinylene) derivatives in the Presence of Oxidants in Dicholoromethane.

Run	[PPV-*g*-PSt] ($\times10^{-3}$ M)	[PPV-*g*-PCL] ($\times10^{-3}$ M)	[DPI] ($\times10^{-3}$ M)	[EMP] ($\times10^{-3}$ M)	[TPS] ($\times10^{-3}$ M)	Conv.[c] (%)	M_n[d] (g·mol^{-1})	M_w/M_n[d]
1	0,5	-	3	-	-	36,2	17400	2,1
2	0,5	-	6	-	-	46,5	10200	3,7
3	0,5	-	12	-	-	61,0	8300	4,5
4[b]	0.5		12	-	-	<1	-	-
5	0,2	-	3	-	-	29,5	21000	1,6
6	0,2	-	6	-	-	40,8	15900	1,7
7	0,2	-	12	-	-	49,5	11000	1,5
8	-	0,2	3	-	-	21,7	6900	4,2
9	-	0,2	6	-	-	39,2	10200	3,7
10	-	0,2	12	-	-	53,2	29100	2,3
11	0,2	-	-	12	-	43,4	10100	1,7
12	-	0,2	-	12	-	32,5	8900	1,7
13	0,2	-	-	-	12	0	-	-
14	-	0,2	-	-	12	0	-	-

[a] λ = 400-500 nm; light intensity = 45×10^{-3} W m^{-2}; irradiation time = 1 h.

[b] In the presence of 2,6-di-*tert*-butylpyridine (12×10^{-3} M)

[c] Determined gravimetrically

[d] Determined by GPC according to polystyrene standards.

It can also be noted from the table that, among the onium salts employed, DPI is the most efficient in electron transfer reactions. This can be explained by the more favorable thermodynamic conditions (Table 4.3). Any change in the environment takes place only if the free energy change ΔG is negative. The feasibility of an electron transfer process from a sensitizer to a ground state onium salt is be estimated using the Rehm-Weller equation based on the excitation energy (E^*) and the oxidation potential (E_{ox}) of the photosensitizer, and the reduction potential of the onium salt (f_c= 96.5 kJ mol^{-1} V^{-1}).

$$\Delta G = f_c\,(E_{ox}(\mathrm{S}) - E_{red}(\mathrm{ox})) - E^*(\mathrm{PS}) \qquad \textbf{(4.1)}$$

In accordance with the ΔG values, TPS does not participate in the electron transfer process while EMP exhibits an intermediate behavior.

Table 4.3 : Free energy changes for the photoinduced electron transfer from excited state PPV derivatives (E_{ox} = 2,4 V)[9] to various oxidants at 400 nm (E^* = 299 kj.mol^{-1}).

Oxidants	E_{ox} (V)^a	ΔG (kj.mol^{-1})^b
DPI	-0.2	-50.9
EMP	-0.7	-2.8
TPS	-1.2	+45.5

^{a} E_{ox} are given vs SCE

^{b} Calculated by Rehm-Weller Equation

Besides cyclic ethers, the polymerizability of vinyl monomers such as isobutyl vinyl ether (IBVE) and *N*-vinyl carbazole (NVC) with the described initiating system was also tested. All monomers underwent polymerizationupon irradiation in the visible range under similar experimental conditions (Table 4.4). Higher conversions and polydispersities noted with NVC and IBVE may be attributed to their strong electron donor nature and dominating chain transfer reactions observed in the cationic polymerization of vinylic monomers. The polymerizability of NVC monomer by free radical mechanism should also be considered.

Table 4.4 : Visible light ınduced cationic polymerization^a of various monomers using PPV-*g*-PSt in the presence of DPI in dicholoromethane.

Monomers	Conv. (%)^b	M_n (g·mol^{-1})^c	M_w/M_n^{c}
CHO	61,0	8300	4,5
IBVE	70,0	10300	6,3
NVC	90,1	8200	8,2

^{a} [Monomer]/ [DPI]/ [PPV-*g*-PSt]: 400/ 24/ 1 , λ = 400-500 nm; light intensity = 45 × 10^{-3} W m^{-2}; irradiation time = 1 h.
^{b} Determined gravimetrically
^{c} Determined by GPC according to polystyrene standards.

More convincing evidence for the polymerization mechanism was obtained by conducting a control experiment in the presence of a proton scavenger such as 2,6-di-*tert*-butylpyridine under identical experimental conditions . As can be seen from Table 4.2 Run 4, experiments in the present of the proton scavenger failed to produce any precipitable polymer indicating the dominant role of protonic acids as the initiating species. The ^{1}H-NMR spectra of the obtained polymers also supports this hypothesis. A plausable photopolymerization mechanism on the example of PPV-*g*-PSt / DPI system is depicted in (Figure 4.7). No aromatic protons corresponding to PPVs were detected. (Figure 4.8).

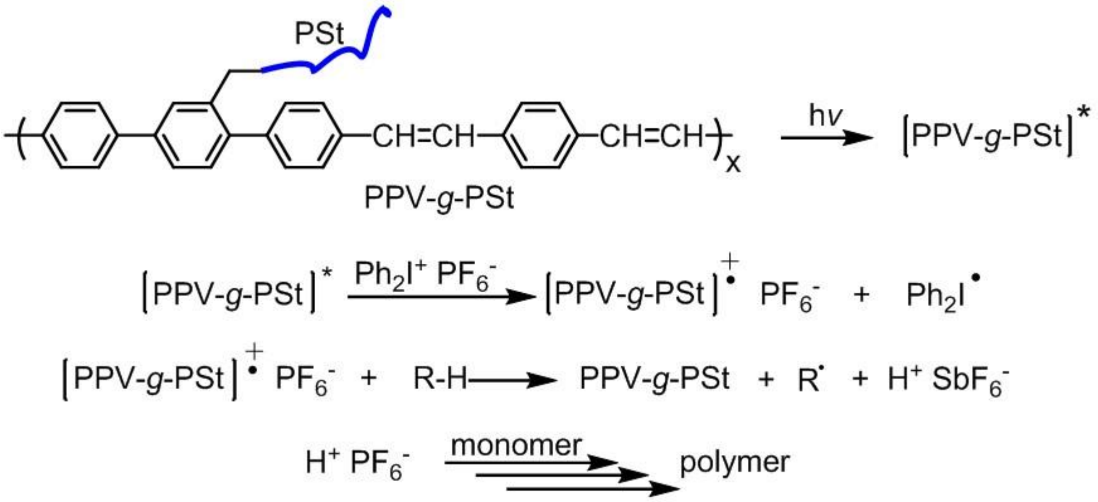


Figure 4.7 : Proposed mechanism for photoinduced cationic polymerization using PPV-g-PSt as photosensitizers.

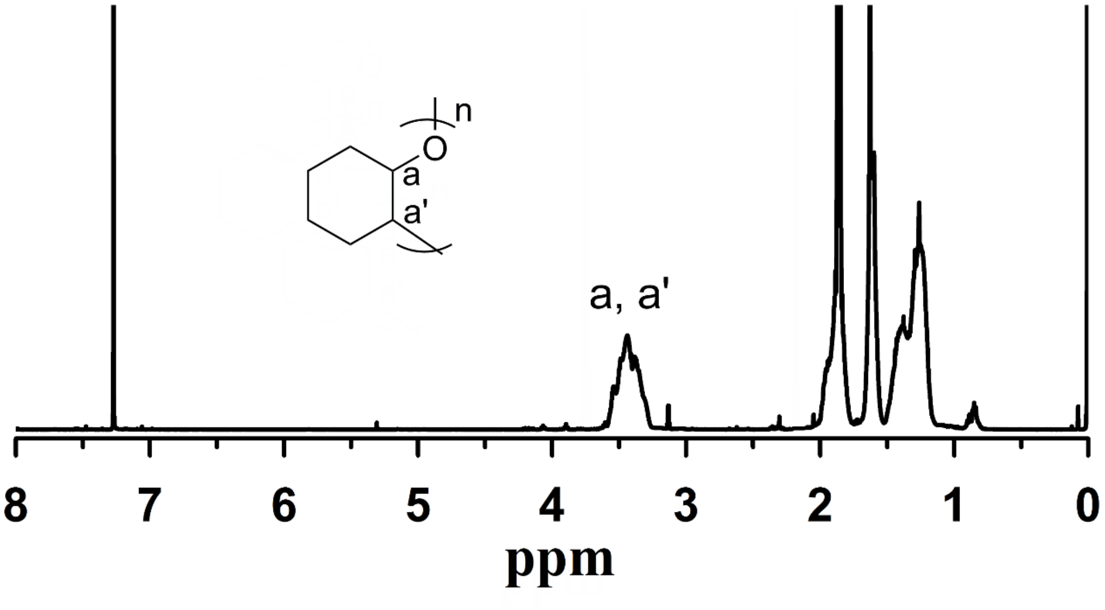


Figure 4.8 : ^{1}H-NMR spectra of PCHO obtained by photoinduced cationic polymerization using PPV-*g*-PSt/DPI initiating system.

The kinetic profiles of the polymerization processes using PPV-*g*-PSt and PPV-*g*-PCL are investigated by Photo-DSC studies. Photo-DSC technique is capable of measuring any liberating heat during the photopolymerization process. This is directly proportional to the number of oxirane bonds reacted in the photopolymerization process. Consequently, the rate of polymerization (the number of monomers being consumed over total number of monomers per time), RP (1/s), can be determined according to eq (4.2):

$$R_P = (Q_t) \times 1000 / [n \times (E_{db})] \qquad \textbf{(4.2)}$$

where Qt ($J\ mol^{-1}\ s^{-1}$) is the amount of released heat at time t, n the number of oxirane rings, and Edb (kJ mol−1) is the energy of ring opening step (~81 kJ mol^{-1}). By integrating the area under RP−t graph, the conversion of the acrylate monomer is obtained. Figure 4.9 depicts the kinetics of the photopolymerization of CHO using both PPVs in the presence of DPI measured by photo-DSC. It can be seen that the photosensitization activity of PPV-g-PSt was higher than that of PPV-g-PCL in agreement with the gravimetric studies.

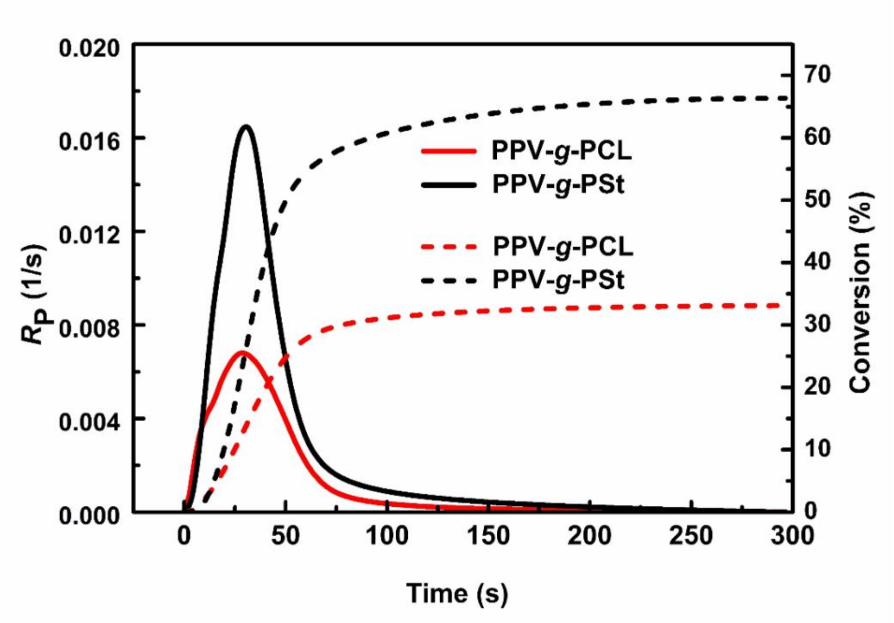


Figure 4.9 : Kinetics of the photopolymerization of CHO using PPV-*g*-PSt and PPV-*g*-PCL in dichloromethane obtained by photo-DSC. Solid lines: rate of polymerization, R_P (1/s); dashed lines: conversion (%).

5. CONCLUSION

In summary, PPVs with PSt and PCL side chains were synthesized and used as photosensitizers in conjunction with various onium salts for visible light induced cationic polymerization of appropriate monomers. It has been postulated that PPVs undego photoinduced electron transfer reactions with onium salts to yield protonic acid, which is responsible for the initiation of cationic polymerization. It is clear that both photosensitizers possess excellent photophysical properties for such initiation route in the visible region which may find use in many specific applications such as holographic recordings, photoresists, integrated circuits, printing plates, nanoscale micromechanics and laser-induced 3D curing. It appears that providing appropriate matching redox and absorption properties the other conjugated polymers may undergo similar photoinduced electron transfer reactions creating wider selectivity for particular applications.

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