

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**SYNTHESIS OF PHTHALOCYANINE CONTAINING POLY(METHYL
METHACRYLATE) BY ATRP**

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2015

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ATRP İLE FTALOSİYANİN İÇEREN POLİMETİLMETAKRİLAT SENTEZİ

YÜKSEK LİSANS TEZİ

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To my family,

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.

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ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
DCM	: Dichloromethane
DSC	: Differential Scanning Calorimetry
FT-IR	: Fourier Transform Infrared Spectroscopy
GPC	: Gel Permeation Chromatography
HOMO	: Highest occupied molecular orbital
H₂Pc-Br	: Metal free phthalocyanine with bromide group
H₂Pc-OH	: Metal free phthalocyanine with hydroxy group
K	: Kelvin
LUMO	: Lowest unoccupied molecular orbital
M_w	: Molecular weight
MMA	: Methyl methacrylate
nm	: Nanometer
Pc	: Phthalocyanine
PMMA	: Poly(methyl methacrylate)
SCE	: Saturated calomel electrode
TGA	: Thermogravimetric analysis
THF	: Tetrahydrofuran
UV-Vis	: Ultraviolet-Visible
ZnPc-Br	: Zinc Phthalocyanine with bromide groups
ZnPc-OH	: Zinc Phthalocyanine with hydroxy group

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SYNTHESIS OF PHTHALOCYANINE CONTAINING POLY(METHYL METHACRYLATE) BY ATRP

SUMMARY

Since their accidental discovery in 1930s, the phthalocyanines have been one of the most studied classes of organic functional materials because of their unusual chemical and physical properties. Their diverse functionality comes from its 18- π electron aromatic system and their ability to coordinate with most of the metal atoms in the periodic table. In addition to their ubiquitous use as highly stable blue and green colorants, phthalocyanines find commercial applications as a photoconductor in Xerography, and in optical data storage as the laser absorption layer within recordable compact discs. Also there is an increasing interest for applications in non-linear optics, molecular electronics, photodynamic cancer therapy, solar energy conversion, various catalytic processes, electrochromic and electroluminescent displays, chromatography, and as the active component of gas sensors. The structure of the phthalocyanine can be modified by the change of the central atom and/or its axial coordination, the change of the meso-atoms in the phthalocyanine macrocycle, and its peripheral modification. Introduction of peripheral substituents like alkyl, alkoxy or alkylthio groups to the phthalocyanine enhances its solubility in common organic solvents and its optical and redox properties.

Phthalocyanines can be incorporated within the the macromolecular structure as either network, main-chain or sidechain polymers. In addition, they can also be present as end-groups, pendant groups or as a core of a polymer which is an active area of research.

It is difficult to obtain the polymer with narrow molecular weight distribution and well-defined structure by traditional radical polymerization, which will affect the property accordingly. In the past few years, controlled/“living” radical polymerization (CLRP) has been widely developed, which provides an efficient way of synthesizing polymers with designed structure and narrow molecular weight distribution. Atom transfer radical polymerization (ATRP), stable free radical polymerization (SFRP), nitroxide mediated radical polymerization (NMRP), and reversible addition-fragmentation chain transfer polymerization (RAFT) are examples of CLRP techniques. Among these techniques, ATRP is one of the very versatile and convenient techniques for polymer synthesis with good control of the molecular weight and relatively low polydispersities. ATRP also allows the synthesis of a variety of polymers with well-defined compositions, architectures, functionalities, and chain topology.

In this study, methyl methacrylate is polymerized by ATRP using brominated phthalocyanines as macroinitiator. Therefore, hydroxy end group containing phthalocyanines are brominated to form reactive bromine groups. Structure of the phthalocyanines were examined by NMR, FT-IR and electrochemical studies.

Bromine functional group take part in initiating the poly(methyl methacrylate) chain growth. Polymerization characteristics, chemical structure, thermal, UV-Vis, fluorescence and transmittance properties were examined by analysis.

ATRP İLE FTALOSİYANİN İÇEREN POLİMETİLMETAKRİLAT SENTEZİ

ÖZET

1930'lardaki kazara bulunuşlarından beri ftalosiyaninler alışılmamış kimyasal ve fiziksel özelliklerinden ötürü en çok araştırma yapılan organik fonksiyonel maddelerden biri olmuştur. Yapılarındaki 18- π elektronlu aromatik sistem ve periyodik tablodaki birçok metal atomu ile koordine olabilmeleri sayesinde farklı işlevselliklere sahiptirler. Metalli ve metallsiz ftalosiyaninler özellikle renklendirici niteliği nedeniyle detaylıca araştırılmıştır. Ftalosiyaninlerin yapısı porfirinlere benzemesine rağmen porfirinler gibi doğada bulunmayan, sentetik materyallerdir. Porfirinlerden farklı olarak dört tane benzil grubu ve mezo konumunda dört tane azot atomu bulunmaktadır.

Ftalosiyaninler iyi derecede termal ve kimyasal kararlılığa sahiptir. Fakat ftalosiyaninlerin en büyük dezavantajlarından biri substitüe olmamış türevlerinin çözünürlüklerinin aşırı derecede az olmasıdır. Bu özelliği, aromatik merkezinin aşırı derecede hidrofobik oluşuna ve ftalosiyanin yığılma eğilimi gösremesine neden düzlemselliğine dayandırılabilir. Ftalosiyaninlerin elektrokimyasal aktiviteleri aromatik halkadan kaynaklanmaktadır. Halkadaki işlemlere ek olarak redoks aktif metaller de etki edebilir. Kobalt, demir ve manganez gibi metallerin elektrokimyasal olarak aktif olmalarına karşın çinko, nikel ve magnezyum elektrokimyasal olarak inatiftir.

Ftalosiyaninler için en önemli spektral analizlerden biri ultraviyole – görünür bölge (UV-Vis) spektroskopisidir. π elektronlarınca zengin oldukları için, $n \rightarrow \pi^*$ ve $\pi \rightarrow \pi^*$ geçişlerinde karakteristik absorpsiyon pikleri gösterirler. Bunlar Q bandı (700-65 nm civarında), B bandı (420-320 nm civarında), N bandı (330-285 nm civarında) ve L bandıdır (270-230 nm civarında). UV-Vis ölçümlerinde metalli ve metallsiz ftalosiyaninler için en büyük fark, metalli ftalosiyaninlerin Q bandında bir adet pik gözlemlenmesine rağmen metallsiz ftalosiyaninlerin Q bandında ikiye yarılmış gibi duran bir pik gözlemlenmesidir.

Ftalosiyaninler yaygın olarak mavi ve yeşil boyar maddeler olarak kullanılırlar ve oldukça kararlı bir yapıya sahiptirler. Boyar madde kullanımının yanı sıra ticari anlamda kserografide fotoiletken ve kaydedilebilen kompat disklerin lazer soğrulma katmanlarında optik veri depolayıcısı olarak kullanılabilirler. Ayrıca doğrusal olmayan optikler, moleküler elektronik, fotodinamik kanser terapisi, güneş enerjisi dönüşümü, çeşitli katalitik prosesler, gaz sensörlerin aktif parçaları ve elektrokromik ve elektroluminesans ekranlar gibi alanlar için ftalosiyanin kullanımında artan bir ilgi vardır. Ftalosiyaninlerin yapısında çeşitli yollarla değişiklikler yapılabilir; bunlar merkez atomun ve/veya aksiyal koordinasyonun değişimi, ftalosiyanin makromolekülündeki mezo-atomların değişimi ve periferik modifikasyondur. Alkil, alkoksil ve alkiltio gibi grupların periferik substituent olarak yapıya dahil edilmeleri

sayesinde ftalosiyaninlerin yaygın organik solventlerdeki çözünürlükleri ve optik ve redoks özellikleri geliştirilebilir.

Ftalosiyaninler ağ, ana zincir veya yan zincir olarak makromoleküler yapılar ile birleştirilmiş halde bulunabilirler. Bunların yanı sıra uç grup, yan grup olarak ve polimerin merkezine merkez grup olarak dahil olabilirler. Ftalosiyaninlerin polimer merkezlerinde bulunduğu durumlarla ilgili çalışmalar yaygınlaşmaya başlamıştır. Yeni polimer-ftalosiyanin bağlarının oluşturulması şu an çalışılmakta olan aktif bir alandır ve yapılan yeni malzemelerde gözlemlenen gelişmiş özellikler bu alandaki çalışmaları hızlandırmaktadır.

Dar molekül ağırlığı dağılımı ve iyi tanımlanma gibi polimerlerin özelliklerini etkileyen faktörleri geleneksel radikal polimerizasyon yöntemleri ile kontrol etmek zordur. Son yıllar içerisinde yaygın bir şekilde geliştirilen kontrollü/yaşayan radikal polimerizasyon (CLRP) tasarlanmış yapıları ve dar bir molekül ağırlığı dağılımına sahip polimerlerin sentezlenmesi için etkili bir yöntem temin etmektedir. CLRP tekniklerine örnek olarak atom transfer radikal polimerizasyonu (ATRP), kararlı serbest radikal polimerizasyon (SFRP), nitroksit aracılı radikal polimerizasyon (NMRP) ve tersinir eklenme-parçalanma zincir transfer polimerizasyonu (RAFT) gösterilebilir. Bu teknikler arasından ATRP, molekül ağırlığını iyi bir şekilde kontrol ve nispeten düşük polidispersiteye sahip polimer sentezi için çok yönlü ve uygun bir tekniktir. ATRP iyi tanımlanmış bileşimlere, mimari yapılara, uç grup işlevselliklerine ve zincir topolojilerine sahip çeşitli polimerlerin sentezlenmesine olanak tanımaktadır.

ATRP, büyüyen radikali kararlı hale getirebilecek ve fonksiyonel grupları olan monomerler için uygulanabilir. Çeşitli vinil monomerleri ATRP ile başarılı bir şekilde polimerleştirilmiştir. En çok incelenmiş olanlar stiren, akrilatlar ve metakrilatların polimerleşmesidir. Her ayrı monomer için farklı spesifik ATRP koşulları bulunmaktadır.

Bu çalışmada, metil metakrilatın polimerleştirilmesi sırasında kullanılacak bir radikal başlatıcı oluşturulmuştur ve bu başlatıcı ATRP reaksiyonunda etkin bir şekilde kullanılmıştır.

İlk aşamada, metalsiz ve çinko metalli hidroksil uç grubu bulunan oktakis(hidroksietiltiyo)-sübstitüentli ftalosiyaninlerin uç grupları modifiye edilmiştir. 2-bromopropiyonil bromür kullanılarak metalli ve metalsiz ftalosiyaninlerin uç gruplarında aktif brom grubu olması sağlanmıştır. Reaksiyon verimi gravimetrik olarak hesaplanmıştır.

Yapılar arasındaki farklar FT-IR ve NMR yöntemleri ile incelenmiştir. Ayrıca yeni oluşturulan metalsiz ve metalli ftalosiyaninlerin elektrokimyasal özellikleri de incelenmiştir. Sentezlenen ftalosiyaninler metil metakrilatın ATRP yöntemiyle polimerleştirilmesinde başlatıcı olarak kullanılmıştır.

Reaksiyon süresinin polimerizasyona etkisi incelenmek üzere metil metakrilat monomerinin elde edilen ftalosiyaninler ile bakır(I)bromür/ *N,N,N',N',N''*-pentametildietilentriamin katalizörülüğünde metalsiz başlatıcı için 12, 24 ve 48 saat ve metalli başlatıcı için 6, 12, 24 ve 48 saat boyunca reaksiyon vermesi sağlanmıştır. Reaksiyon sonunda elde edilen çözelti üzerine tetrahidrofuran eklenip kısa alümina kolonda geçirilerek ortamdaki fazla bakırdan kurtulması sağlanmıştır. Solvent uçurulmuş ve polimerler metanol içerisine çöktürülüp sonrasında süzümüştür.

Jel Geçirgenlik Kromatografisinde ile polimetimetakrilatların moleküler ağırlıkları (M_n) ve moleküler ağırlık dağılımları (PDI) incelenmiştir. Beklenildiği üzere reaksiyon süresinin artması polimerin molekül ağırlığı artmış ve molekül ağırlık dağılımı düşmüştür. Oluşan polimerlerin yapısı FT-IR ve NMR yöntemleri ile incelenmiştir. Hem ftalosiyanin başlatıcılarının hem de polimerlerinin elektrokimyasal özellikleri incelenmiştir ve birbirlerine benzer karakterde özellikleri olduğu gözlemlenmiştir. Ayrıca başlatıcıların ve polimerlerin elektronik absorpsiyon ve floresans özelliklerine bakılıp gerekli karşılatırmalar yapılmıştır. Elektronik absorpsiyon özelliklerinden elde edilen en önemli sonuç, beklenildiği üzere metalsiz başlatıcıyla sentezlenen polimerlerin içerisinde metal bulunan polimerlerle benzer elektronik absorpsiyon spektrumları vermesidir. Bunun nedeni ortamın sıcaklığı ve ortamda bulunan fazladan bakır kompleksleri nedeniyle ATRP sırasında metalsiz ftalosiyaninlerin merkezine bakır atomunun yerleşmesidir. Floresans spektrumlarından çıkarılan sonuç ise düşük ağırlıklı polimerlerin floresans özelliğini koruduğu fakat molekül ağırlığı arttıkça kendiliğinden sönümlemelerin gözlenmeye başlanmasıdır. Son olarak geçirgenlik özellikleri incelenmiş, ftalosiyaninlerin başlatıcı olarak kullanılmasının polimetilmetakrilatların geçirgenlik özelliklerini olumsuz yönde etkilemediği gözlemlenmiştir.

1. INTRODUCTION

Since their first laboratory synthesis in 1930's, scientists shown great interest to phthalocyanines because of their unusual physical and chemical properties. Their diverse functionality comes from its 18- π electron aromatic system and their ability to coordinate with most of the metal atoms in the periodic table. Today, they are used in many fields. Phthalocyanines are well-known organic dyes with common applications in advanced technologies such as industrial catalytic systems [1]; photosensitizers for photodynamic therapy of cancer [2]; materials for electro photography, ink-jet semiconductors, chemical sensors, and electrochromic devices, functional polymers and liquid crystals [3]; nanotechnology [4], and non-linear optics [5]. The structure of the phthalocyanine can be modified by the change of the central atom and/or its axial coordination, the change of the meso-atoms in the phthalocyanine macrocycle, and its peripheral modification [6] which is more efficient. Introduction of peripheral substituents like alkyl, alkoxy or alkylthio groups to the phthalocyanine enhances its solubility in common organic solvents and the use for tuning of optical and redox properties of phthalocyanines designed for specific high-tech. applications [7-8].

The development of new polymer-phthalocyanine bound is an active area of research, especially improved properties of new materials accelerated the research efforts in this area. Recently, polymers containing phthalocyanines as end group or pendant unit have been widely studied. However, there have not many studies concerning the preparation of four armed polymers with phthalocyanine core.

It is difficult to obtain the polymer with narrow molecular weight distribution and well-defined structure by traditional radical polymerization, which will affect the property accordingly. In the past few years, controlled/"living" radical polymerization (CRP) has been widely developed, which provides an efficient way of synthesizing polymers with designed structure and narrow molecular weight distribution. Atom transfer radical polymerization (ATRP), one of the most

investigated CRP, can provide polymers with well-defined structure using suitable initiators [9-10].

This thesis will concern to polymerize methyl methacrylate by ATRP as using brominated phthalocyanines as macroinitiator. Therefore, -OH end group containing phthalocyanines are brominated to form bromine reactive groups. This functional group take part in initiating the PMMA chain growth. Polymerization characteristics, chemical structure, thermal, electrochemical, UV-Vis, fluorescence and transmittance properties were examined by analysis.

2. THEOROTICAL PART

2.1 Phthalocyanine

2.1.1 History of phthalocyanines

Phthalocyanines are planar macrocyclic structures which contain 18 π -electron system. They are consist of four isoindole units. They have ability to make complexes with most of the metals. These properties give phthalocyanines several chemical and physical properties and allow it to have a wide range of applications. Free and metallophthalocyanines were been researched in detailed way especially because of their colouring agent properties. Although their structure is similar to porphyrins, they are synthetic materials and can not be found in the nature like porphyrins. Phthalocyanines have four benzo unit and four nitrogen atoms in meso position different from porphyrins (Figure 2.1) [11-12].

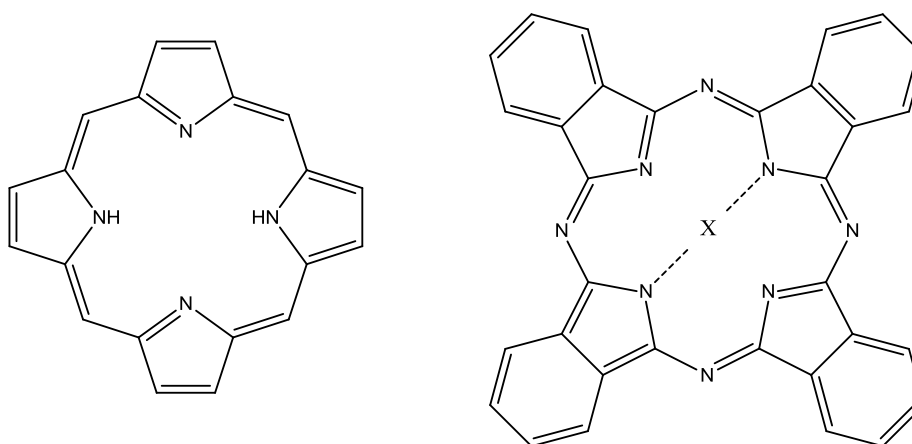


Figure 2.1 : Porphyrin and phthalocyanine (X: 2H or metal).

The word “phthalocyanine” was derived from the Greek terms naphta (rock oil) and cyanine (dark blue). After twenty six years from its accidental discovery, the word phthalocyanine was first used by Professor P. Linstead (Imperial College of Science and Technology) in 1933 to define metal free or di hydrogen phthalocyanine, metal phthalocyanines and their derivatives [13].

The discovery of phthalocyanine is made by the workers of South Metropolitan Gas Company in London, Braun and Tcherniac in 1907. They found a blue substance after heating o-cyanobenzamide (Figure 2.2) [14]. In 1927 while De Diesbach and Von der Weid from University of Fribourg making a reaction with o-dibromobenzene and cuprous cyanide (CuCN) refluxing with pyridine to synthesis nitriles of benzene, they obtained a product with blue colour with 23% yield (Figure 2.3) [15]. Later on Hindsight clarified that the first byproduct was metal free phthalocyanine, and the second one copper(II) phthalocyanine.

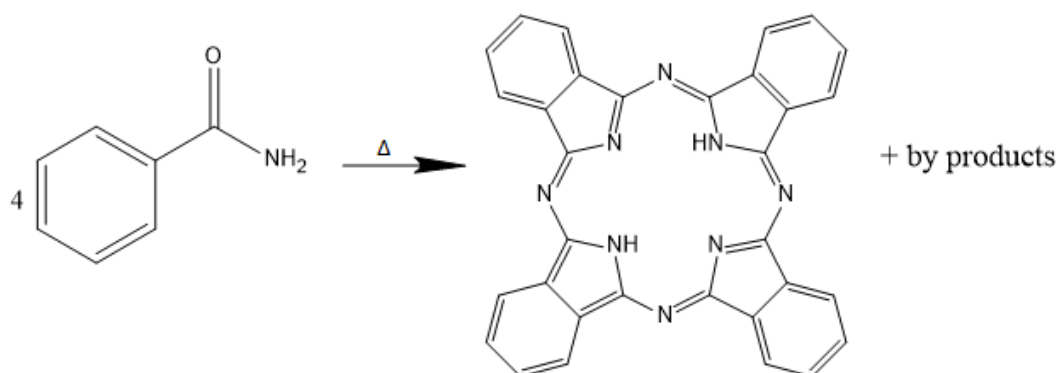


Figure 2.2 : Synthetic routes to phthalocyanine used by Braun and Techerniac.

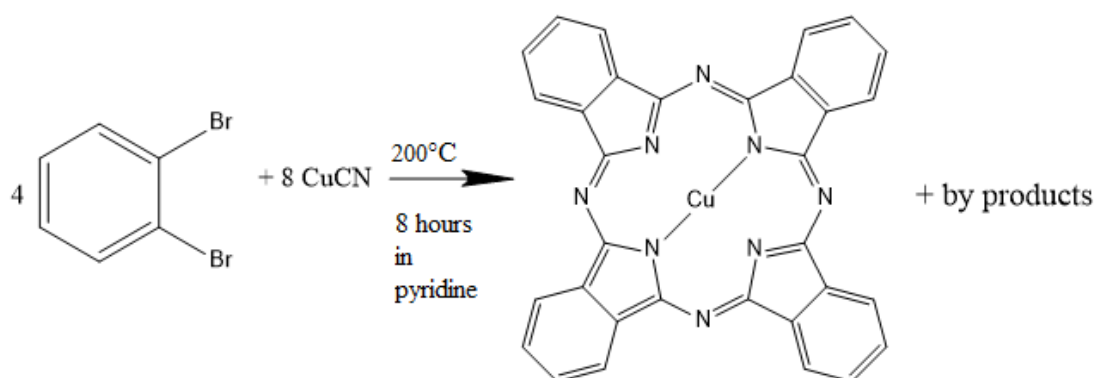


Figure 2.3 : Synthetic routes to phthalocyanine by Diesbach.

Up to this point, none of these researchers characterized the phthalocyanine products, so the discovery of phthalocyanines attributed to chemists at Scottish Dyes Ltd. In 1928 while producing phthalimide from phthalic anhydride and ammonia, a green/blue imprutiyy was found which was coming from the iron vats. The compound was very stable, insoluble, and resitant to heat and identified as iron (II)

phthalocyanine [16]. Starting from 1929 Professor Linstead and his students, supported by the Imperial Chemical Industries, determined and announced the structure of phthalocyanine and several metallophthalocyanines in 1933 and 1934 [17]. Also the structure was analyzed by X-ray diffraction studies, made by Robertson [18-20].

The potential of phthalocyanines as pigments was immediately obvious to workers at Imperial Chemical Industries, which began trading copper (II) phthalocyanine under the name Monastral Blue in 1935 [21]. In 1936 and 1937 I.G. Farben Industry and Dupont followed the developments. Industrial manufacture of phthalocyanine was based on the methodology developed by Wyler at the ICI research center at Blackley, Manchester. The Wyler method involves heating inexpensive phthalic anhydride in a melt of urea, metal salt, and suitable catalyst (e.g., ammonium molybdate) and this is still the method of choice for industrial-scale manufacture of phthalocyanine colorants. Water-soluble dyes based on sulfonated phthalocyanines and, subsequently, reactive dyes for permanent textile coloration were developed in the 1950s and 1960s.

Since their discovery and identification, phthalocyanines have been extensively used as dyes and pigments in paint, printing, textile and paper industries, due to their intense blue-green color. Today, many thousands of tons of phthalocyanines are produced worldwide, per annum, to help satisfy the demand for colorants and optoelectronic materials.

2.1.2 Properties of phthalocyanines

Phthalocyanines belong to the tetrapyrrole macrocycle class as their structure contain an alternating nitrogen atom-carbon atom ring. They form an important class of macrocyclic compounds which do not occur naturally. Phthalocyanines are man's analogues of nature's pigments of life, the porphyrins, such as chlorophyll and hemoglobin. This class also includes porphyrins and porphyrazines [22-23].

Phthalocyanines possess large nonlinearity, along with synthetic flexibility as well as thermal stability. Phthalocyanines have a conjugated, 18 π electron aromatic planar structure. This π system is localized over alternate carbon and nitrogen atoms and provide the unique chemical and physical properties. 18 π electron conjugated system gives it characteristic blue-green colour. The structure has sixteen ring sites

for possible substitution and the diversity of applications of phthalocyanines can be extended by incorporating different substituents to these sites. These sixteen sites can be divided into two categories. The positions 2, 3, 9, 10, 16, 17, 23, 24 are peripheral (p) sites or α -positions and 1, 4, 8, 11, 15, 18, 22, 24 are non-peripheral (np) sites or β -positions [6]. These alterations change the properties of phthalocyanines like solubility. Solubility can be varied by changing the central metal ions, axial ligands and ring substituents (Figure 2.4) [24].

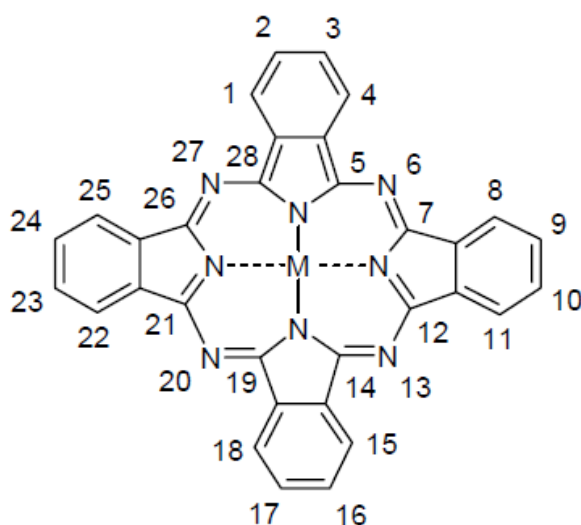


Figure 2.4 : Peripheral and non-peripheral sites of phthalocyanines.

Structure determination of phthalocyanine and its metal derivatives was carried out by Linstead [25].

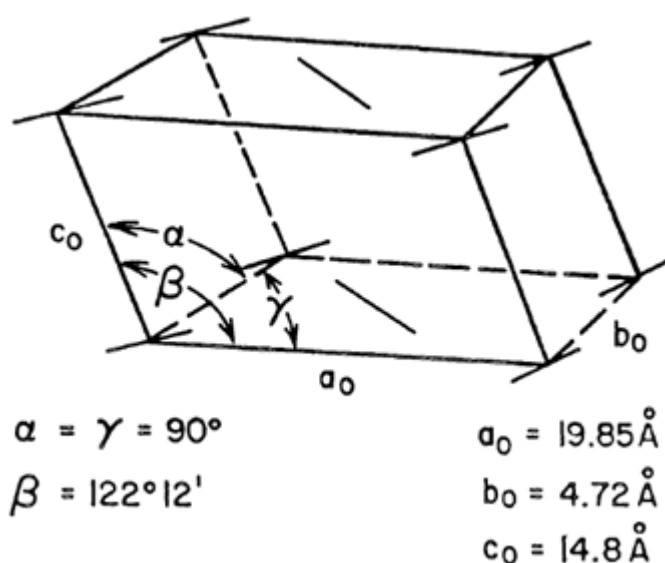
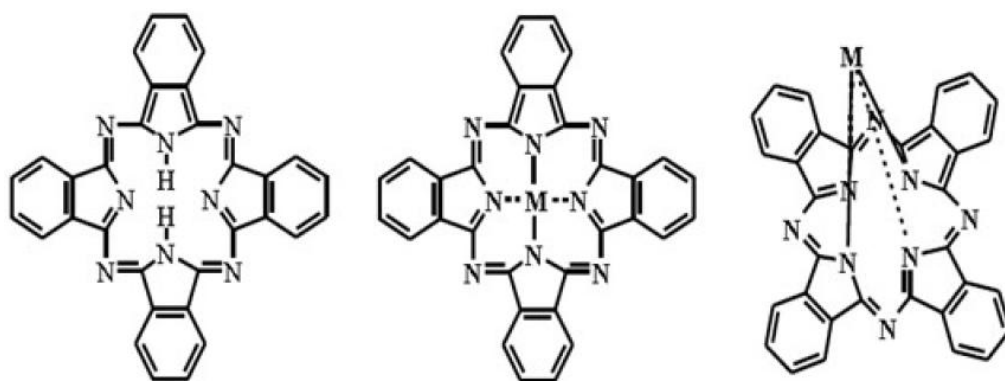


Figure 2.5 : The unit cell of metal-free phthalocyanine.

[illegible]

As it can be seen in Figure 2.7 metallophthalocyanines have D_{4h} geometry while metal free phthalocyanines have a D_{2h} symmetry. Replacing the two hydrogen atoms with a metal leads to an increase in symmetry from D_{2h} to D_{4h} . However because of their larger ionic size, some metal ions like Pb, Sb, and Ta do not perfectly fit in the cavity. The size of the phthalocyanine cavity is found as 396 pm [26], large metal ions tend to misshape the geometry of phthalocyanines. This behavior leads to a change in planarity to a square pyramidal and a reduction of the symmetry from D_{2h} to a C_{4v} symmetry [27-28].



7

2.1.2.1 Physical and chemical properties

Phthalocyanines have good thermal and chemical stability and high LUMO energy level. If they are compared with porphyrins, phthalocyanines have greater stability toward heat and oxidation because of their four aza nitrogens. Up to 100 °C, atmospheric oxygen can not oxidize phthalocyanines. Mild oxidation may lead to the formation of oxidation intermediates that can be reduced to the original products. Phthalocyanine ring is completely destroyed and oxidized to phthalimide when it is introduced to aqueous solutions of strong oxidants. Also the central metal atom of the phthalocyanine may cause oxidation. Manganese phthalocyanine, for instance, can be produced in these different oxidation states, depending on the solvent [29].

A notorious disadvantage of phthalocyanines is the extreme insolubility of their unsubstituted derivatives. This can be primarily traced to the extreme hydrophobicity of the aromatic core and planarity of the phthalocyanine, which leads to a tendency to stack upon themselves and results in highly stable crystal structures with high molecular lattice energies. Phthalocyanines have poor solubility in most organic solvents and insoluble in water. Phthalocyanines poor solubility is due to strong interactions which cause aggregation of the phthalocyanines [30-31]. The solubility of unsubstituted phthalocyanines in the more universal organic solvents like sulpholane, dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) is negligible. Even highly aromatic solvents such as quinoline and 1-chloronaphthalene rarely give solutions of concentrations exceeding 10^{-5} M. Axial ligation takes place if there is a metal atom in the central cavity of phthalocyanine. Axial substitution in phthalocyanine complexes generally increases solubility, reduces molecular aggregation and evokes relevant changes to the electronic structure of the molecule by altering the π electron distribution attributed to the dipole moment of the central metal-axial ligand bond [32].

Phthalocyanines are resistant to attack by weak mineral acids and alkalis and are also stable with respect to water vapour and many common gases in the absence of light. Films made from phthalocyanines can last a year in air without displaying deterioration as phthalocyanines exhibit a very high involatility. Most compounds do not melt but sublime above 200 °C. Copper compound can be sublimed without decomposition at 500–580 °C under an inert gas and normal pressure and at 900 °C

under vacuum. It decomposes vigorously, however, at 405-420 °C in air and in nitrogen between 460–630 °C [33].

Phthalocyanines can be organized in columns at a supramolecular level, giving rise to conducting properties. The cofacial stacking of metallophthalocyanines enables electron delocalization along the main axis of the column through π - π orbital overlapping. Metallophthalocyanines generally crystallize in an inclined stacked insulating arrangements called α or β - modifications that do not allow an appropriate overlap of π - π orbitals and hence no formation of a conduction band [34]. Phthalocyanines are not semiconductors in normal conditions. However, phthalocyanine radicals like LiPc can form charge carriers by themselves and show conductivity [35]. Phthalocyanines can also show conductivity when they form discotic liquid crystals or Langmuir-Blodgett films.

2.1.2.2 Electrochemical properties

Electrochemistry of phthalocyanines were not investigated for a long time because of their poor solubility and hence relative purity. Phthalocyanines have the capacity to gain or lose electrons. The Pc skeleton exists as a dianion, Pc^{2-} , successive removal of up to two electrons from the HOMO results in the formation of Pc^{1-} and Pc^0 cation radicals, respectively [36].

The phthalocyanine ring redox activity is directly related to the frontier orbitals in the molecule. When oxidation takes place there will be removal of electron from HOMO and for reduction there will be addition of an electron to LUMO.

The electrochemical activity of metal free phthalocyanines is related to processes occurring on the ring. In addition to ring process, metallophthalocyanines containing electro active central metals exhibit electro activity associated with the central metals. Examples of electro active metals include cobalt, iron and manganese while electrochemically inactive metals include zinc, nickel and magnesium. Furthermore, electro active ligands substituted on the phthalocyanine also demonstrate their own characteristic redox peaks or couples [37].

Multiple and often reversible redox processes can be used for characterization of metallophthalocyanines which have active central metals, both in solution or when adsorbed on electrode surfaces. The Pc^{2-} ring can be oxidized ($\text{Pc}^{2-} \rightarrow \text{Pc}^{1-} \rightarrow \text{Pc}^0$) or can be successively reduced ($\text{Pc}^{2-} \rightarrow \text{Pc}^{3-} \rightarrow \text{Pc}^{4-} \rightarrow \text{Pc}^{5-} \rightarrow \text{Pc}^{6-}$). The electro active

metallophthalocyanines like Cr, Mn, Co and Fe whose orbitals lie between HOMO and LUMO of the phthalocyanine ligand have their metal oxidations or reductions occurring in between those corresponding to ligand reduction or oxidation, in the presence of coordinating species that would stabilize the metal center [38-41]. For Metallophthalocyanines which do not have active central metals like Ni, Cu, Zn, Pd, the redox processes take place on the phthalocyanine ring.

Changes in the nature of the peripheral substituents affects the electron density and consequently the electrochemistry of phthalocyanines. Electron-donating substituents like amine, ether, thioether, methoxy shift redox processes towards negative potentials while the presence of an electron withdrawing group like fluoro, sulphonate, nitro, ester, carboxylic acid shift redox processes towards positive potentials [42-44].

2.1.3 Spectral analysis

The most important spectral analysis of phthalocyanines is Ultraviolet-Visible (UV-Vis) spectroscopy. As phthalocyanines are rich in π -electrons, they show characteristic absorption peaks in UV-Vis spectroscopy related to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. These characteristic peaks are Q-band (around 700-650 nm, related to $\pi \rightarrow \pi^*$ transitions), B-band (around 420-320 nm, related to $n \rightarrow \pi^*$ transitions), N-band (around 330-285 nm, related to $\pi \rightarrow \pi^*$ transitions) and L-band (around 270-230 nm, related to $\pi \rightarrow \pi^*$ transitions).

All the electronic transitions generating the four typical Pc bands involve orbitals which are mainly associated with the inner pyrrole rings of the Pc macrocycle. For example, the Q band is originated by electronic charge transfer from the pyrrole skeleton to the condensed benzene rings. The variations of electron density due to the Qband transition do not induce local charge excesses but spread all over the molecular area. On the other hand, the B band produces a redistribution of the electronic density which provokes an increase of electron density in correspondence with the bridging atoms of the azamethine group. The nature of the N band is strongly related to the variations of electron density on the pyrrole nitrogen atoms. These atoms are responsible for the coordination of the central atom in the MPc complex formation. It is therefore expected that the nature of metals will play a

decisive role in the determination of the N band features when the metallophthalocyanines are considered [45].

The exact location and shape of these bands may change related to few parameters. The first important parameter is substituent position. Q-band shifts to longer wavelength if substituents are in non-peripheral position [46]. Aromatic solvents also change the position of the Q-band, they shift Q-band to longer wavelength as they stabilize LUMO [47]. Finally the most important parameter is the metal effect (Figure 2.8). Q-band is the result of transition from HOMO to LUMO. Metallophthalocyanines have D_{4h} symmetry as the four nitrogen atoms at the center of the molecule are equal; which will result in a single peak in Q-band. However, in metal-free phthalocyanines, two hydrogen atoms at the center changes the symmetry of the molecule to D_{2h} . This results in a degradation in LUMO and two allowed transitions at different energy levels happen (Figure 2.8). Because of these two transitions, metal-free phthalocyanines show a splitted Q-band [48].

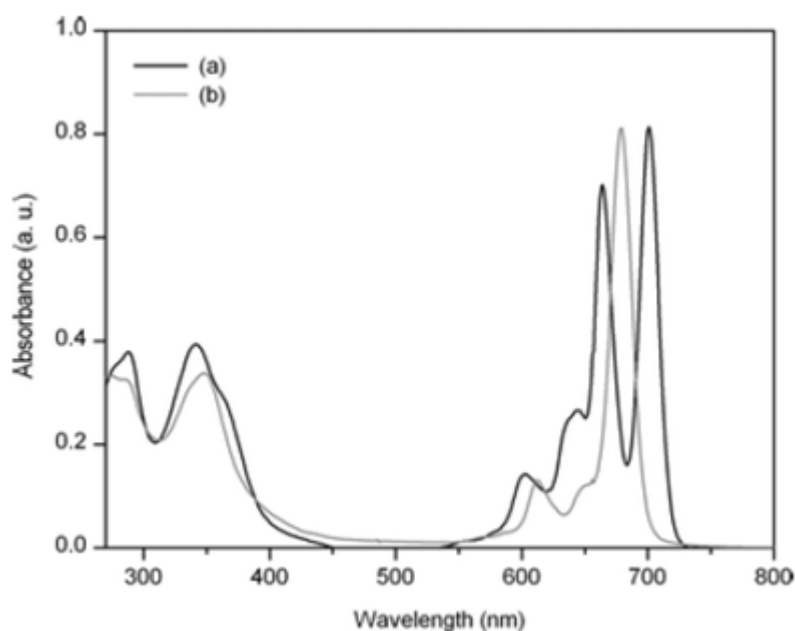


Figure 2.8 : UV-Vis spectra of a) metal-free phthalocyanine , b) metallophthalocyanine.

2.1.4 Applications

Phthalocyanines are used in a number of applications because of their increased stability, architectural flexibility, diverse coordination properties and improved spectroscopic characteristics (Figure 2.9). In addition to their ubiquitous use as highly stable blue and green colorants, phthalocyanines find commercial applications

as a photoconductor in Xerography, and in optical data storage as the laser absorption layer within recordable compact discs (R-CDs). Also there is an increasing interest for applications in non-linear optics (including optical limitation), molecular electronics, photodynamic cancer therapy, solar energy conversion (most recently as photosensitisers for cheap, amorphous semiconductors), various catalytic processes, electrochromic and electroluminescent displays, chromatography, and as the active component of gas sensors [49].

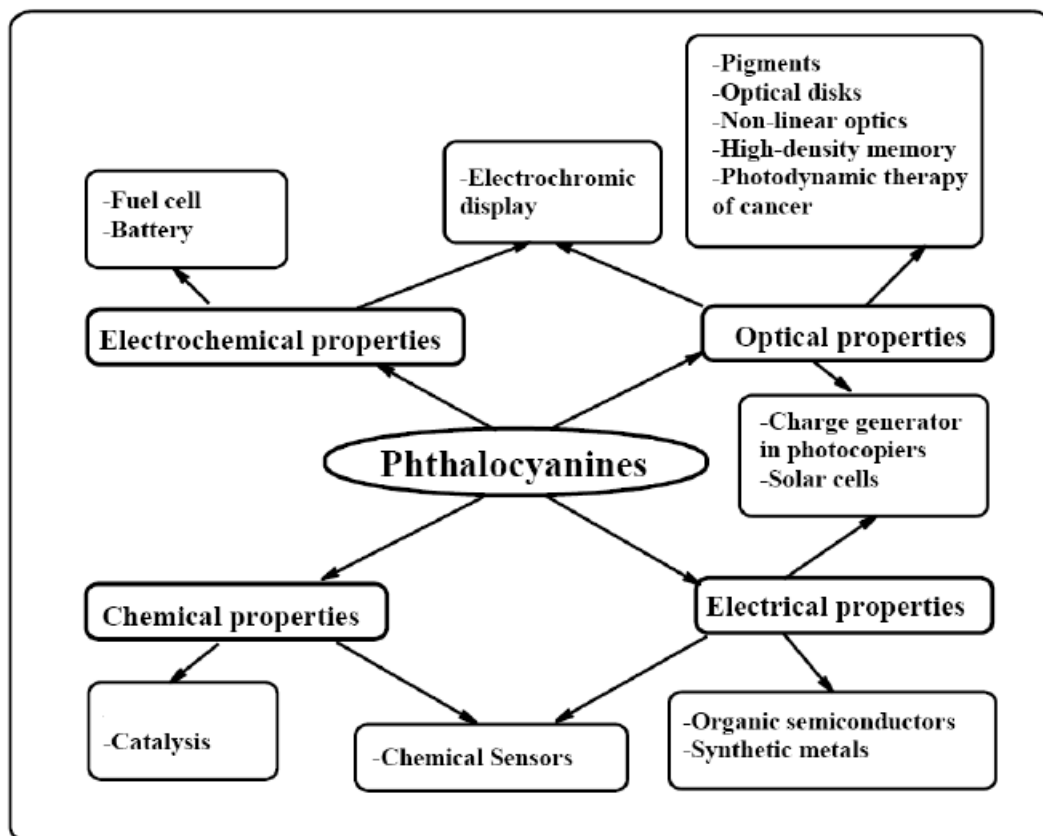


Figure 2.9 : Usage of phthalocyanines.

2.1.4.1 Dyes and pigments

Phthalocyanines are highly delocalized 18 π electron aromatic molecules showing strong absorption in the visible region, for this reason, they are extensively used as dyestuffs for textiles and printing inks. Their characteristic blue-green color and robustness account for their traditional use as industrial dyes pigments. Phthalocyanines are second only to the ubiquitous azo colorants in terms of commercial importance.

While textile dyes based on phthalocyanines are of rather limited importance, the phthalocyanines provide by far the most important blue and green organic pigments [50].

The major blue used within the coatings industry is copper phthalocyanine blue (PB 15), with its usage far outweighing other blues such as Indathrone blue (PB 60). Metal-free phthalocyanine blue (PB 16) is normally manufactured via the sodium salt of phthalonitrile. Acid pasting is used to condition the crude and give the pigment.

Copper phthalocyanine is commercially available in two crystal forms known as the α and β . The α form is described by the designations Pigment Blue 15, 15:1, and 15:2 and is a bright red-shade blue pigment. The β form is described as Pigment Blue 15:3 and 15:4 and is a bright green or peacock shade. The α form is meta-stable and requires special treatment to stabilize the crystal against its tendency to revert to the more stable, green-shade β crystal. If either of the unstable α crystal forms (PB 15 or 15:1) is used with strong solvents, conversion to the β form will occur upon storage of the system. Conversion from the α to the β form is usually accompanied by an increase in crystal size with subsequent loss of strength and shift to a greener hue.

Pigment Blue 15 is an α crystal with the reddest shade of the types commonly available. It is the least stable of the family and as such is often referred to as crystallizing red-shade (CRS) blue. This crystal form cannot be used in any solvent containing systems.

Pigment Blue 15:1 is also an α crystal, but chemical modifications have been made to stabilize the structure against crystallization. Most commonly the molecule is chlorinated to the extent of introducing one chlorine molecule to give monochlor blue. Another technique involves the use of a substituted phthalocyanine, added to the pigment at levels approaching 10 to 15%, that confers crystal stability to the system. The monochlorinated grade is, as a consequence of the introduced chlorine atom, greener than the additive-stabilized crystal.

Pigment Blue 15:2, described as “noncrystallizing nonflocculating” red-shade blue, is widely used within the coatings industry. The product is an α crystal that is stabilized against both crystallization and flocculation using additive technology.

Pigment Blue 15:3 represents the green-shade, β crystal phthalocyanine blue and, as it exists in the stable crystal form, it is less susceptible to crystallization. Most commercial grades of Pigment Blue 15:3, however, contain from 4 to 8% of the α crystal, which will be adversely affected by strong solvent systems. A 100% β blue is too dull, opaque, and weak to be commercially attractive; hence, a proportion of the α crystal is left in the system, contributing considerably to the attractiveness of the system.

Pigment Blue 15:4 represents a β blue that has been modified with phthalocyanine-based additives to give a green-shade blue that is resistant to flocculation and can be used in strong solvent systems.

Copper phthalocyanine approximates the ideal pigment. It offers strength, brightness, economy, and all-around excellent fastness properties. Perhaps the pigment's only disadvantages are its tendencies to change to a coarse, crystalline, nonpigmentary form in strong solvents and to flocculate or separate from white pigments when used in paints and lacquers.

The major green pigment used as a self shade in the coatings industry is based on halogenated copper phthalocyanine and, as such, is termed phthalocyanine green. The Colour Index names are Pigment Green 7 and Pigment Green 36.

Pigment Green 7, the blue-shade green, is based on chlorinated copper phthalocyanine with a chlorine content that varies from between 13 to 15 atoms per molecule.

Pigment Green 36, the yellower shade, is based on a structure that involves the progressive replacement of chlorine on the phthalocyanine structure with bromine. The composition of Pigment Green 36 varies with respect to the total halogen content, chlorine plus bromine, and in the ratio of bromine to chlorine.

These pigments are ideal, since their tinctorial and fastness properties allow their use in the most severe application situations. They possess outstanding fastness to solvents, heat, light, and outdoor exposure. They can be used in masstone shades and tints down to the very palest of depths.

Phthalocyanine greens are manufactured by a three-step process: crude phthalocyanine blue is first manufactured, then halogenated to give a crude copper phthalocyanine green, and finally conditioned to give the pigmentary product [51].

Phthalocyanines are widely used in paint and plastic industries. The noncolorant applications include catalysts, lubricating greases, analytical reagents, clinical diagnostic agents and electrical devices.

The insolubility of phthalocyanines necessitates preparation of soluble derivatives for application as dyes for textile fibres. Phthalocyanine pigments in the form of aqueous dispersions are used in pad-dyeing with resin emulsions. Because of their excellent stability to acids, alkalis and solvents phthalocyanines are particularly useful in spin dyeing. They have also been used in coloring polyvinylchloride fibres, viscose, cuprommonium cellulose, nylon, etc. Phthalocyanines have found wide use as paint pigments. Metal surfaces can be coated by forming the metal phthalocyanine directly on them [52]. Large metal surfaces can be coated with metal phthalocyanine by dipping in a solution of phthalonitrile in acetone, drying, and subjecting the metal to temperatures of around 350°C in a sealed oven. The coating is very adherent and the shade of colour depends on the metal used.

Phthalocyanines have been used to color rubber, polystyrene, polyurethane foams, cellulose acetate sheeting, polyesters, polyamides, vinylchloride polymers and other plastic and polymeric materials. Copper phthalocyanine-sodium sulfonate has been used in photographic processes to produce colored prints. Copper phthalocyanine is also used as a certified food color .

2.1.4.2 Analytical reagent

Copper phthalocyanine in concentrated sulphuric acid has been used as a reagent for the detection of oxidizing agents such as NO_2^- , NO_3^- , ClO_3^- , BrO_3^- , IO_3^- , $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- . Copper tetrasulphophthalocyanine is used as a redox indicator in the cerimetric determination of iron (II) and ferrocyanide. It was found that copper 4,4',4'',4''' tetrasulphophthalocyanine (CuTSP) is a suitable indicator for the titration of Fe(II) in 0.5 - 2.5 M HCl or H_2SO_4 or $\text{Fe}(\text{CN})_6^{4-}$ in 0.5 N H_2SO_4 with 0.01 N to 0.001 N Ce^{4+} . CuTSP is stable towards HCl, H_2SO_4 and H_3PO_4 . A 0.1 % solution of CuTSP is used as the indicator solution.

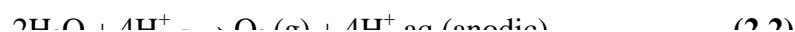
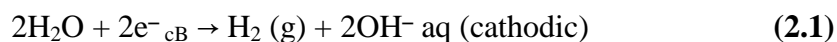
2.1.4.3 Catalyst

Activation of molecular hydrogen is the first mention of phthalocyanines as a catalyst and found that crystals of phthalocyanine and copper phthalocyanine catalyze atomic interchange between molecular hydrogen and water vapour, and oxygen [53-54]. Phthalocyanines catalyze the oxidation of many organic compounds. They can catalyze the oxidation of α -pinene to verbenone, and the autooxidation of saturated ketones such as 2-octanone, 4-heptanone and cyclohexanone at 120-130°C to α -diketones and aldehyde. Cobalt and other phthalocyanines derivatives have been used as rubber emulsification catalysts. When cobalt tetrasulphophthalocyanine is attached to poly (vinylamine) it can catalyses the autooxidation of thiols [55].

2.1.4.4 Photovoltaic and photogalvanic devices

Phthalocyanines show photoconductivity. Their properties have been studied for use in electrophotographic systems, diodes, laser printers, photovoltaic cells, photoelectrochemical devices and vidicon tubes [56-58].

Cobalt (II) tetrasulfophthalocyanine (CoTSP) can be covalently bound to the surface of titanium dioxide particles. Upon irradiation with light having energy exceeding the band gap energy of TiO_2 , Co(II) TSP is reduced to Co(I) TSP. This photochemical reduction is reversible in presence of oxygen. The photochemical stability and the high quantum yields for oxygen reduction makes this newly developed material applicable as a potent and stable oxidation catalyst. The interest shown in these systems is due to the simultaneous formation of dihydrogen and dioxygen from water. An overall transfer of conduction band electrons e^-_{CB} and valence band holes h^+_{VB} is required to achieve this direct storage of solar energy in the form of chemical energy. The reactions taking place can be seen at the (2.1) and (2.2).



Cobalt tetrasulfophthalocyanine covalently bound on the surface of titanium dioxide. Particles act as efficient electron relays to compete with the e^-/h^+ recombination and thus achieve reasonable but still rather small, quantum yields.

Efficient organic solar cells and field effect transistors also have been fabricated using various phthalocyanines. Photovoltaic solar cells made from *p*- and *n*-type silicon have commercial efficiencies of 15 to 20% and gain great importance for the conversion of solar energy into electrical energy. In 2011 module costs were US\$ 1.25 W⁻¹. It is expected that also organic solar/photovoltaic cells (OPV) will soon be available. To set an example, Figure 2.10 can be examined. It shows schematically the configuration of a single heterojunction “pin” cell. In this cell type “i” is the intrinsic absorber layer for visible light consisting of ZnPc or CuPc as *p*-type and C₆₀ (fullerene) as *n*-type conductor. Also 1,8,15,22-tetrafluorophthalocyanine can act as absorber and *p*-conductor, and hexadecafluorophthalocyanine is employed as absorber and *n*-conductor [59].

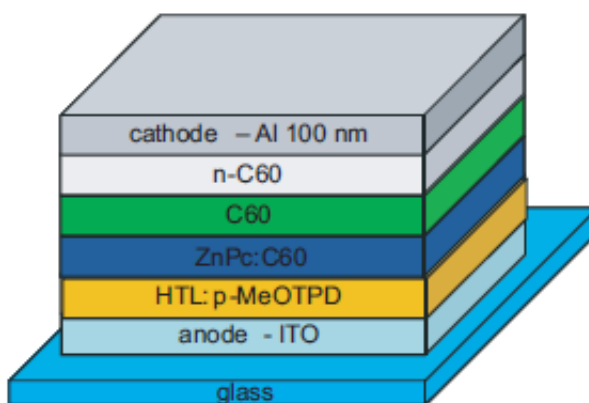


Figure 2.10 : Configuration of a single heterojunction pin cell.

2.1.4.5 Photodynamic therapy

Photodynamic therapy is a medical treatment directed against target tissue in which a molecular photosensitizer is selectively adsorbed and then irradiated to catalytically generate singlet oxygen. The localized concentration of singlet oxygen attacks and kills the tissue. The phthalocyanine chromophore has been found to be among the most effective photosensitizers in this application. The critical features are a selective uptake of the dye into the target tissue or tumor, a strong absorption in the far red or near IR, a long triplet excited state lifetime, a good photooxidative stability, and an excretion from the body after therapy.

A selective uptake into the target tissue is a challenge for the design of peripheral groups, which involves considerations of water solubility, lipophilicity, and penetration of cell membranes. A strong absorption in the far red and near IR

accommodates a good depth of penetration by the light into the tissue. The phthalocyanine and naphthalocyanine chromophores in the monomeric state meet this feature nicely. The triplet excited state lifetime is an aspect where phthalocyanine aggregation is also a very important concern. Photochemical stability correlates with the triplet excited state lifetime as well as with the solvent and electron withdrawing and donating character of peripheral substituents.

Factors that extend the excited state triplet lifetime are the selection of the metal ion and, in particular, a resistance to aggregation. Phthalocyanines complexed with paramagnetic ions have shortened excited state lifetimes and diminished photoactivity compared with those complexed with diamagnetic metal ions. Complexed ions, such as Al, Zn, and Si, are reported to have longer excited state triplet lifetimes. Aggregation of phthalocyanines is reported to markedly shorten the excited state lifetimes and reduce the efficiency of singlet oxygen production [2].

2.1.4.6 Electrochromic displays

Electrochromic effect is the production, by faradaic reaction, of a color change in materials localized at an electrode surface. A thin film of metal diphtalocyanine deposited on optically transparent electrode shows change in absorption spectrum of polarisation in contact with an aqueous electrolyte [60].

Electrochromism of phthalocyanines are very interesting for developing new type displays and have been investigated for many years. Liquid crystal displays (LCD) can be examined as an example. In the LCDs metallophthalocyanines display two of the three colour components that are responsible for their intense colour and absorption of visible light in certain wavelength ranges. To display colours, a colour layer (color filter) consists of a two-dimensional periodic arrays of colour absorptive surfaces in the three primary colors red, green and blue of the additive color mixture. All colours can be represented including white and black. A pixel now contains subpixel for each of the three primary colours, which are also driven separately by a transistor. For large-scale LCD monitors in high definition resolution for 25 million addressable points also 25 million transistors must be available. To the colorants of the three primary colors particular requirements are addressed: color fastness, color uniformity, color intensity, color stability. To avoid light scattering, the colorants must be present as nanoparticles of about 20 to 30 nm in uniform and globular form

that do not grow together to form agglomerates. To meet these demands, the development of suitable nano-pigments was required. It was found that phthalocyanines cover two of the three primary colours. For the primary color blue the ϵ modification of copper phthalocyanine is employed. For the primary colour green the halogenated $\text{CuPcCl}_{-4}\text{Br}_{-12}$ is appropriate. For the colour red, e.g. diketopyrrolopyrrole (DPP), are used [59].

2.1.4.7 Nonlinear optics

The structural prerequisite for nonlinear optics material is the presence of a conjugated, delocalized π electron orbital network. The conjugated structure affords high polarizability properties and thus fast charge redistribution on interaction with intense magnetic radiation, such as laser radiation. Organic and organometallic materials have emerged as promising candidates for limiting laser radiation intensity. Among nonlinear optics materials, metallophthalocyanines are of great interest because they have several advantages over the inorganic material currently in use for optical limiting. The laser light advantages includes fast response times (subpicosecond). The faster the response is, the better the optical limiter small dielectric constants ease of fabrication or processing and low cost of production. The discovery of phthalocyanines as active nonlinear optic materials in optical limiting applications has been widely recognized. Up until recently, the feasibility of phthalocyanines as nonlinear optic materials has been devoted to the measurements of nonlinear properties, together with a basic understanding of the origin of nonlinearities [61].

2.1.4.8 Batteries

Phthalocyanines and phthalocyanine derivatives have been used as cathode materials in batteries especially in fuel cells and air cathode batteries. In batteries the porous electroconductive material is loaded with metal phthalocyanine and a perfluoro compound. This composite material is used as the catalyst layer

2.1.4.9 Gas sensors

Devices based on metal phthalocyanine show useful response towards NO_2 . A thin film metallophthalocyanine sensor has successfully been used to monitor NO_x produced by short firing in coal mines [62]. Phthalocyanine based devices offer

much promise as resistance modulating sensors for toxic gases, sensors against toxic gases can be developed using the conductivity changes of phthalocyanines. They are thus complementary to metal oxide devices which are most useful in the detection of flammable gases

2.2 Controlled/Living Free Polymerization

Free radical polymerization (FRP) is one of the most common and practical techniques for producing commodity polymers. FRP possesses great tolerance to material and operational impurities, along with high compatibility with a wide range of vinyl monomers making it a very robust and cost effective process that accounts for a significant portion of polymer production. Mechanistically, FRP with a thermal initiator can be broken down into three basic steps – initiator decomposition and initiation, propagation, and termination by combination or disproportionation (Figure 2.11) [63].

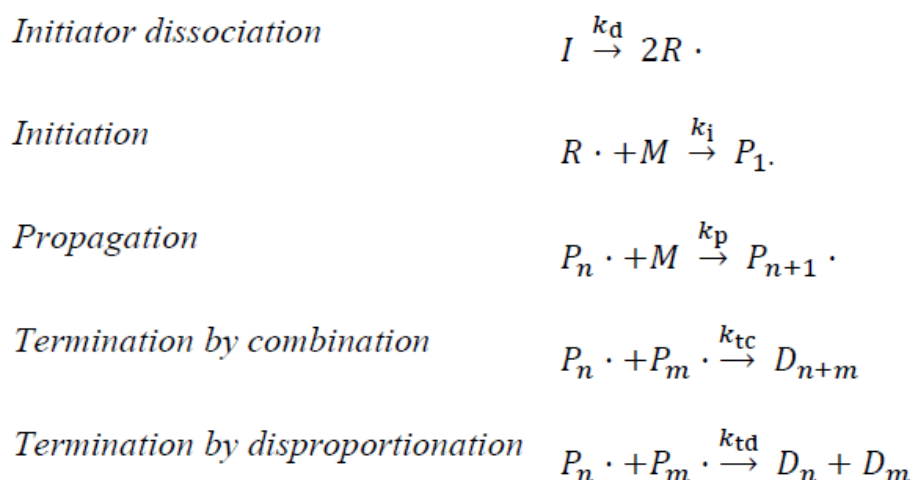


Figure 2.11 : General mechanism of free radical polymerization.

The disadvantages of conventional radical polymerization is the poor control of macromolecular structures including degrees of polymerization, polydispersity index, and also the practical impossibility to synthesize block copolymers, and other advanced structures. Various processes have been developed to control of free radical polymerization during the last decade and thus polymers with low polydispersities, compositions, architectures and functionalities were synthesized (Figure 2.12) [64].

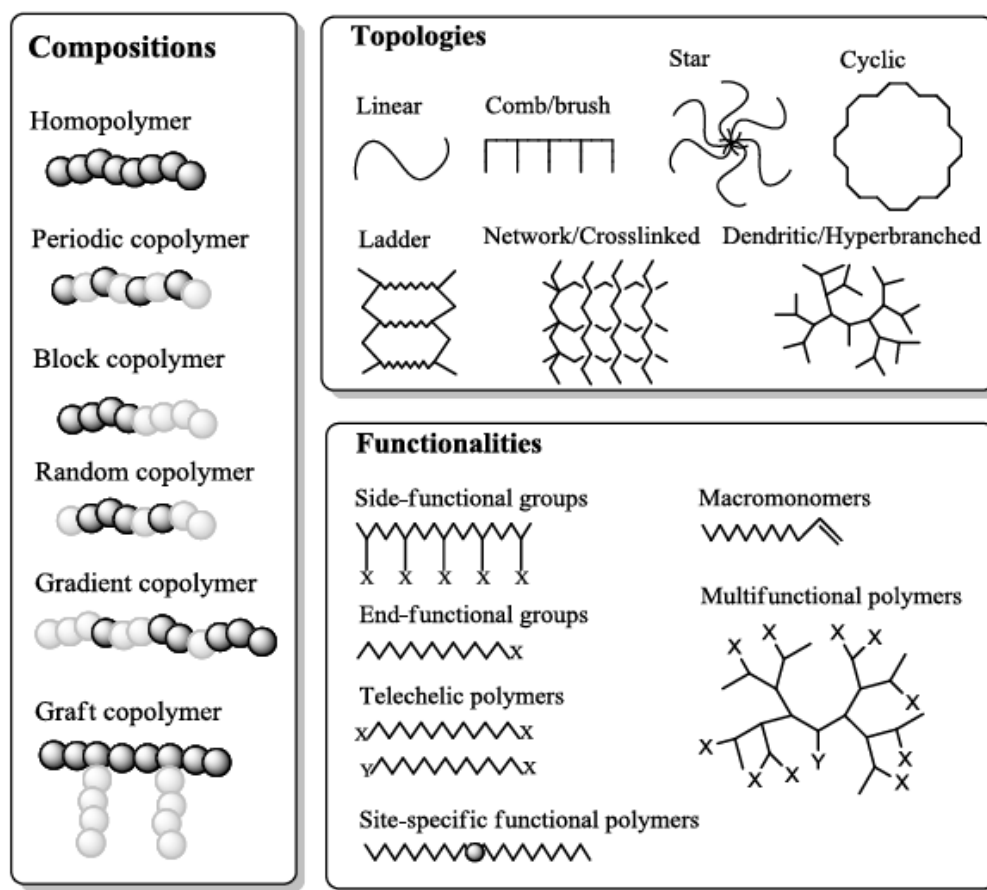


Figure 2.12 : Polymers obtained by controlled/living free radical polymerization.

The importance of the synthesis of polymers with such control has been augmented due to the rising demands for the specialty polymers. Obviously, living polymerization is an essential technique for synthesizing polymers with controlled structures. Moreover, living polymerization techniques allow preparation of macromonomers, macroinitiators, functional polymers, block and graft copolymers, and star polymers. In this way, the need for specialty polymers having a desired combination of properties can be fulfilled. Control of complex architectures by living polymerization has largely been achieved using living anionic and cationic as well as group transfer polymerization techniques. From the practical point of view, however, these techniques are less attractive than free-radical polymerization, because the latter can be performed much more easily. Moreover, ionic techniques are limited to a very few vinyl monomers, whereas practically all vinyl monomers can be homo and copolymerized by a free-radical mechanism long-lasting goal has been the development of controlled/living radical polymerization methods. Radical polymerization suffers from some defects (i.e., the control of the reactivity of the polymerizing monomers and, in turn, the control of the structure of the resultant

polymer). In ionic living systems, however, the chain ends do not react with one another due to the electrostatic repulsion. On the other hand, the growing radicals very easily react with each other at diffusion controlled rates via combination and/or disproportionation. Therefore, controlled/living radical polymerization has long been considered impossible. Following the discovery of living anionic and cationic polymerization, many attempts have been made to find controlled/living radical polymerization systems to achieve a high level of control over molar mass, polydispersity, end groups, and architecture. Despite considerable progress, a truly controlled/living radical polymerization has not been developed until a little more than two decades ago [65].

In the 1990s, several methods were developed that enable controlled radical polymerization. These methods include: stable free-radical polymerization (SFRP), best represented by polymerization mediated with TEMPO 2,2,6,6-tetramethylpiperidine-*N*-oxyl [66], metal-catalyzed atom transfer radical polymerization (ATRP) [67], reversible addition–fragmentation chain transfer (RAFT) [68] and diphenylethene method (DPE) [69]. Using these polymerization methods, the molecular weight of the polymers linearly increases with conversion and the polydispersities are small.

2.3 Atom Transfer Radical Polymerization (ATRP)

The pioneering work on ATRP was conducted independently by two groups in 1995. Kato *et al.* demonstrated the polymerization of MMA using a ruthenium based complex [10], while at the same time Wang and Matyjaszewski showed the polymerization of styrene using a copper based mediator [9]. Since then, an immense amount of literature has been published on ATRP in bulk and solution, mostly using copper bound to a nitrogen based ligand as the mediating species due to its low cost and versatility compared to other transition metals.

The term Atom Transfer Radical Polymerization was coined by Matyjaszewski, whereas Kato's groups termed this type of reaction Metal Catalyzed Living Radical Polymerization. The name atom transfer radical polymerization originates from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP has its roots in atom transfer radical addition (ATRA), which targets the formation of 1:1 adducts of alkyl halides and alkenes,

also catalyzed by transition metal complexes. ATRA is a modification of Kharasch addition reaction, which usually occurs in the presence of light or conventional radical initiators. Because of the involvement of transition metals in the activation and deactivation steps, chemo-, regio-, and stereoselectivities in ATRA and Kharasch addition may be different [67].

In ATRA (Figure 2.13), a copper (I) complex undergoes a one-electron oxidation with concomitant abstraction of a halogen atom from a starting compound. This reaction generates an organic radical and a copper (II) complex, and substituents on the organic halide can facilitate the reaction by stabilizing the resulting radical. The organic radical can then add to an unsaturated group in an inter- or intramolecular fashion and then reabstract a halogen atom from the copper (II) complex to reform the original copper (I) complex and to form the product. Compounds derived from the self-reaction of radicals (i.e., termination) comprise very little of the product, because the copper (II) complex act as a persistent radical and controls the concentration of the intermediate radicals. Substrates for this reaction are typically chosen such that if addition occurs, then the newly formed radical is much less stabilized than the initial radical and will essentially react irreversibly with the copper (II) complex to form an inactive alkyl halide product ($k_{act} \gg k'_{act}$). Thus, in ATRA, usually only one addition step occurs; however, if starting and product alkyl halides possess similar reactivities toward atom transfer, then it should be possible to repeat the catalytic cycle and add multiple unsaturated groups as in a polymerization reaction [70].

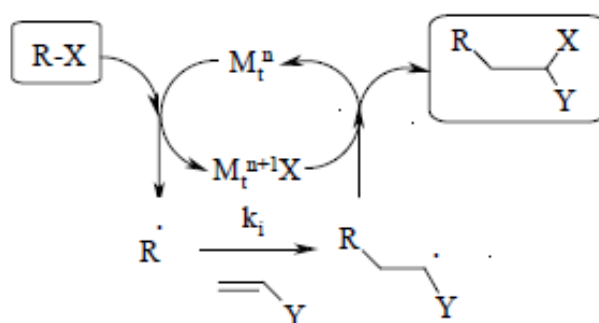


Figure 2.13 : Mechanism of ATRA.

ATRP has roots in the transition metal catalyzed telomerization reactions. These reactions, however, do not proceed with efficient exchange, which results in a nonlinear evolution of the molecular weights with conversions and polymers with

high polydispersities. ATRP also has connections to the transition metal initiated redox processes as well as inhibition with transition metal compounds. These two techniques allow for either activation or deactivation process, however, without efficient reversibility. ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the polymerization conditions such that the molecular weights increased linearly with conversion and polydispersities were typical of a living process. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [67]. However, the major problem related to ATRP is the removal of catalyst from the final polymer which can make the product colored and toxic.

2.3.1 Mechanism of ATRP

The mechanism involves the transfer of a halogen atom from the polymer to a metal catalyst yielding an active chain end (a radical), hence the term Atom Transfer Radical Polymerization (ATRP). Reaction takes place through a reversible redox reaction involving the transition metal catalyst (Mt), which is oxidized as the polymer is converted from the dormant state (PX) to the active species (P[•]) through the transfer of the halogen (X). The metal catalyst is bound in a complex with a multidentate ligand (L), which assists in binding the halogen. The deactivation reaction is kinetically favored in the equilibrium ($k_d \gg k_a$) thus rendering only a small concentration of active radical species present at a given time. Ideally, this eliminates the possibility of two activated polymer chain ends encountering to give termination, while in practice termination does occur.

The mechanism can be seen on the Figure 2.14. The halogen-bound polymer chain (P-X) is converted to an activated form (P[•]), which can propagate the monomer (M). Activation is facilitated by the transfer of the halogen (X) to the metal-ligand complex (Mt/L). k_a , k_d , k_p and k_t are the rate constants of activation, deactivation, propagation and termination, respectively.

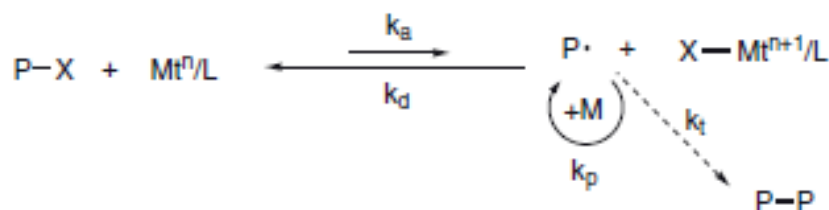


Figure 2.14 : Mechanism of ATRP.

2.3.2 ATRP equilibrium

The dynamics of the ATRP equilibrium are very important to the polymerization rate and control imposed over the final macromolecular structure. As briefly discussed, the deactivation of growing chains must be fast in order to suppress unwanted radical termination. In addition, fast activation is required in order to maintain a reasonable rate of polymerization as well as to ensure that all chains are initiated at the same time. This ensures that all polymer chains grow at the same rate and undergo similar numbers of activation/deactivation cycle, statistically leading to a narrow final molecular weight distribution. As copper complexes are most often used in ATRP, the rate of polymerization for an ATRP system assuming negligible bimolecular termination can be approximated as [67] :

$$R_p = k_p[M][P^\bullet] = k_p[M] \frac{k_{\text{act}}}{k_{\text{deact}}} [R-X]_0 \frac{[Cu^I]}{[Cu^{II}X]} \quad 2.3$$

where k_p is the monomer propagation rate coefficient; $[M]$, $[P^\bullet]$, $[R-X]_0$ are monomer, propagating chain, and alkyl halide initiator concentrations respectively; k_{act} and k_{deact} are the rate constants of activation and deactivation which combine to form the ATRP equilibrium constant; and $[CuI]$ and $[CuIIX]$ are the concentrations of the activator and deactivator species. Of the variables in 2.3, the rate constants of activation (k_{act}) and deactivation (k_{deact}) exhibit the largest variance with polymerization conditions and are the key to successfully controlling the final molecular structure using ATRP.

The ATRP equilibrium can be theoretically broken down into 4 separate reversible reactions (Figure 2.15). It is important to note that while analysis of the ATRP equilibrium as dissected into these four elementary steps can generate useful trends, the physical relevance to how the reaction proceeds is less meaningful. The four

reversible reactions are: oxidation of the metal complex (electron transfer, K_{ET}), alkyl halide bond homolysis (K_{BH}), reduction of a halogen to a halide ion (electron affinity, K_{EA}), and association of the halide ion to metal complex (halidophilicity, K_X) [71]. The product of these four elementary rate constants gives rise to the overall ATRP equilibrium (K_{ATRP}).

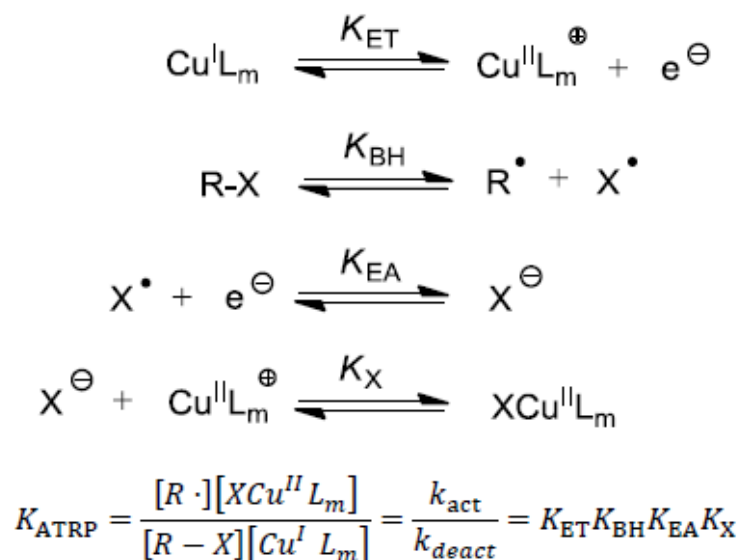


Figure 2.15 : Breakdown of ATRP equilibrium.

2.3.3 Components of ATRP

2.3.3.1 Monomers

ATRP can be carried out with monomers that have a functional group, which can stabilize the propagating radical (Figure 2.16). Various vinyl monomers have successfully been polymerized with ATRP. Most investigated are polymerization of styrenes, acrylates and methacrylates, but other monomers such as acrylonitrile, (meth)acrylamide and other compounds containing substituents that can stabilize a propagating radical have proven successful as well. These monomers have been polymerized under different ATRP conditions, and which conditions that should be used are specific for each monomer. Dienes have been difficult to polymerize due to the lack of proper alkyl substituent to stabilize the propagating radical. The polymerization of other monomers such as vinyl acetate, vinyl chloride and ethylene in a controlled manner still remains a challenge because of the difficulty in activation of their less reactive carbon-halogen bond.

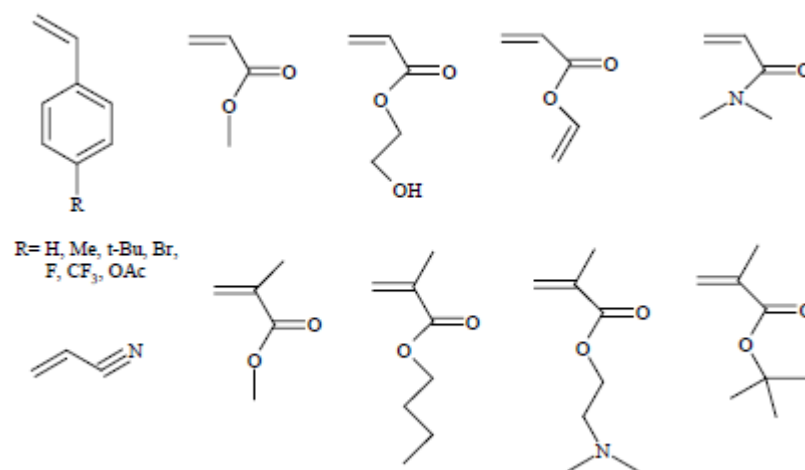


Figure 2.16 : Examples of monomers that can be used in ATRP.

2.3.3.2 Initiators

The initiator generates the growing chains, thus, the initiator concentration determines the molecular weight of the resulting polymer. The theoretical degree of polymerization (DP) can be calculated according to equation 2.4 [67].

$$DP = \frac{[M]_0}{[I]_0} * \text{conversion} \quad 2.4$$

In ATRP the initiator is typically an alkyl halide (RX) (Figure 2.17). It is important that the initiation rate is higher than the propagating rate, in order to get all the chains growing at the same time. If initiation is incomplete at the beginning of the reaction this will lead to higher molecular weights than the targeted ones and higher polydispersities [72]. Another important factor is that the initiator shows little or no tendency to undergo side reactions. It has been shown that tertiary alkyl halides are better initiators than secondary ones, which are better than primary ones. Other variables that are important to take into account when choosing an initiator are steric, polar and redox properties [73]. One easy rule to follow is that the R-group in the alkyl halide should be similar in structure to that of the monomer. For example, (1-bromoethyl)benzene is usually used when polymerizing styrene. Compounds such as ethyl 2-bromoisobutyrate and ethyl 2-bromopropionate are used for meth(acrylates) and 2-bromopropionitrile can be used for acrylonitriles. However, other initiators work well for different monomers. The alkyl is usually bromide or chlorine. ATRP of acrylates and styrene with iodine-based initiators has been reported. Fluorine does

not work in ATRP due to the strong H-F bond, which cannot undergo homolytic cleavage.

Polyhalogenated initiators were found to act as bifunctional initiators [74]. Structural similarity between the initiator and the monomer has a considerable effect in ATRP. For instance, although methyl methacrylate is more reactive than styrene, benzyl halides are more active towards styrene polymerization than methyl methacrylate polymerization due to their similar structures [73].

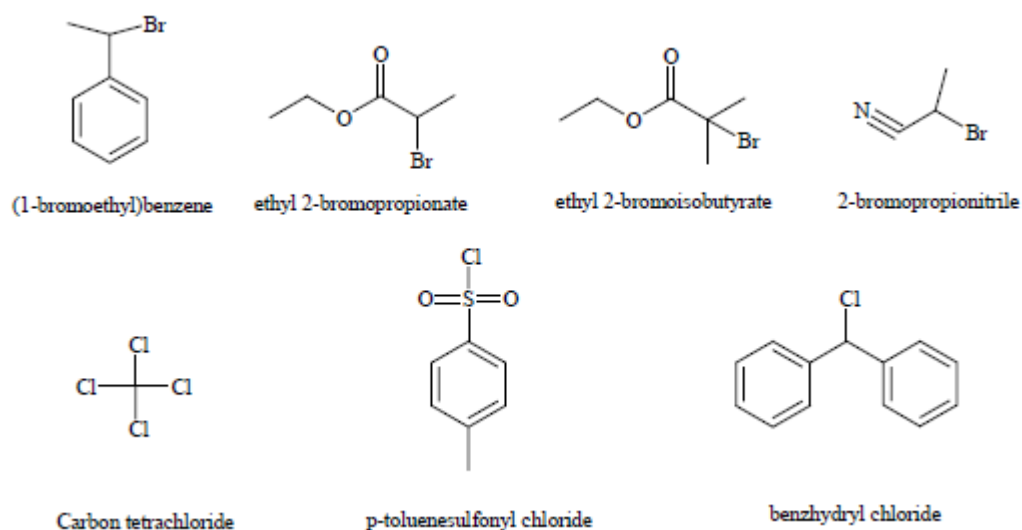


Figure 2.17 : Examples of initiators.

2.3.3.3 Catalysts

Compared to conventional free radical polymerization, the new and the key component in ATRP is the catalyst. As a catalyst the role of transition complex is to induce reversible activation of a dormant carbon-halogen bond via single electron oxidation/reduction of the metal center thereby controlling the equilibrium constant and dynamics between the active and dormant species. An ideal ATRP catalyst should not participate in side reactions and should be able to deactivate at rapid rate with diffusion controlled rate constants. There are no set rules for designing catalysts, but there are several requirements which a metal center of catalyst should met [75-76]: a) need to have two accessible oxidation states separated by one electron, b) strong affinity for ligand complexation, c) reasonable affinity towards halogens, and d) co-ordination sphere should be able to expand upon oxidation to be able to accommodate halogen. Several transition metal complexes such as ruthenium, iron, rhodium, copper, nickel, rhenium, palladium, and molybdenum have been used

for ATRP. The most extensively studied catalyst is copper halide. The Cu(I) based catalyst was first reported by Wang and Percec for the polymerization of styrene [77]. Cu(I) systems have been subsequently applied for a wide range of monomers ever since.

2.3.3.4 Ligands

The ligand plays an important role in solubilizing the transition metal salt in the organic medium and thus maintaining the homogeneity of the ATRP system, which allows homogeneous redox process during the polymerization [78-79]. An appropriate ligand for the metal is chosen in tailoring the redox properties of transition metal complexes and stabilizing them. The rate of activation of the catalyst depends on the nature of the binding site of the ligand. The nitrogen based ligands like tetramethylethylenediamine (TMEDA), 1,1,4,7,10,10-hexamethyltriethylene-tetraamine (HMTETA), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), 2,2'-bipyridine (bpy) etc. in combination with CuI salts have been efficiently used and studied for variety of monomers. The fastest activating catalysts are the ones containing alkyl amine or pyridine binding sites. In general the reactivity of the N-based ligands decreases in the following order: alkyl amine \approx pyridine > alkyl imine > aryl imine > aryl amine. Among the N-based ligands simple amines like PMDETA, HMTETA, TMEDA, etc. are advantageous to use because a) they are less expensive, b) copper complexes of simple amines are relatively less colored and c) coordination spheres of copper and simple amines have low values of redox potential leading to faster polymerization rates. Several other ligands such as phosphorus based ligands, cyclopentadienyl, indenyl and 4-isopropyl toluene have also been used in combination with transition metals to form complexes in ATRP systems.

2.3.3.5 Solvents

ATRP can be carried out in bulk, solution and in heterogenous system (e.g emulsion, suspension) at temperatures ranging from -20 °C to 130 °C. Several solvents, polar and nonpolar, have been used for different types of monomers. Except halogenated solvents, all aromatic and aliphatic solvents can be used for ATRP. Factors which affect the choice of solvent are:

- 1) Solubility of monomer, polymer and the catalyst.

- 2) Minimal chain transfer and side reaction involving solvent.
- 3) Acceleration and better control of polymerization.

Traditionally used solvents such as toluene, acetone, diphenyl ether, dimethyl formamide and various alcohols can be used for ATRP, but more surprisingly polymerization can in some cases also take place in water, which has aroused interest due to the obvious advantages of low solvent price, environmental considerations and eliminated handling precautions. Supercritical carbon dioxide as a solvent has also attracted attention because of environmental friendliness and cost reduction. In general, solvents reduce propagation rate, but polar solvents can increase the rate of reaction, in some cases providing better control over the product [80].

2.3.4 Limitations of ATRP

A number of functional groups in the monomer are not tolerated in ATRP including carboxylic acid and certain ionic groups, which react with the catalyst, thereby impeding the establishment of the equilibrium. Carboxylic acid groups can, however, be introduced by polymerization of the carboxylic acid salt instead. This was first realized by the group of Armes, who polymerized methacrylic acid in aqueous media at pH~9 using a poly(ethylene oxide) macroinitiator. Other monomers such as vinyl acetate and halogenated alkenes can not be polymerized by ATRP, due to insufficient stabilization of the formed radical.

The main concern in using ATRP for synthesis, industrial or otherwise, is removal of the catalyst. The metal catalyst-ligand complex is undesired in the product, as the transition metal induces aging in the polymer, but also for aesthetic (coloration) and toxicological reasons removal is important. Catalyst removal is both difficult and costly, but several methods are presently in use. One procedure is to immobilize the catalyst by having it attached to solid supports during reaction, but this can give loss of control, perhaps due to reduced mobility. Other purification methods include passing the raw product through an alumina column, precipitation of polymer and use of an absorbant [81].

3. EXPERIMENTAL PART

3.1 Materials

Octakis(hydroxyethylthio)-substituted phthalocyanines (Figure 3.1) were taken from Prof. Dr. Esin Hamuryudan (Department of Chemistry, Faculty of Science and Letters, Istanbul Technical Chemistry). M_w of metal-free phthalocyanine and metal phthalocyanine are 819.01 g/mol and 882.37 g/mol respectively. Both the metal free and metallophthalocyanine have strong, dark green colour.

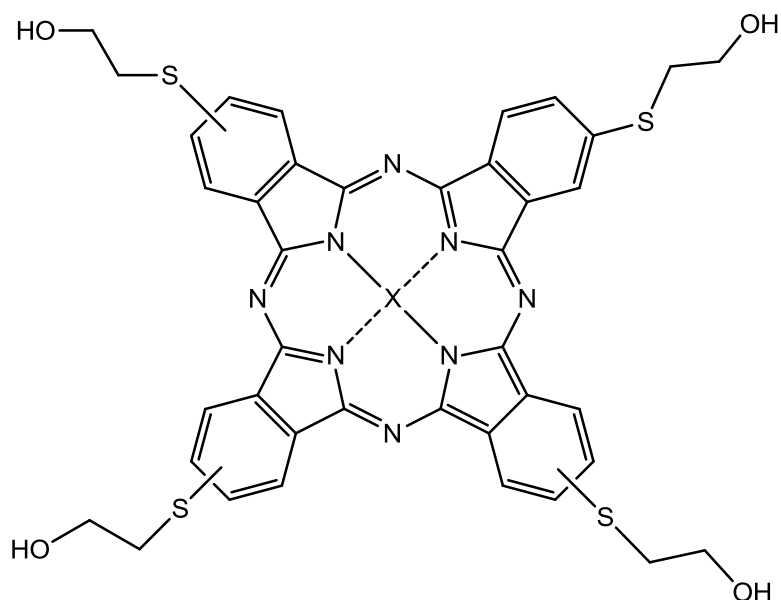


Figure 3.1 : Octakis(hydroxyethylthio)-substituted phthalocyanines (X: 2H or Zn).

2-Bromopropionyl bromide (97%, Sigma Aldrich) (Figure 3.2) is used as received. Density is 2.061 g/ml.

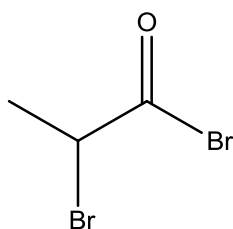


Figure 3.2 : 2-Bromopropionyl bromide.

Triethylamine (TEA, 99%, Acros) (Figure 3.3) is used as received. Density is 0.7255 g/ml.

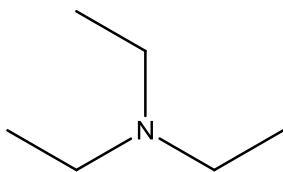


Figure 3.3 : TEA.

4-Dimethylaminopyridine (DMAP, Fluka) (Figure 3.4) is used as received. M_w is 112.17 g/mol.

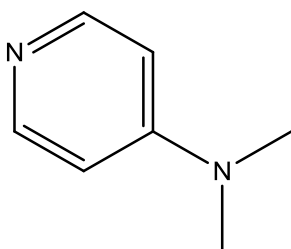


Figure 3.4 : DMAP.

Dimethylformamide (DMF, $\geq 99.5\%$, Merck) (Figure 3.5) is used as received. Density is 0.948 g/ml.

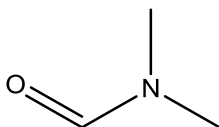


Figure 3.5 : DMF.

Sodium carbonate (Lachema) is used as received.

Methyl methacrylate (MMA, 98%, Fluka) (Figure 3.6) was passed through an alumina column before use to remove the inhibitor. MMA is distilled in vacuo over CaH₂ just before use.

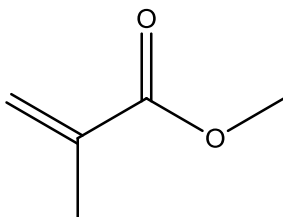


Figure 3.6 : MMA.

Anisole ($\geq 99\%$, Acros) is used as received. Density is 0.995 g/ml.

Copper(I)bromide (98%, Sigma Aldrich) is used as received.

***N,N,N',N',N''*-pentamethyldiethylentriamine (PMDETA, 97%, Aldrich)** (Figure 3.7) was distilled over NaOH prior to use.

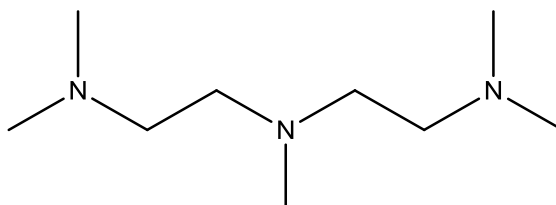


Figure 3.7 : PMDETA.

Tetrahydrofuran (THF, 99.8 %, J. T. Baker) was dried and distilled over benzophenone-Na.

Methly alcohol ($\geq 99\%$, Sigma) is used as received.

3.2 Equipments

3.2.1 Fourier transform infrared spectroscopy (FT-IR)

Analyses were performed with Thermo Scientific Nicolet IS FT-IR Spectrometer. Resolution mode is 4 cm^{-1} . Sixteen scans were averaged for each sample in the range $4000\text{-}400\text{ cm}^{-1}$.

3.2.2 Nuclear magnetic resonance (NMR)

^1H -NMR analyses were performed with Agilent VNMRS spectrometer at 500 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated chloroform (CDCl_3) were used as solvent.

3.2.3 Gel permeation chromatography (GPC)

Analyses were performed with a set up consist of Agilent pump and refractive index detector and three Agilent Zorbax PSM 1000S, 300S, 60S columns ($6.2 \times 250\text{ mm}$, 5 micron) measuring in the range of $10^4\text{-}10^6$, $3 \times 10^3\text{-}3 \times 10^5$, $5 \times 10^2\text{-}10^4$ respectively. THF

was used as the eluent at a flow rate of 0.5 ml/min at 30°C. M_w s were calculated with the aid of pMMA standards.

3.2.4 Ultraviolet-Visible (UV-Vis) spectroscopy

Analyses were performed with a Shimadzu PharmaSpec UV 1700 UV-Vis Spectrometer. Chloroform was used for blank solution.

3.2.5 Differential scanning calorimetry (DSC)

Analyses were performed with TA DSC Q10 instrument in a flowing nitrogen atmosphere from 30°C at scanning rate of 10°C/min.

3.2.6 Thermogravimetric analyser (TGA)

Analyses were performed with TA Q50 instrument under the nitrogen atmosphere at a heating rate of 20°C/min rising from room temperature to 750°C. The weights of samples are between 6-10 mg. Calibration was achieved with indium as reference material.

3.2.7 Fluorescence spectroscopy

Analyses were performed with Varian Clay Eclipse Fluorescence Spectrophotometer. Excitation wavelength is 630 nm.

3.2.8 Cyclic voltammetry and square wave voltammetry

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were recorded on a Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode cell configuration at room temperature in DMF. The working electrode was glassy carbon electrode with a surface area of 0.071 cm². A Pt wire served as the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode. Scan rate is 25 mV/s.

3.2.9 Transmittance

Transmittance of the films was measured in the spectral range of 300–1100 nm using an Agilent 8453E UV-Vis spectrophotometer.

3.3 Synthesis

3.3.1 Synthesis of H₂Pc-Br

H₂Pc-OH (0.27 g, 0.33 mmol), TEA (3.96 mmol, 0.56 mL), DMAP (0.033 mmol, 0.0042 g) were added to the three-necked flask charged with DMF (25 mL) and cooled to 0°C under a nitrogen atmosphere. 2-bromopropionyl bromide (3.3 mmol, 0.35 mL) was added dropwise to the solution, the mixture was stirred for 1 hour at 0°C and then 96 hours at room temperature. DCM solution was added to the reaction mixture and it was washed with deionized water and 5% Na₂CO₃ solution. After the solvent removal, the crude product was purified by column chromatography on silica (eluent: chloroform-methanol). Yield was 87%.

3.3.2 Synthesis of ZnPc-Br

ZnPc-OH (0.397 mmol, 0.35 g), TEA (5.56 mmol, 0.78 mL), DMAP (0.0397 mmol, 0.0049 g) were added to the three-necked flask charged with DMF (25 mL) and cooled to 0°C under a nitrogen atmosphere. 2-bromopropionyl bromide (4.76 mmol, 0.5 mL) was added dropwise to the solution, the mixture was stirred for 1 hour at 0°C and then 96 hours at room temperature. DCM solution was added to the reaction mixture and it was washed with deionized water and 5% Na₂CO₃ solution. After the solvent removal, the crude product was purified by column chromatography on silica (eluent: chloroform-methanol). Yield was 79%.

3.3.3 Synthesis of PMMA with the initiator H₂Pc-Br

To a schlenk tube equipped with a magnetic stirrer, vacuum and dry nitrogen was applied three or four times, then MMA (3.2 mL), anisole (1 mL), CuBr (0.015 g), PMDETA (44 µL) and initiator (H₂Pc-Br; 0.02 g) were added in the order mentioned under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then tube was immersed in an oil bath and held by a thermostat at 95°C, with rigorous stirring. The polymerization was performed for 12, 24 and 48 hours. Then the tube was cooled to room temperature and the contents were dissolved in large amount of THF.

The THF solution was passed through a short neutral alumina column to remove copper complex and then excess THF was removed by evaporation. The polymer

was precipitated into excess methanole, isolated by vacuum filtration and dried at room temperature *in vacuo*. The conversion was determined gravimetrically.

3.3.4 Synthesis of PMMA with the initiator ZnPc-Br

To a schlenk tube equipped with a magnetic stirrer, vacuum and dry nitrogen was applied three or four times, then MMA (4.5 mL), anisole (1.4 mL), CuBr (0.021 g), PMDETA (62 μ L) and initiator (ZnPc-Br; 0.03 g) were added in the order mentioned under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then tube was immersed in an oil bath and held by a termostate at 95°C, with rigorous stirring. The polymerization was performed for 12, 24 and 48 hours. Then the tube was cooled to room temperature and the contents were dissolved in large amount of THF. The THF solution was passed through a short neutral alumina column to remove copper complex and then excess THF was removed by evaporation. The polymer was precipitated into excess methanole, isolated by vacuum filtration and dried at room temperature *in vacuo*. The conversion was determined gravimetrically.

3.3.5 Film preparation

Thin polymer films were spin-coated (1000 rpm for 30 s) using a SCS P6700 spin coater onto a clean and dried glass substrate using solutions of the synthesized polymers with concentrations of 20 mg in 5ml of chloroform. After spin-coating, the polymer films were annealed for 2 h at 120°C in an oven. By this procedure, glass substrate was completely covered with the polymers.

4. RESULTS AND DISCUSSION

In this thesis, H₂Pc-OH and ZnPc-OH were functionalized to obtain initiator that was used for polymerization of methyl methacrylate. For this purpose, H₂Pc-OH and ZnPc-OH were brominated to create reactive bromine groups.

Synthesized H₂Pc-Br and ZnPc-Br were used for polymerization of methyl methacrylate. For characterization NMR, FT-IR, GPC, DSC, TGA, UV-VIS spectroscopy, Floresence spectroscopy, CV and SWV techniques were used.

4.1 Synthesis of H₂Pc-Br and ZnPc-Br

H₂Pc-Br and ZnPc-Br were synthesized according to the procedure (Figure 4.1 and Figure 4.2) mentioned in section 3.3.1 and 3.3.2. Reaction of H₂Pc-OH or ZnPc-OH with 2-bromopropionyl bromide, in the presence of DMAP and TEA, in DMF at room temperature for four days gave H₂Pc-Br and ZnPc-Br, respectively. The resulting product was checked by NMR and FT-IR spectroscopy techniques.

The FT-IR spectra of H₂Pc-OH and H₂Pc-Br are given in Figure 4.2. The differences between these two spectra are the dissappearance of the characteristic peak of hydroxyl group at 3330 cm⁻¹ and the appearance of carboxyl group peak at 1735 cm⁻¹ and C-Br band at 670 cm⁻¹. There is a N-H streching band becasue of inner core imino group and for H₂Pc-OH and H₂Pc-Br, and they are around 3284 cm⁻¹. Moreover, alkyl-CH band can be seen at 2859-2921 cm⁻¹ and 2843-2917 cm⁻¹ for H₂Pc-OH and H₂Pc-Br, respectively.

The FT-IR spectra of ZnPc-OH and ZnPc-Br are given in Figure 4.3. The differences between these two spectra are the dissappearance of the characteristic peak of hydroxyl group around 3280 cm⁻¹ and the appearance of carboxyl group peak at 1728 cm⁻¹ and C-Br band at 677 cm⁻¹. Inner core imino group peak is replaced with a metal-nitrogen (M-N) streching band as Zn is placed in the inner core [82] and it can be seen around 910 cm⁻¹ for both ZnPc-OH and ZnPc-Br. Also, alkyl-CH band is at 2868-2925 cm⁻¹ and 2917-2962 cm⁻¹ for ZnPc-OH and ZnPc-Br, respectively.

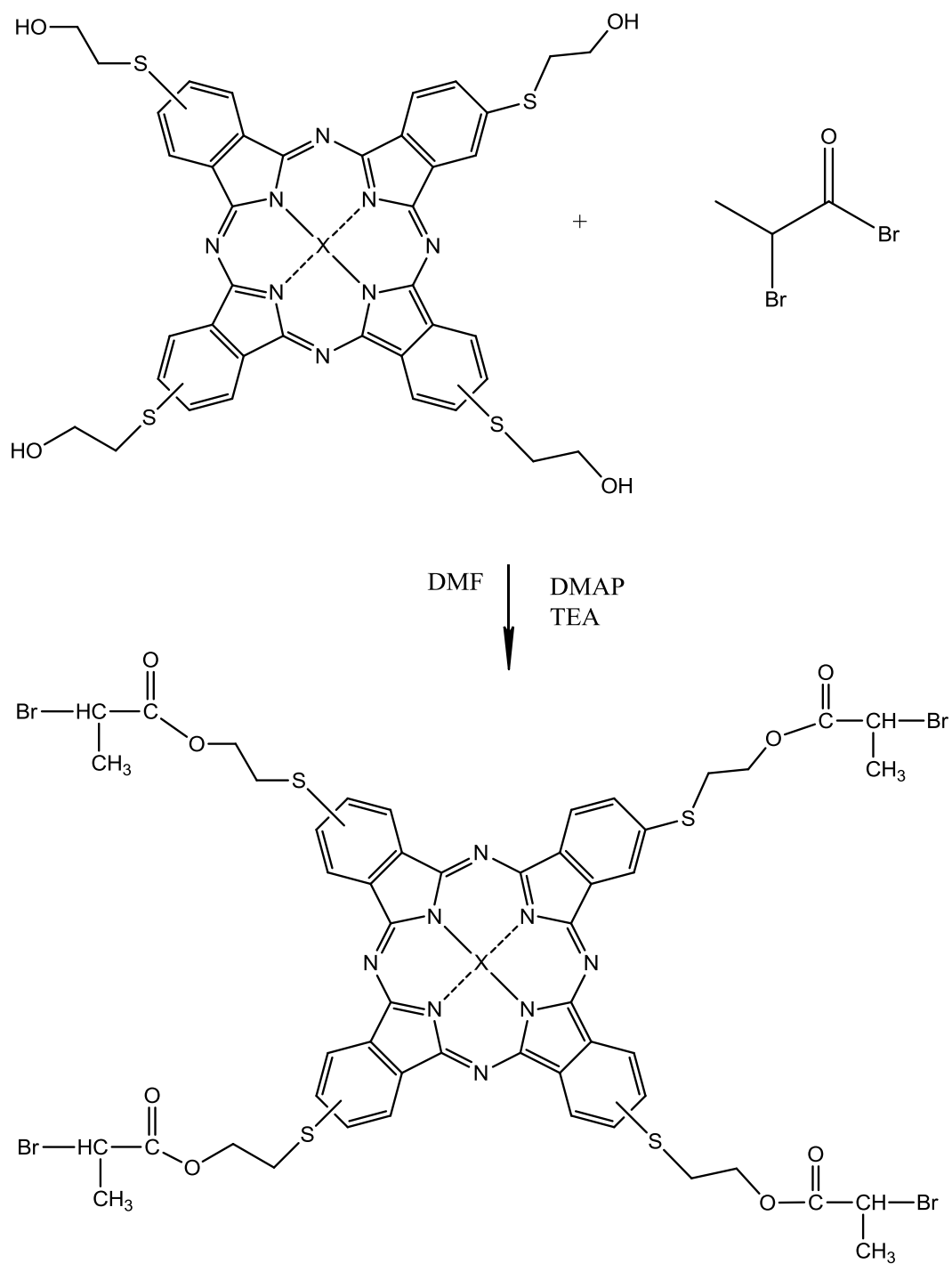


Figure 4.1 : Synthesis of XPc-Br (X: 2H or Zn).

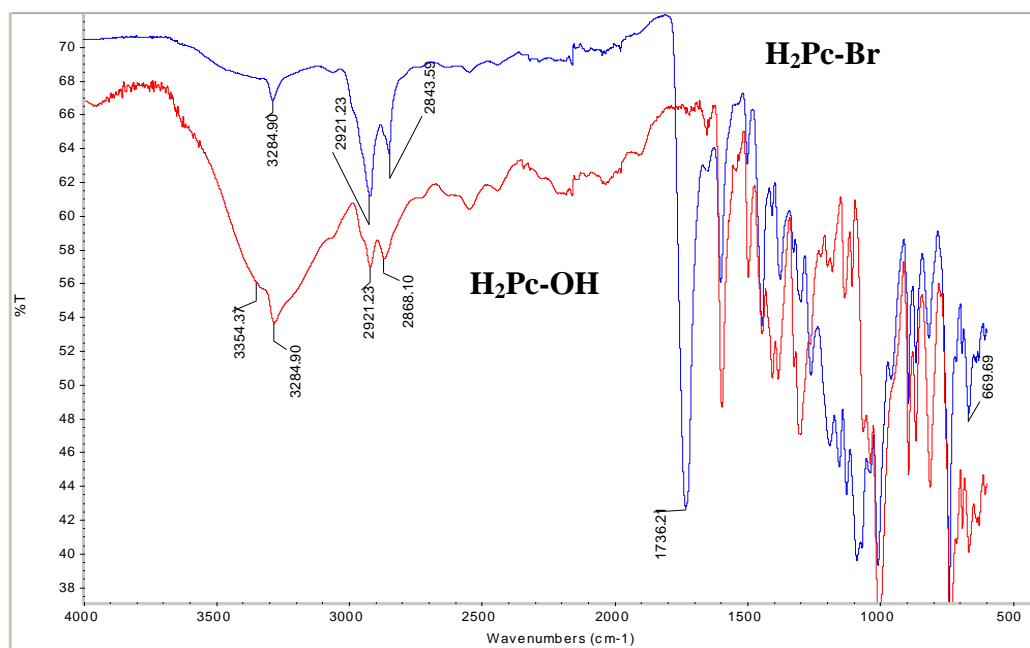


Figure 4.2 : FT-IR spectrum of H_2Pc-OH and H_2Pc-Br .

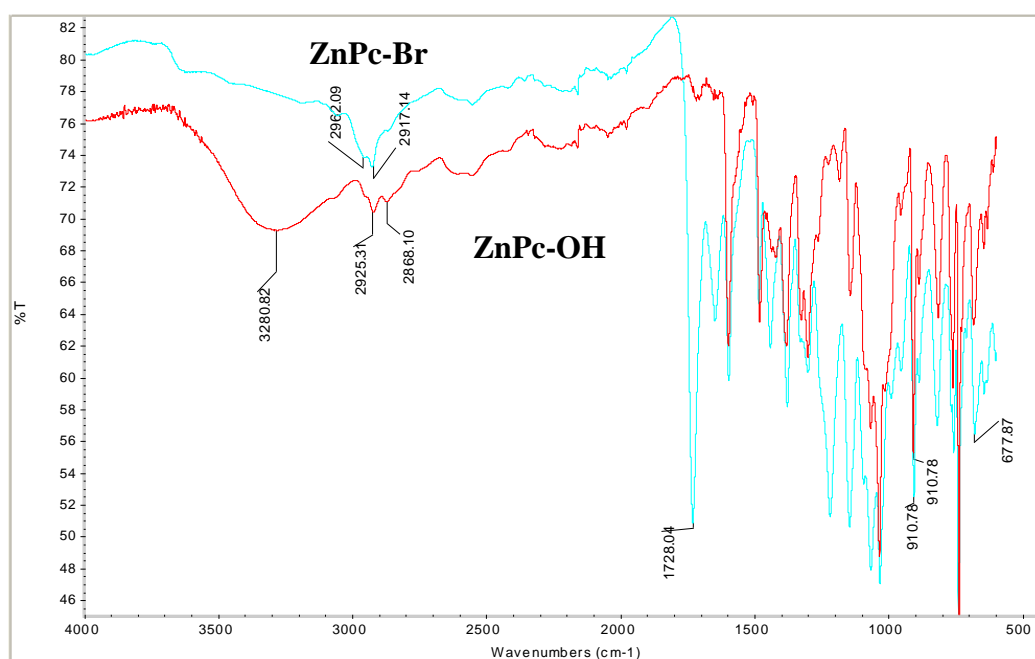


Figure 4.3 : FT-IR spectrum of $ZnPc-OH$ and $ZnPc-Br$.

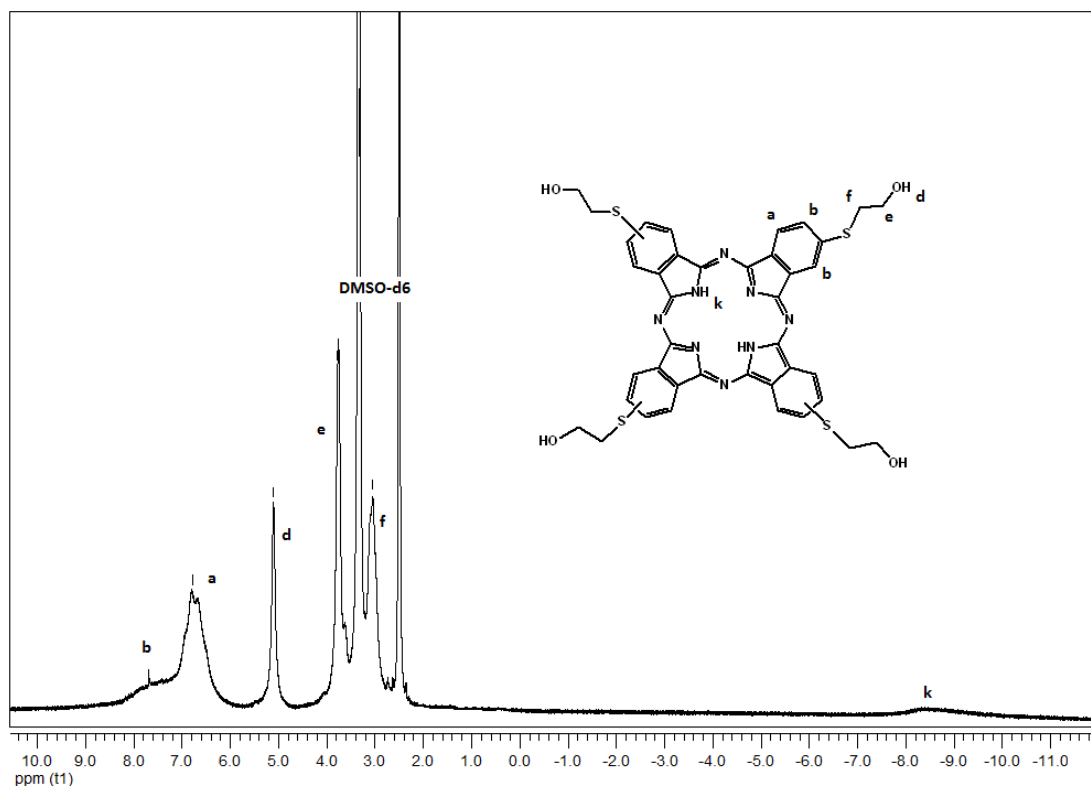


Figure 4.4 : ^1H -NMR spectrum of $\text{H}_2\text{Pc-OH}$.

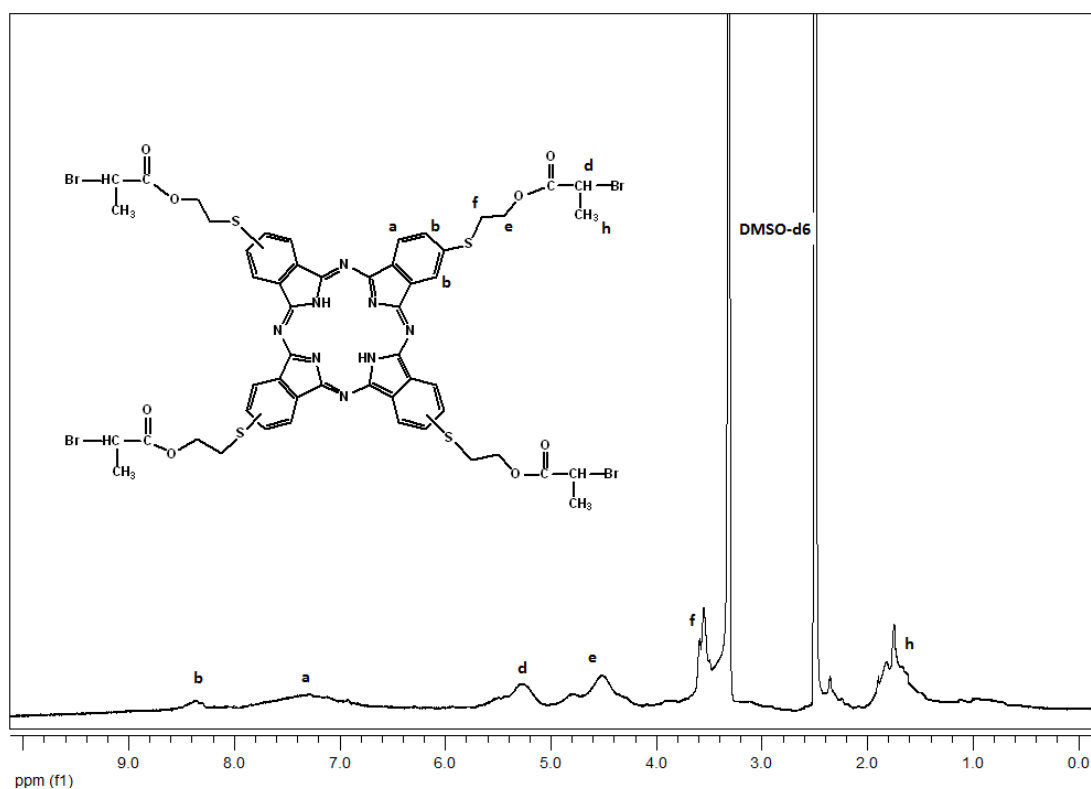


Figure 4.5 : ^1H -NMR spectrum of $\text{H}_2\text{Pc-Br}$.

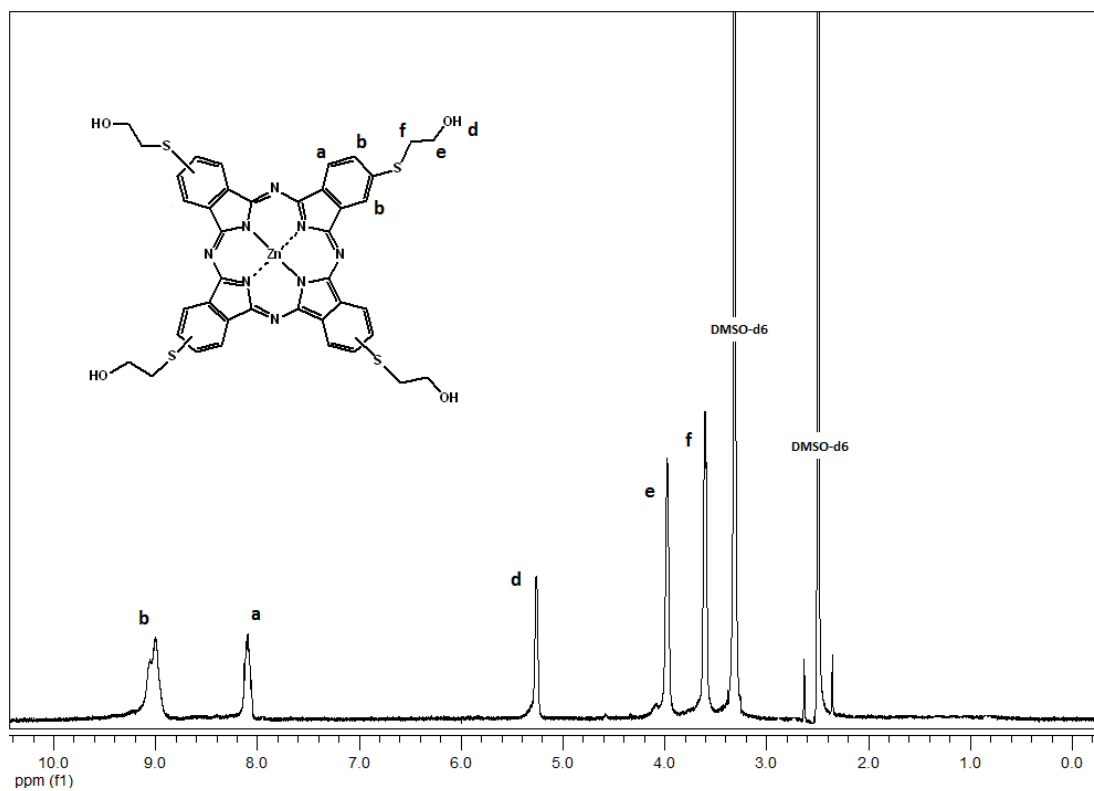


Figure 4.6 : ^1H -NMR spectrum of ZnPc-OH.

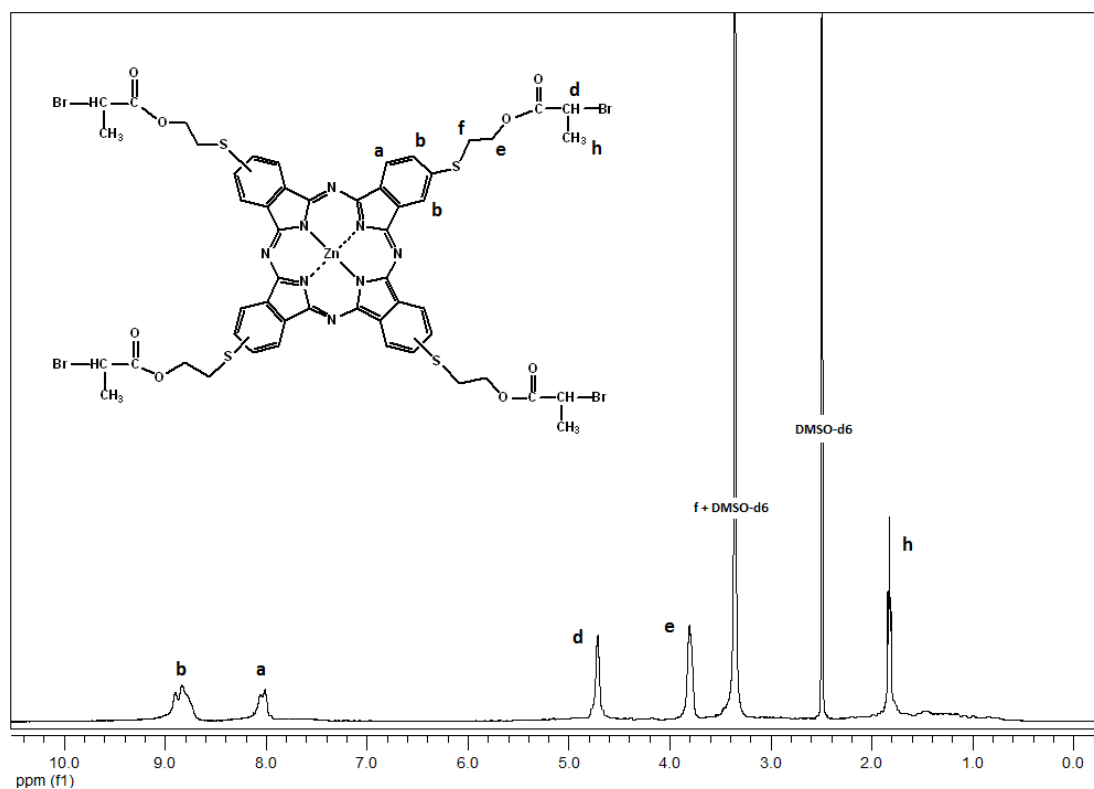


Figure 4.7 : ^1H -NMR spectrum of ZnPc-Br.

^1H -NMR spectra of $\text{H}_2\text{Pc-OH}$ and $\text{H}_2\text{Pc-Br}$ were recorded in DMSO-d_6 . For $\text{H}_2\text{Pc-OH}$, the peak observed between -9.0 and -8.0 ppm corresponded to N-H protons at the inner core imino group. The intensity of the peak was low, this could be attributed to the strong aggregation of the phthalocyanine molecule [83]. Spectrum also indicated the presence of *Ar*-H protons between 6.1 - 8.1 ppm, -OH protons at 5.1 ppm, $-\text{OCH}_2$ protons at 3.8 ppm and $-\text{SCH}_2$ protons at 3.04 ppm. For $\text{H}_2\text{Pc-Br}$ new peaks appeared at 5.25 ppm and 1.7 ppm corresponded to CH-Br and CH_3 , respectively. Spectrum also indicated the presence of eight *Ar*-H protons at 8.35 ppm, four *Ar*-H protons at 7.3 ppm, O- CH_2 protons at 4.5 ppm and S- CH_2 protons at 3.55 ppm.

^1H -NMR spectra of ZnPc-OH and ZnPc-Br were recorded in DMSO-d_6 . For ZnPc-OH , spectrum indicated the presence of eight *Ar*-H protons at 9.05 ppm, four *Ar*-H protons at 8.1 ppm, -OH protons at 5.25 ppm, $-\text{OCH}_2$ protons at 4.0 ppm and $-\text{SCH}_2$ protons at 3.6 ppm. For ZnPc-Br new peaks appeared at 4.71 ppm and 1.81 ppm corresponded to CH-Br and CH_3 , respectively. Spectrum also indicated the presence of eight *Ar*-H protons at 8.84 ppm, four *Ar*-H protons at 8.05 ppm and $-\text{OCH}_2$ protons at 3.8 ppm. The peak for $-\text{SCH}_2$ protons were not very clear because it was overlapped with the peak of DMSO-d_6 .

Electrochemical studies were also made on phthalocyanines. All redox reactions should be resulted from the 18 π electrons system of the phthalocyanine ring as both $\text{H}_2\text{Pc-Br}$ and ZnPc-Br had redox inactive center. Altering the metal center with redox inactive metal ions and substituents of $\text{H}_2\text{Pc-Br}$ and ZnPc-Br just affect the character of phthalocyanine ring electron transfer reactions and stabilities of the electrogenerated anionic and cationic forms of phthalocyanines. Electrochemical character of $\text{H}_2\text{Pc-Br}$ and ZnPc-Br were performed in solution. Basic electrochemical parameters taken from the voltammograms of $\text{H}_2\text{Pc-Br}$ and ZnPc-Br could be seen in Table 4.1. Basic electrochemical parameters of the phthalocyanines are in harmony with the similar complexes in the literature [84-85].

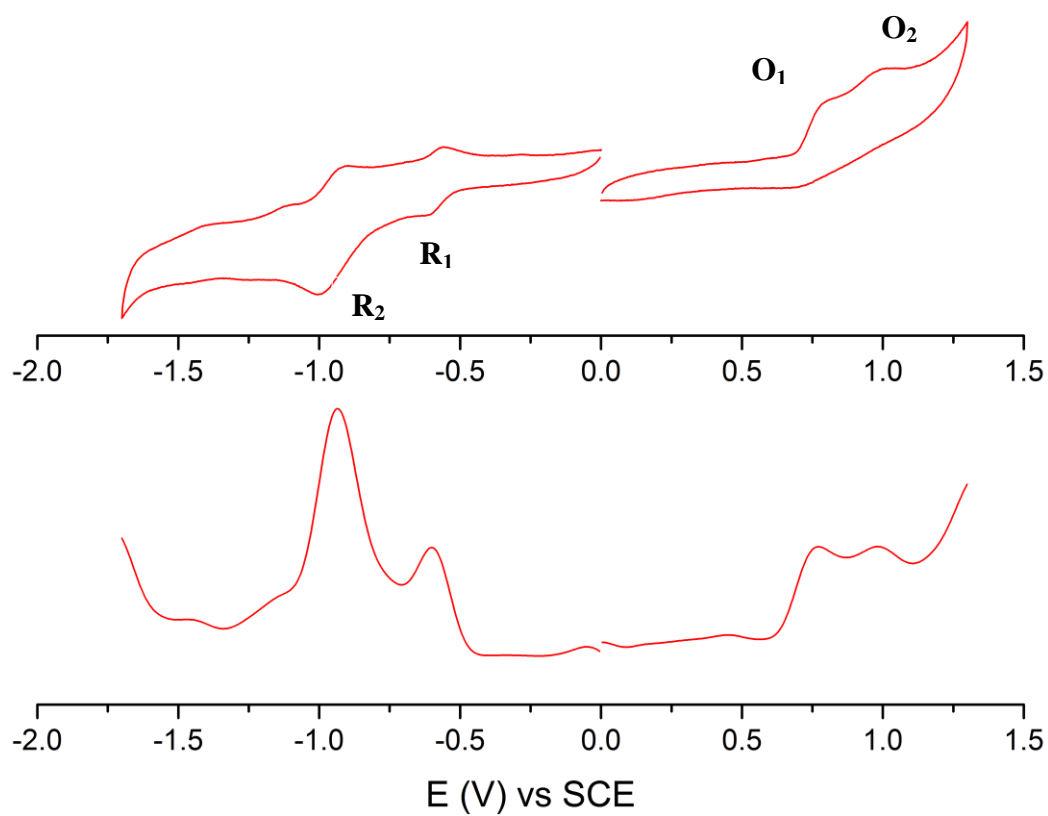


Figure 4.8 : CV and SWV of $\text{H}_2\text{Pc-Br}$.

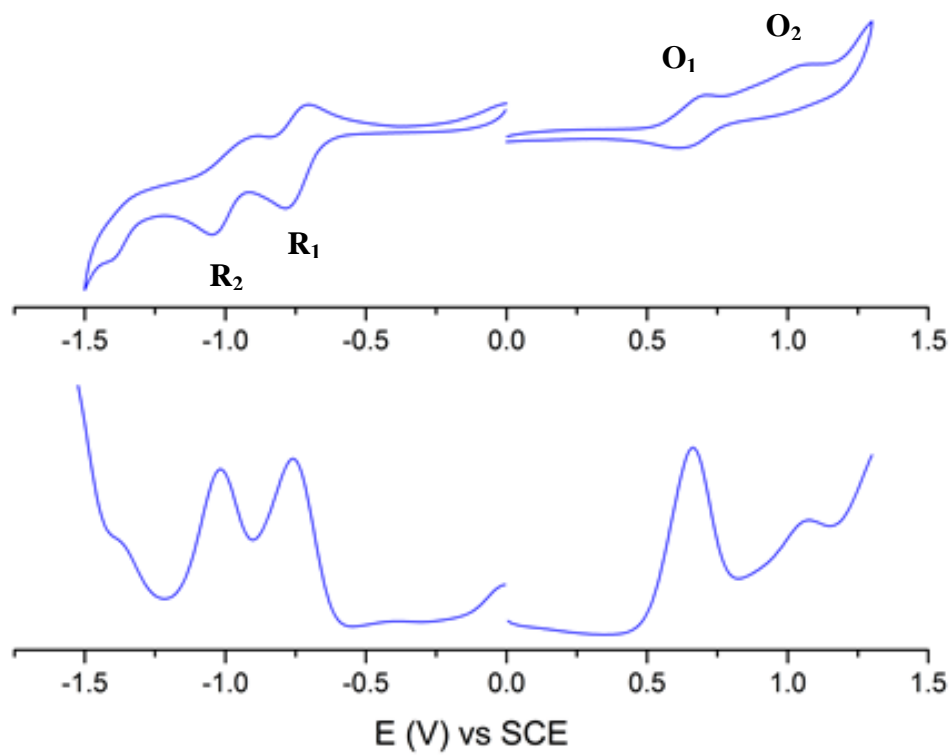


Figure 4.9 : CV and SWV of ZnPc-Br .

Table 4.1 : Oxidation and reduction potentials of H₂Pc-Br and ZnPc-Br.

Compound	R ₁ (V)	R ₂ (V)	O ₁ (V)	O ₂ (V)
H ₂ Pc-Br	-0.6	-0.93	0.75	0.98
ZnPc-Br	-0.76	-1.01	0.66	1.07

The first reduction and second reaction had an electrochemically reversible character when the potential was switched just after the reduction reaction. Also phthalocyanines gave two oxidation reactions. The results came from cyclic voltammetry were also confirmed by square wave voltammetry which is a more precise method.

4.2 ATRP of Methylmethacrylate

Atom transfer radical polymerization, a radical process that is more tolerant to impurities, is a good method for the synthesis of polymers with well-defined compositions, architectures, and functionalities. H₂Pc-Br and ZnPc-Br initiators with bromine group were used to initiate the ATRP of MMA to obtain four armed polymers (Figure 4.10 and Figure 4.11). Typical results concerning the ATRP of monomers are presented in Table 4.1.

The data indicate that the polymerization of MMA in anisole has uncontrolled character resulting in rather broad molecular weight distribution (MWD) and higher experimental Mn values (GPC) than the calculated ones. The PDI values remain about 1.71–1.36. On the other hand, by increasing the time, the conversions of PMMA increase from 5.25 to 14.37%.

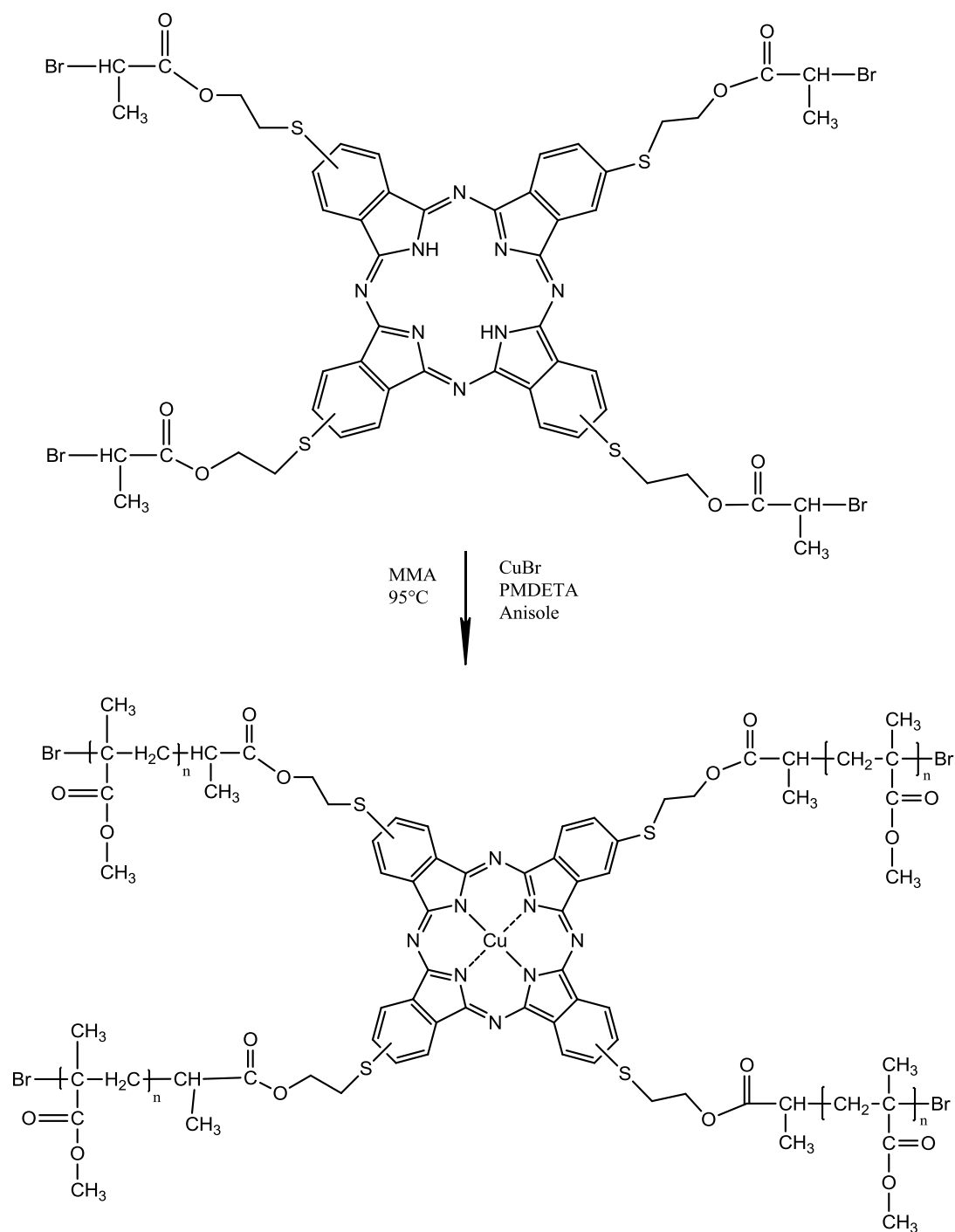


Figure 4.10 : Synthesis of PMMA using H_2Pc-Br as initiator.

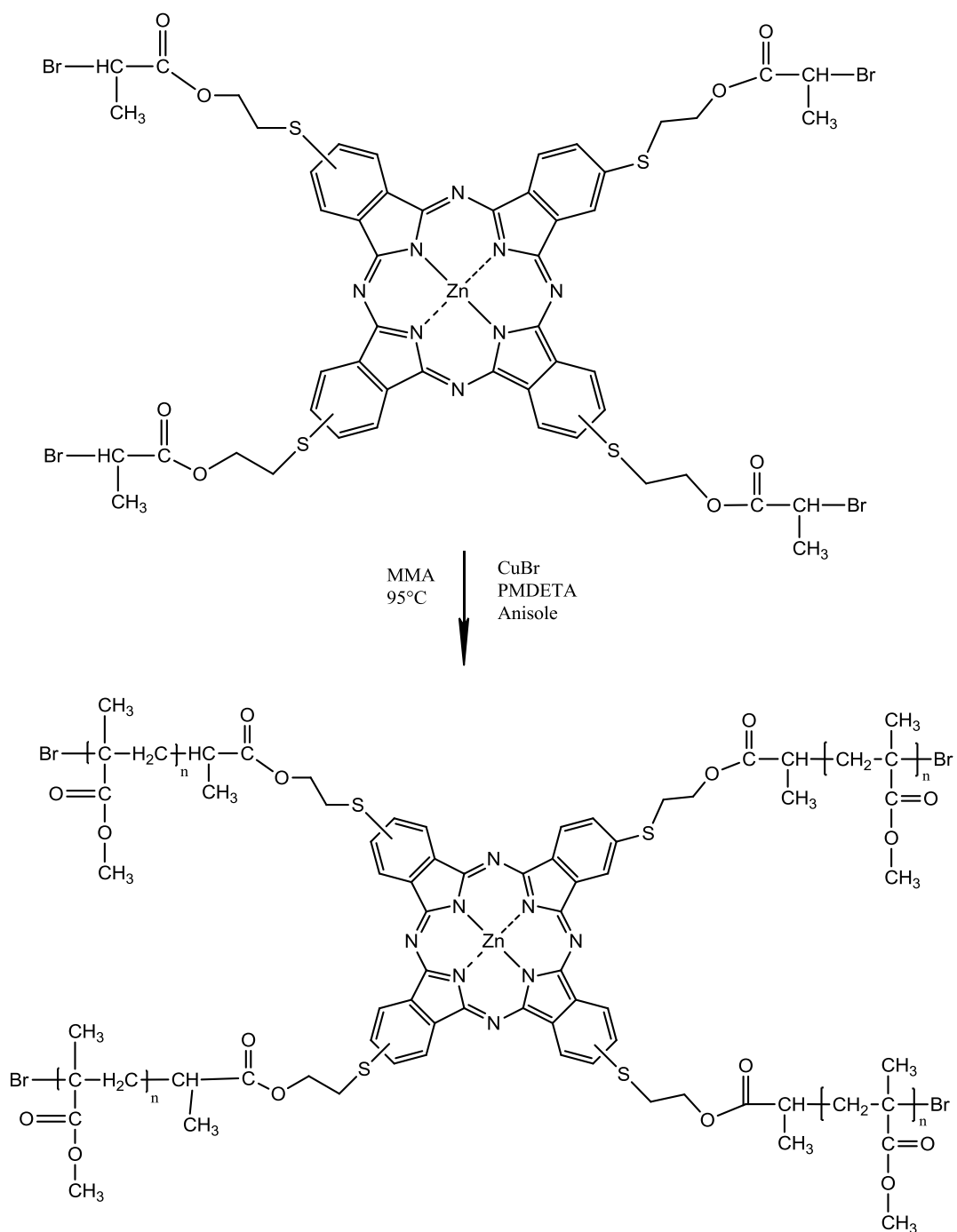


Figure 4.11 : Synthesis of PMMA using ZnPc-Br as initiator.

Table 4.2 : Polymerization characteristics of Polymethylmethacrylates.

Initiator	Run	Time (h)	[M ₀]/[I ₀]	Conv. (%) ^b	M _{n, th} ^c	M _{n, exp} ^d	M _w /M _n ^d
H ₂ Pc-Br	CuPc-PMMA1	12	2000	5.25	11,871	30,331	1.53
H ₂ Pc-Br	CuPc-PMMA2	24	2000	11.85	25,087	43,317	1.52
H ₂ Pc-Br	CuPc-PMMA3	48	2000	13.51	28,411	70,811	1.41
ZnPc-Br	ZnPc-PMMA4	6	2000	5.22	11,854	19,937	1.71
ZnPc-Br	ZnPc-PMMA5	12	2000	9.8	21,045	37,502	1.58
ZnPc-Br	ZnPc-PMMA6	24	2000	12.75	26,952	47,217	1.55
ZnPc-Br	ZnPc-PMMA7	48	2000	14.37	30,196	50,120	1.36

^a [I]₀ : [CuBr]₀ : [PMDETA]₀ : [Monomer]₀ = 1 : 7 : 14 : 2000 in anisole at 95°C for PMMA.

^b Determined gravimetrically.

^c Calculated by $M_{n, th} = ([M_0] / [I_0]) \times (\text{conversion \%}) \times \text{Monomer}$.

^d Determined by means of GPC calibrated with PMMA standards.

Table 4.2 shows the increase of monomer conversion with time, which is a basic requirement for living systems. Also it can be seen that, as the conversion increased with the time, polydispersities decreased during the polymerizations.

From the very beginning of the reaction, $M_{n, exp}$ values are higher than $M_{n, th}$ values. This could be due to low initiation efficiency of the initiator. In ATRP reactions not all initiators are good for all monomers. For a good controlled ATRP, it is necessary to better correlate structures of the initiator with the monomer. Having more similar chemical structure of the initiator to the monomer, causes more efficient initiation [86]. It was assumed that in the absence of side reactions only a small amount of H₂Pc-Br and ZnPc-Br initiated the polymerization, causing $M_{n, exp}$ of the product to be much higher than $M_{n, th}$ and the molecular weight distribution to be relatively narrow.

The uncontrolled behavior could be explained due to the steric hindrance of H₂Pc-Br and ZnPc-Br, it could be difficult to react with the monomers in the first step of the reaction, so the PDI values will be high. This can cause chain termination that, it could get difficult to add a new, so the chains preferred termination by combining two growing chains resulting in high Mn and PDI. In our some results, for some polymers $M_{n, exp}$ nearly two times higher than $M_{n, th}$. This can be explained by

investigations of imperfections such as slow initiation, termination, transfer, and slow exchange and their effects on kinetics, molecular weight, and polydispersities of “living” chain growth polymerization [87]. During the polymerization initiating efficiency is decreasing, this could be due to some chains in polymer lost its active end during the polymerization because of the termination reactions. Very reactive initiators may produce too many radicals, which will terminate at early stages. This will reduce efficiency of initiation, produce too much of the deactivator.

Figure 4.12 and Figure 4.13 shows, the semi-logarithmic kinetic plot of $\ln([M]_0/[M]_t)$ versus time, t , where $[M]_0$ is the initial concentration of the monomer, and $[M]_t$ is the monomer concentration at any time and also plots of M_n and polydispersity indexes (M_w / M_n) as a function of conversion. The linearity of the plot indicates that the concentration of growing radicals is constant. $[M]/[I]/[Cu]/[PMDETA] = 2000/1/7/14$, $[M_{MMA}]_0 = 7.07$ M for polymerization with H_2Pc-Br and $[M_{MMA}]_0 = 7.085$ M for polymerization with $ZnPc-Br$.

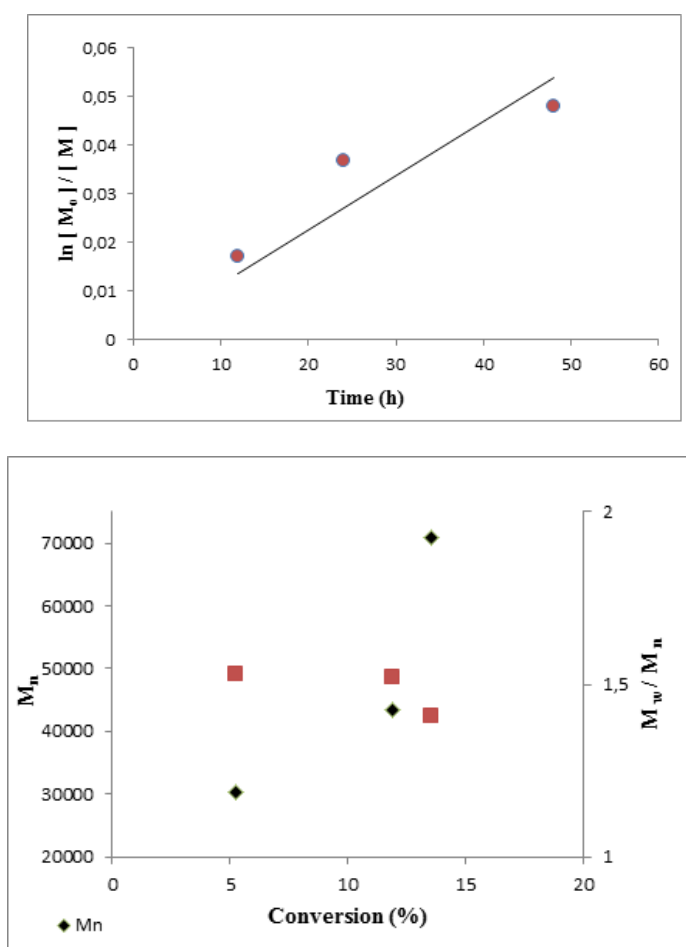


Figure 4.12 : First order kinetic plots for polymerization of MMA using H_2PcBr as initiator and $CuBr$ as catalyst in anisole at 95° .

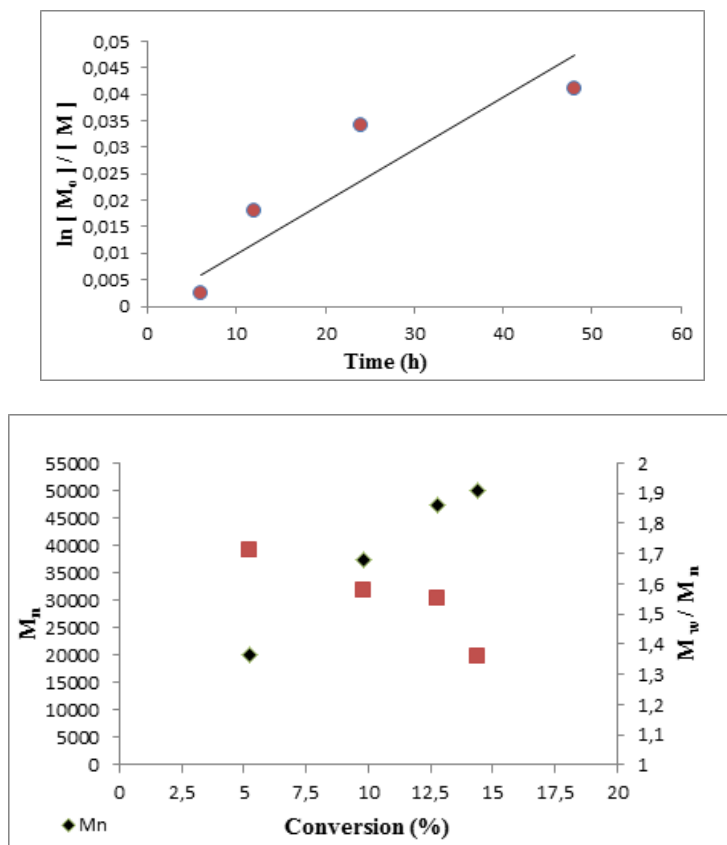


Figure 4.13 : First-order kinetic plots for the polymerization of MMA using ZnPc-Br as initiator and CuBr as catalyst in anisole at 95°C.

All PMMAs showed the same FT-IR spectra (Figure 4.14). It can be seen that there was an absorption band from 1144 cm^{-1} to 1238 cm^{-1} , which could be attributed to the C-O-C stretching vibration. The two bands at 1385 cm^{-1} and 747 cm^{-1} could be attributed to the α -methyl group vibrations. The band at 984 cm^{-1} was the characteristic absorption vibration of PMMA, together with the bands at 1062 cm^{-1} and 841 cm^{-1} . The band at 1732 cm^{-1} showed the presence of the acrylate carboxyl group. The band at 1438 cm^{-1} could be attributed to the bending vibration of the C-H bonds of the $-\text{CH}_3$ group. The two bands at 2995 cm^{-1} and 2946 cm^{-1} could be assigned to the C-H bond stretching vibrations of the $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively. On the basis of the above discussions, it could be concluded that the prepared polymer was indeed macromolecular PMMA [88]. The disappearance of C-Br signal proved that Br functions took part in initiating the PMMA chain growth. Also metal-nitrogen (M-N) stretching band (Cu-N and Zn-N) which came from the initiator could be seen at 910 cm^{-1} .

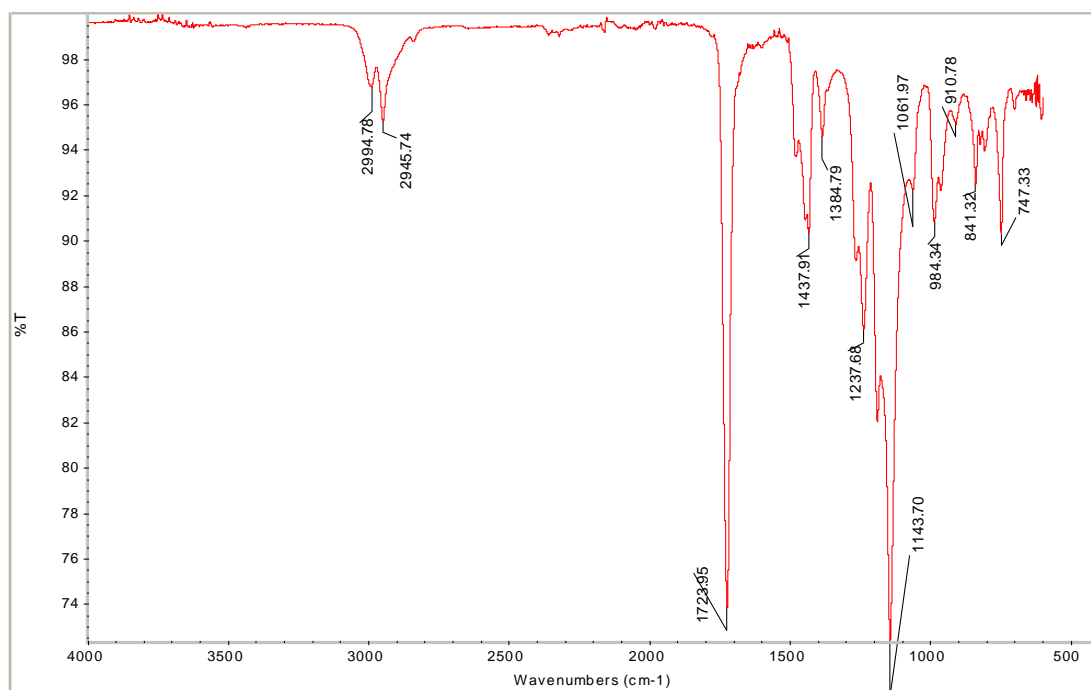


Figure 4.14 : FT-IR spectrum of PMMAs.

In the both two ^1H -NMR spectra of PMMAs, the complete disappearance of initiator CH-Br signals indicated that Br functions took part in initiating the PMMA chain growth. In the ^1H -NMR spectrum of PMMA synthesized with $\text{H}_2\text{Pc-Br}$ (Figure 4.15), the chemical shifts at 7 ppm and 8 ppm corresponded to the benzene ring protons of initiator. Spectrum indicated the presence of $-\text{SCH}_2$ at 3.8 ppm and $-\text{OCH}_2$ at 4.9 ppm which came from the initiator. The signals observed between 0.5 – 2.1 ppm corresponded to the methylene protons of PMMA and the initiator. Also the peak at 3.6 ppm corresponded to methyl of the ester group of PMMA. In the ^1H -NMR spectrum of PMMA synthesized with ZnPc-Br (Figure 4.16), the chemical shifts at 8.2 ppm and 9.4 ppm corresponded to the benzene ring protons of initiator. Spectrum indicated the presence of $-\text{SCH}_2$ at 3.8 ppm and $-\text{OCH}_2$ at 4.5 ppm which came from the initiator. The signals observed between 0.5 – 2.0 ppm corresponded to the methylene protons of PMMA and the initiator. Also the peak at 3.6 ppm corresponded to methyl of the ester group of PMMA.

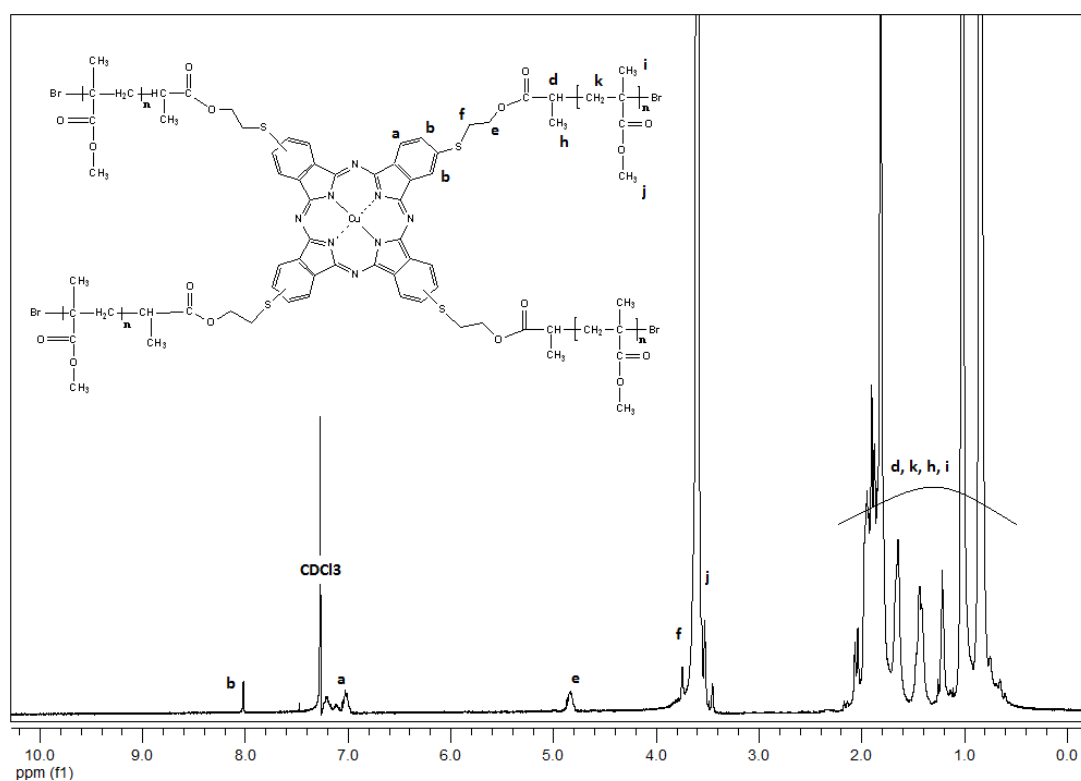


Figure 4.15 : ^1H -NMR spectrum of CuPc-PMMA.

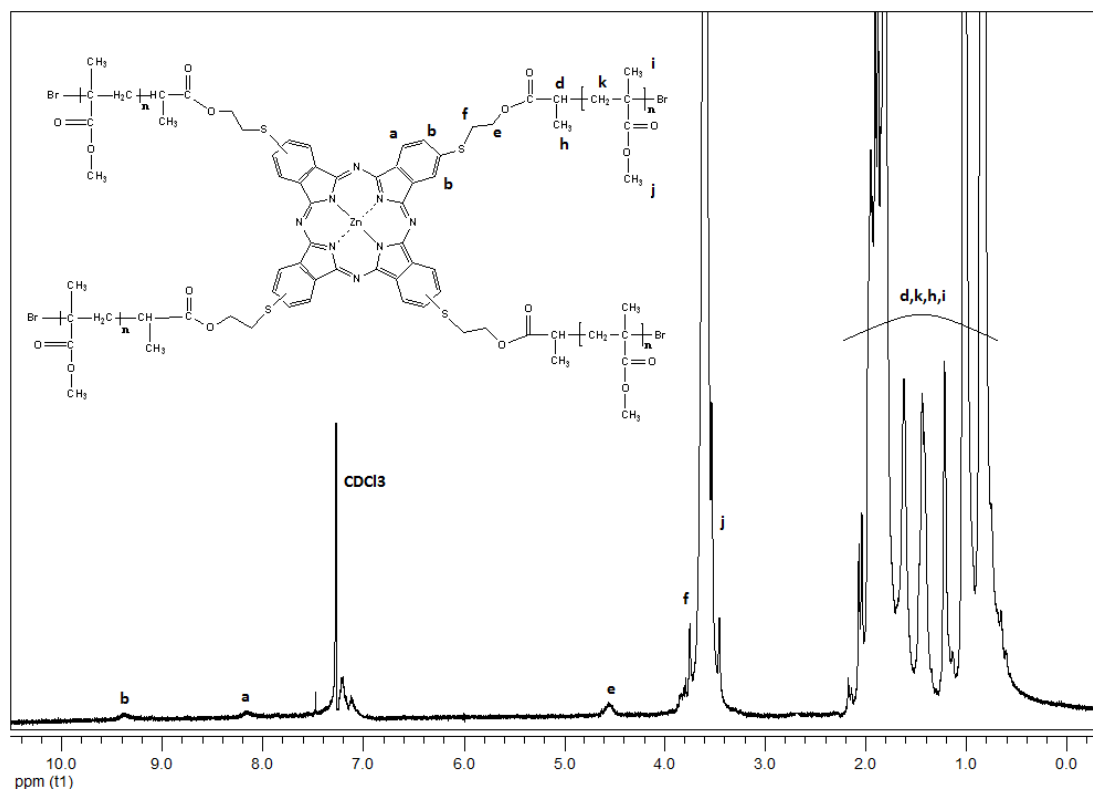


Figure 4.16 : ^1H -NMR spectrum of ZnPc-PMMA.

Electrochemical studies were also made on PMMAs synthesized with phthalocyanines. All redox reactions should be resulted from the 18 π electrons system of the phthalocyanine ring. Electrochemical character of PMMAs were performed in solution. All PMMAs showed similar electrochemical properties. Basic electrochemical parameters taken from the voltammograms of PMMAs (Figure 4.17) could be seen in Table 4.3.

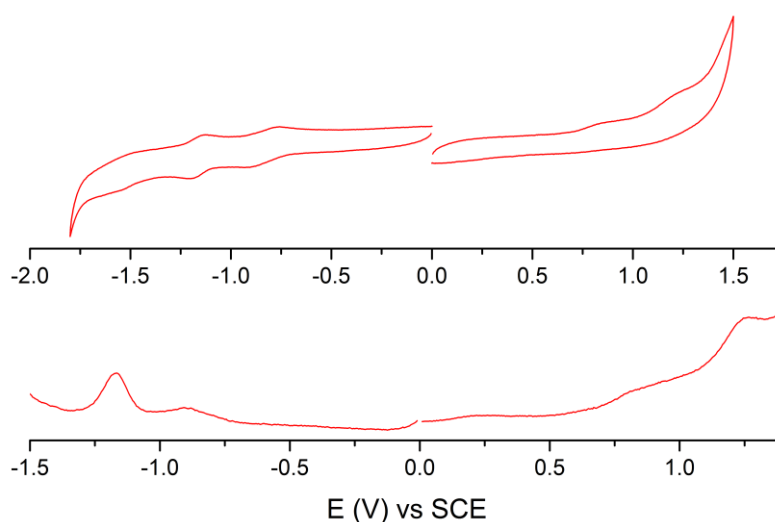


Figure 4.17 : CV and SWV of PMMAs.

Table 4.3 : Electrochemical properties of PMMAs.

Compound	R ₁ (V)	R ₂ (V)	O ₁ (V)	O ₂ (V)
PMMA	-0.88	-1.17	0.85	1.25

4.3 Thermal Behaviour of PMMA

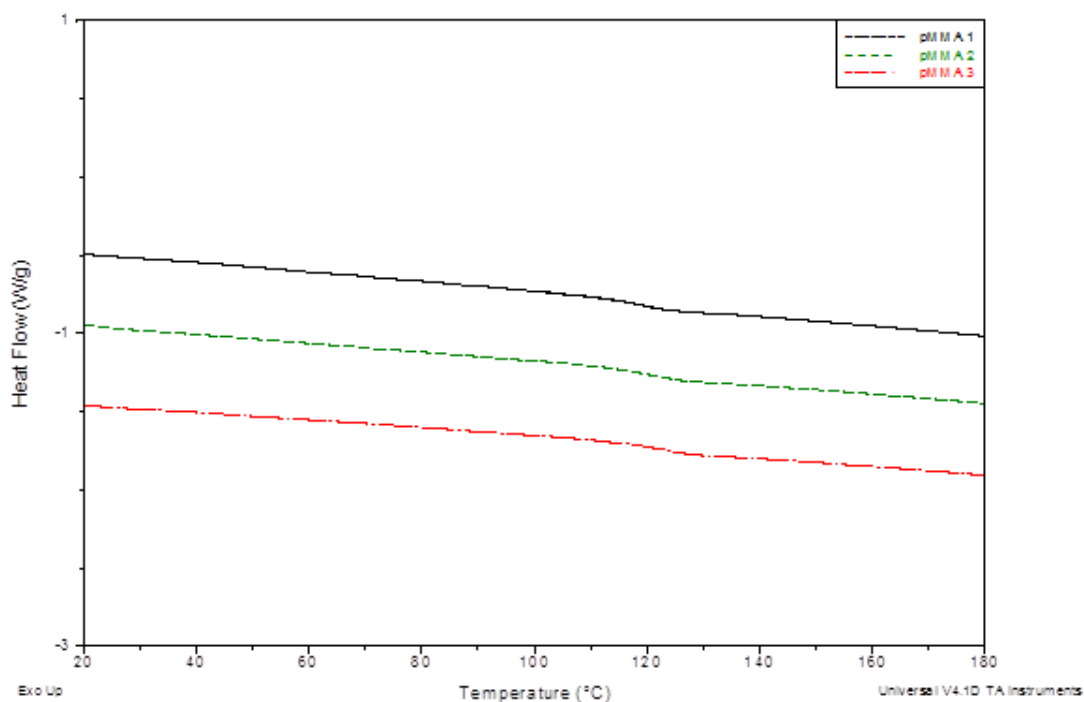
Thermal behaviours of polymers were investigated with DSC and TGA methods. DSC measurements were conducted with a heating rate of 10 °C/min. The thermal stability measurements were evaluated by TGA under nitrogen at a heating rate of 20 °C/min. The results of thermal analysis are summarized in Table 4.4.

Table 4.4 : DSC and TGA results for PMMA.

Polymer	T _g (°C)	T _{%50} (°C)	Residue at 500°C
CuPc-PMMA1	119	397.5	9.1
CuPc-PMMA2	121	396.6	2.7
CuPc-PMMA3	123	393.6	3.1
ZnPc-PMMA4	117	400.1	6.1
ZnPc-PMMA5	123	393.5	3.7
ZnPc-PMMA6	122	394.1	4.8
ZnPc-PMMA7	125	392.9	1.3
STD PMMA ^a	120	391.6	2.0

^a Molecular weight of pure PMMA is 30.350 g/mol.

The T_g values of pMMA were in the range of 119-125 °C. These values were not really different from the T_g value of standard PMMA (Figure 4.18 and Figure 4.19) so it could be said that the macrocyclic compound which we used as an initiator could not affect T_g as the molecular weight's of PMMAs are high.

**Figure 4.18 :** DSC thermograms of CuPc-PMMA_s.

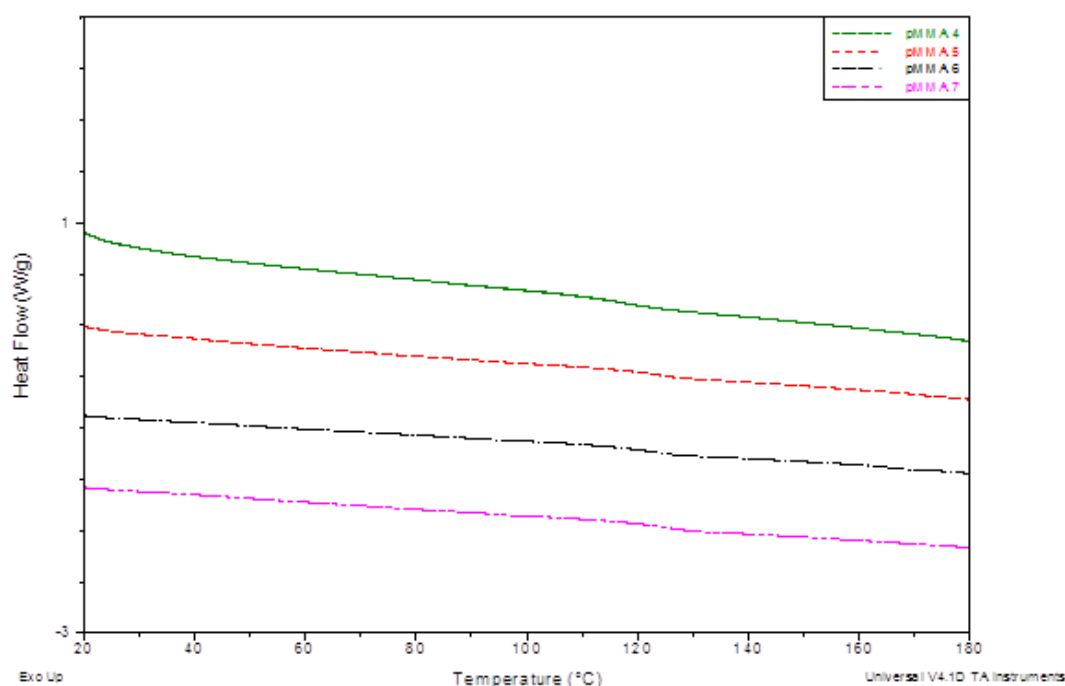


Figure 4.19 : DSC thermograms of ZnPc-PMMA.

Figure 4.20 and Figure 4.21 show the weight loss of PMMAs in a nitrogen atmosphere as a function of temperature. It can be 50% decomposition temperature decreases when the molecular weight of the polymer increases. When the molecular weight of polymers increase, there will be less chain ends which will cause smaller residue values but still they do not have a linear relationship.

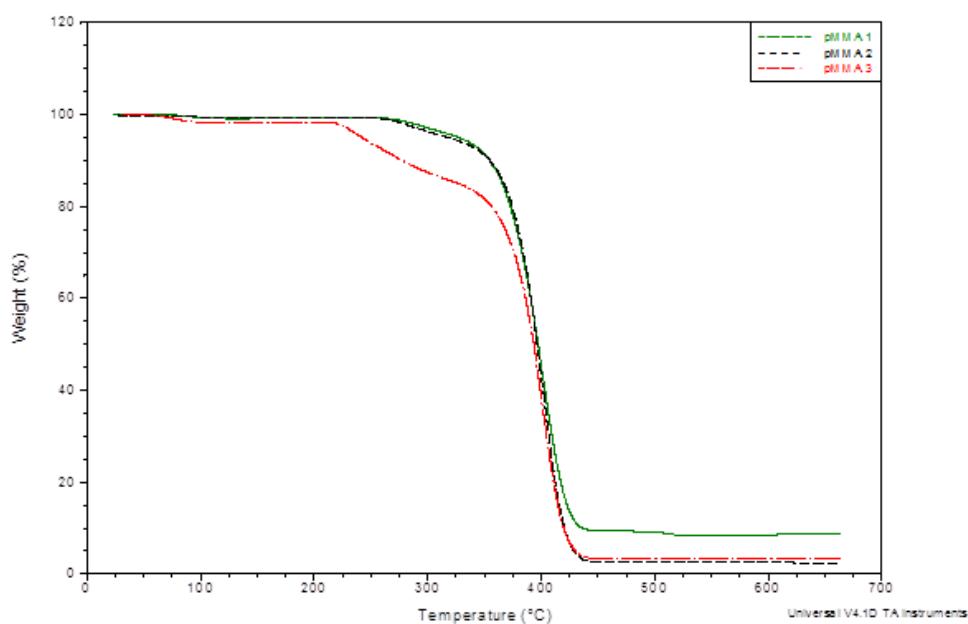


Figure 4.20 : TGA thermograms of CuPc-PMMA.

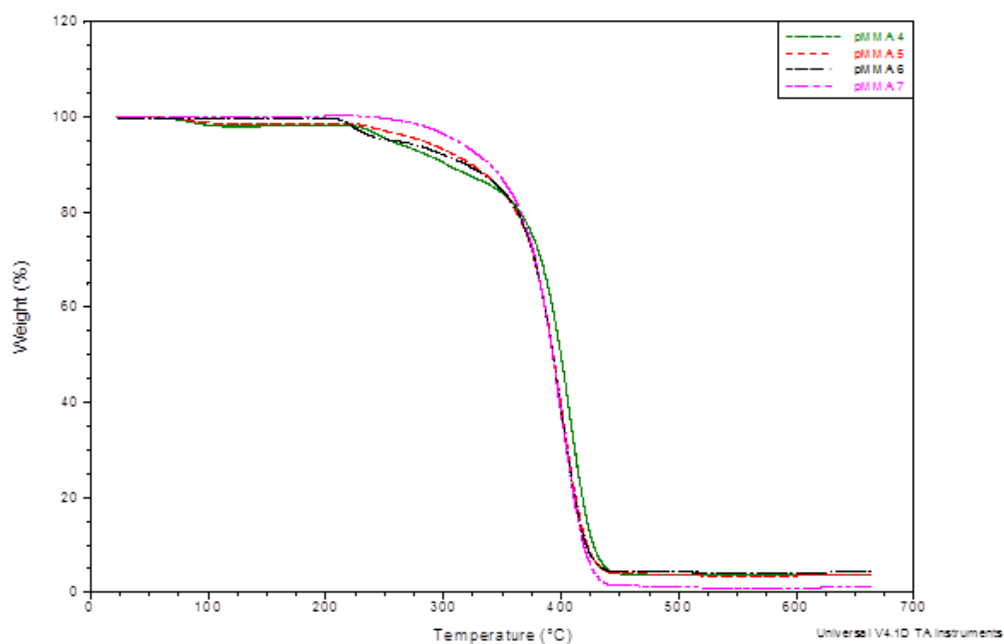


Figure 4.21 : TGA thermograms of ZnPc-PMMA.

4.4 Electronic Absorption and Fluorescence Spectra

The phthalocyanines exhibit typical electronic spectra with two strong absorption bands, the B band at around 300-400 nm and the Q band at 600-750 nm. Q band of phthalocyanine gives information about whether it contains metal at the center or not. While the spectrum of metal free phthalocyanines are splitted due to the electronic transition from a doubly degenerate HOMO to LUMO of the molecule, the spectrum of metallophthalocyanines has one intense band [89]. This difference could be observed from the Figure 4.22. The absorption bands of H₂Pc-Br were observed at 348 nm in the UV region corresponding to the B band and at 710 and 675.5 nm corresponding to the Q band in the visible region. ZnPc-Br exhibited an intense Q band at $\lambda_{\text{max}} = 687.5$ nm and B band at 358 nm.

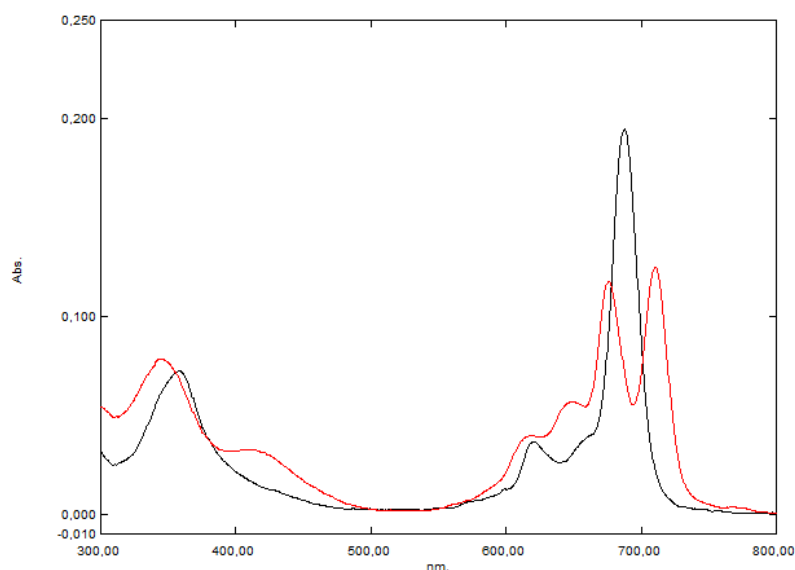


Figure 4.22 : Electronic absorption spectra of H₂Pc-Br (red line) and ZnPc-Br (black line) in chloroform.

Figure 4.23 and Figure 4.24 shows the changes in the visible spectra of H₂Pc-Br and ZnPc-Br in chloroform with concentration. It can be seen that the intensity of absorption of the Q band increases as the concentration increases from 4×10^{-5} to $0.8 \times 10^{-6} \text{ mol dm}^{-3}$, which can be attributed to the effect of nonaggregation.

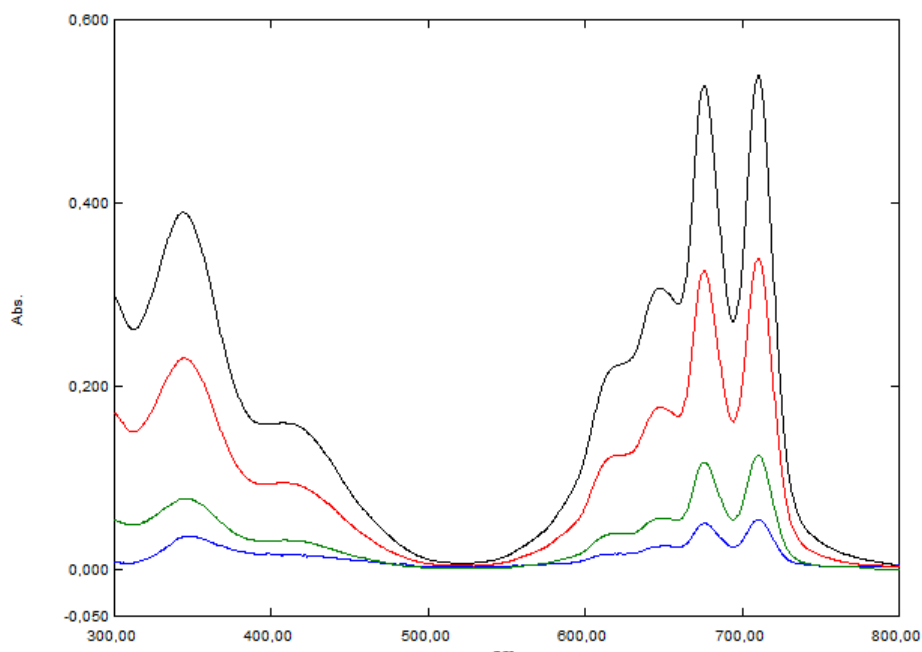


Figure 4.23 : Electronic absorption spectra of H₂Pc-Br in chloroform a concentration range of a 4×10^{-5} (black line), 0.6×10^{-5} (red line), 0.2×10^{-5} (green line), 0.8×10^{-6} (blue line) mol dm^{-3} .

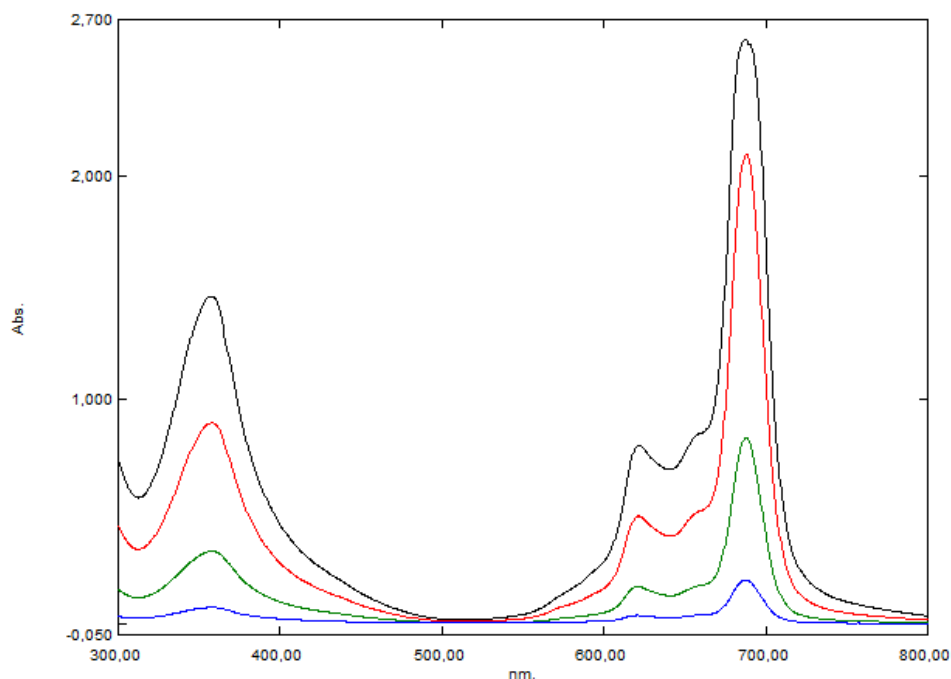
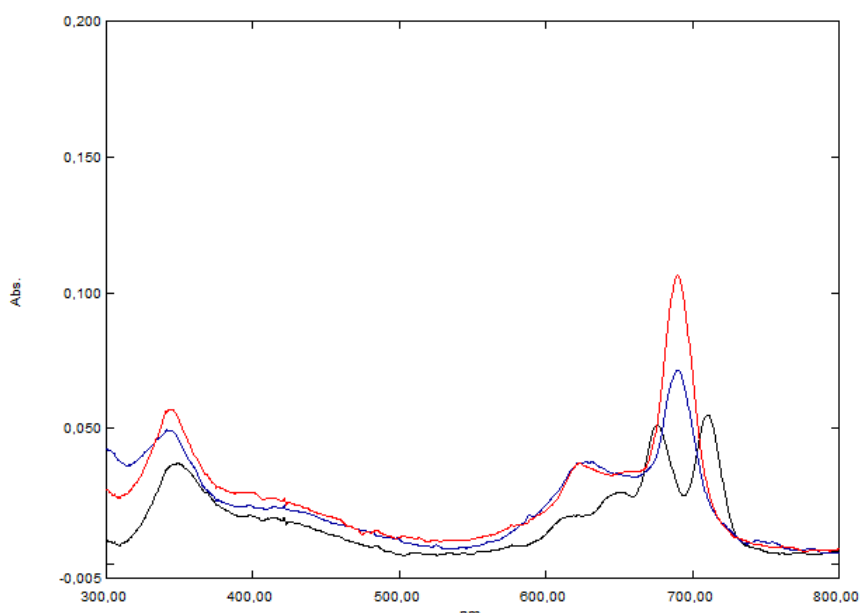


Figure 4.24 : Electronic absorption spectra of ZnPc-Br in chloroform a concentration range of a 4×10^{-5} (black line), 0.6×10^{-5} (red line), 0.2×10^{-5} (green line), 0.8×10^{-6} (blue line) mol dm^{-3} .

For all compounds, Q band maximas and B band maximas are summarized in the Table 4.5. When we compare the UV-Vis spectra of H₂Pc-Br and PMMA synthesized using H₂Pc-Br as initiator (Figure 4.25), instead of a splitted peak we can see a one intense peak at the Q band. This confirms the metallation of the H₂Pc-Br while the ATRP because of the usage of Cu(I)Br as catalyst. The excee of copper locates in the core of phthalocyanine. The introduction of copper ion into the core of phthalocyanine causes a reduction on the peaks at Q band from four to two. The appearance of the Q and B bands in the UV-Vis spectra of ZnPc-Br matchs up with all PMMAs synthesized from it (Figure 2.26).

Table 4.5 : Electronic absorption spectral data.

Compound	Q band, λ_{\max} (nm)	B band, λ_{\max} (nm)
H ₂ Pc-Br	710.0 675.5	348.0
ZnPc-Br	687.5	358.0
CuPc-PMMA 1	689.5	344.0
CuPc-PMMA 2	690.0	343.0
CuPc-PMMA 3	690.0	341.0
ZnPc-PMMA 4	688.0	357.0
ZnPc-PMMA 5	688.0	357.0
ZnPc-PMMA 6	688.0	359.5
ZnPc-PMMA 7	688.5	359.0

**Figure 4.25 :** Electronic absorption spectra of H₂Pc-Br (black line), CuPc PMMA1 (red line), CuPc-PMMA2 (blue line) in chloroform.

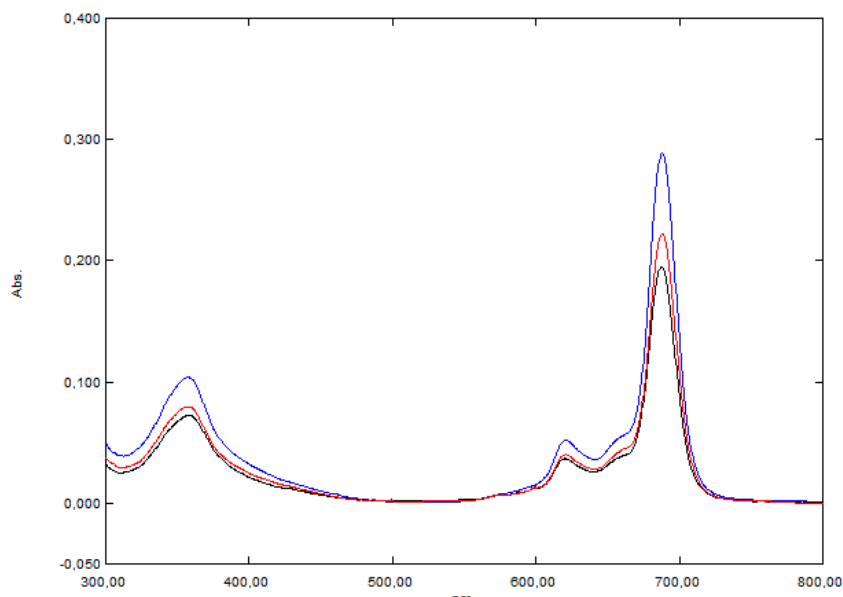


Figure 4.26 : Electronic absorption spectra of ZnPc-Br (black line), ZnPc-PMMA4 (red line), ZnPc-PMMA5 (blue line) in chloroform.

The steady-state fluorescence spectra of the phthalocyanines and PMMAs were performed in chloroform, upon excitation at the 630 nm Q band wavelength (Figure 4.27). Calculated stokes shift values were typical of phthalocyanine complexes. Fluorescence spectra of ZnPc-PMMA4 is similar to the phthalocyanines but the spectra of CuPc-PMMA1 had some differences. When we took fluorescence spectra of the increasing molecular weighted PMMAs, quenching was started (Figure 4.28). The self-quenching effect could be related with the increasing molecular weight and loss of the fluorescence effect of phthalocyanine initiator.

Comparative method (Eq. (4.1)) was used to determine the quantum yields of the phthalocyanines as described in [90]. In this method, the quantum yield of a compound is determined by using a standard which has similar fluorescence properties as the tested compound has. All measurements of the standard and the compound must be performed at the same environmental conditions with the same instrumental settings.

$$\Phi_F = \Phi(\text{Std}) \frac{F A_{\text{Std}} \eta^2}{F_{\text{Std}} A \eta_{\text{Std}}^2} \quad (4.1)$$

where F and F_{Std} are the areas under the fluorescence curves of phthalocyanines derivatives and the standard, respectively. A and A_{Std} are the respective absorbance of the sample and standard at the emission and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc-1 was employed as a

standard in chloroform ($\Phi_F = 0.23$). The fluorescence quantum yield (Φ_F) values for the H₂Pc-Br and ZnPc-Br were found to 0.155 and 0.29, respectively, which were similar to metal free and zinc phthalocyanines in the literature. The fluorescence quantum yield of PMMA4 could not be calculated because there was not any references available for them.

Table 4.6 : Absorption and fluorescence emission spectral data.

Compound	Q band λ_{max} , (nm)	Emission λ_{Em} , (nm)	Stokes shift (nm)	Φ_F	Reference
H ₂ Pc-Br	710.0	716.0	6.0	0.155	
ZnPc-Br	687.5	696.0	8.5	0.290	
CuPc-PMMA1	689.5	697.0	7.5	-	
ZnPc-PMMA4	688.0	696.0	8.0	-	
ZnPc-1	677.0	687.0	10.0	0.230	[91]

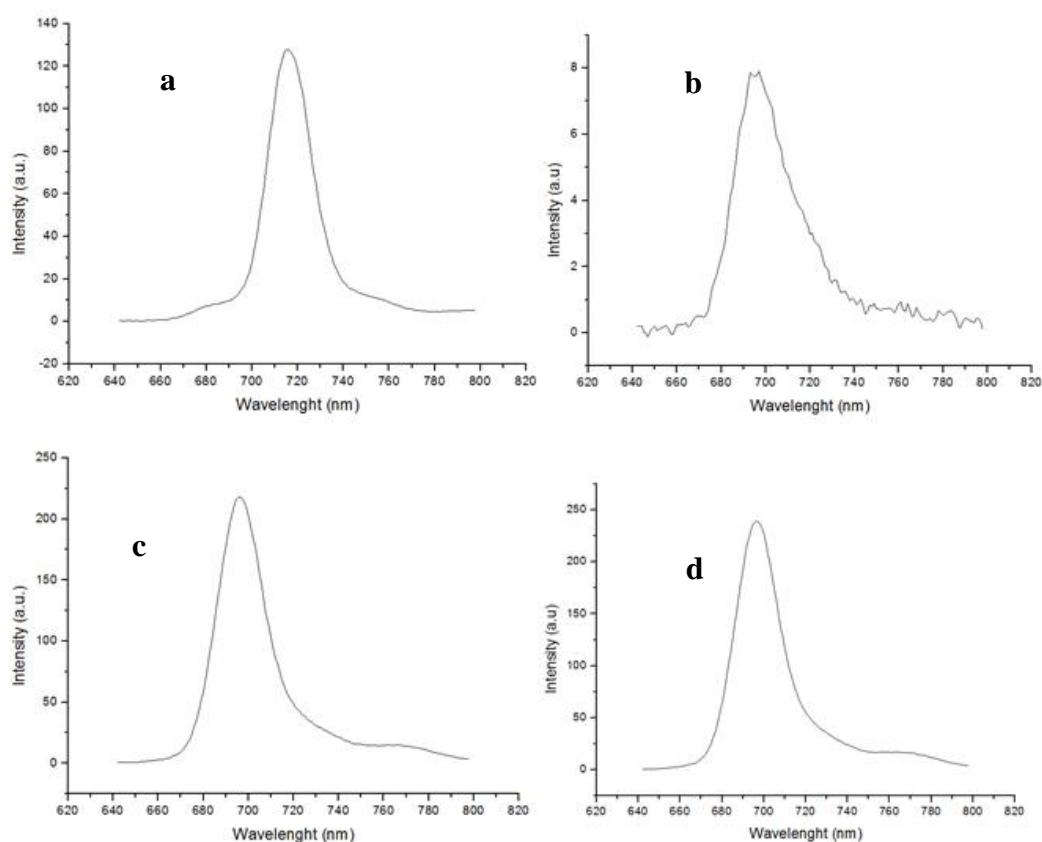


Figure 4.27 : Fluorescence emission spectra of (a) H₂Pc-Br, (b) CuPc-PMMA1, (c) ZnPc-Br, (d) ZnPc-PMMA4.

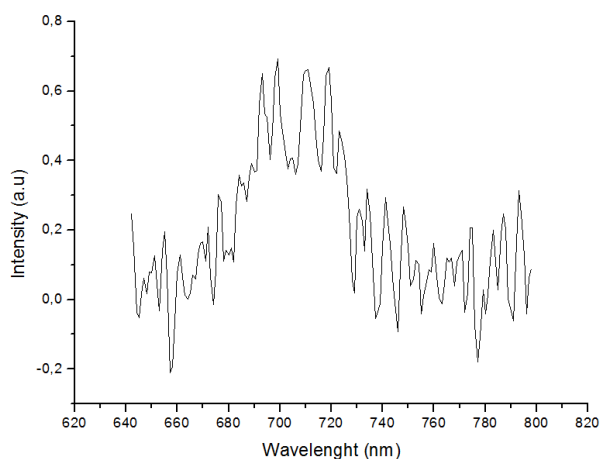


Figure 4.28 : Fluorescence emission spectra of CuPc-pMMA2.

4.5 Transmittance Properties

Transmittance properties of thin film made by phthalocyanines and polymers on a glass substrate were observed by UV-Vis spectrometer. Table 4.7 shows the data taken from transmittance spectra. It can be seen that the transmittance of pure PMMA and PMMA synthesized using phthalocyanine as initiator do not have much difference so we can say that using phthalocyanine as initiator do not have negative effect on the transmittance of the films. Also the transmittance results of phthalocyanines indicate that they can be used as an optic filter between 300–400 nm and 600–700 nm.

Table 4.7 : Transmittance spectral data.

Compound	%T (visible region) ^a	%T (near-UV region) ^b
H ₂ Pc-Br	94	90
ZnPc-Br	93	88
Cu-PMMA1	90	89
Zn-PMMA4	90	90
Std PMMA	92	93

^a Visible region values were taken between 600-700 nm.

^b Near-UV region values were taken between 300-400 nm.

5. CONCLUSION

The aim of this study is to synthesize novel tetra terminal alkynyl-substituted phthalocyanines and use them as macronitiators to have four armed polymers. In this study, new ATRP initiators, H₂Pc-Br and ZnPc-Br, having active bromine group were synthesized and used to perform ATRP of MMA in the presence of CuBr/PMDETA. The structures of the initiator and polymers were thoroughly characterized and confirmed using NMR and FT-IR spectroscopy. Also electrochemical studies were performed on phthalocyanine initiators and the results were compatible with the similar complexes in the literature. Synthesized PMMAs had relatively narrow molecular weight distrubition. A linear relationships between both $\ln[M]_0/[M]$ vs. time and molecular weight vs. conversion indicated controlled/living polymerization of MMA using H₂Pc-Br and ZnPc-Br as ATRP initiator. The DSC results correlate well with the results of pure PMMA polymer. Introducing the phthalocyanines as core into the polymer did not change residue in the TGA analysis much. UV-Vis analysis showed that PMMAs had similar properties with metallophthalocyanines but they started to lose their fluorensence properties with the increasing molecular weight. Transmittance properties of initiators and PMMAs were also examined and it showed that there were not any negative influences on transmittance when PMMAs were synthesized using H₂Pc-Br and ZnPc-Br as initiator.

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