

**SYNTHESIS AND CHARACTERIZATION OF NOVEL AROMATIC MAIN
CHAINS DIAZO POLYMERS. THEIR SOME PROPERTIES AND
POSSIBLE APPLICATION AREAS**

**by
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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF NOVEL AROMATIC MAIN CHAINS DIAZO POLYMERS. THEIR SOME PROPERTIES AND POSSIBLE APPLICATION AREAS

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In this study, the aim was to prepare, characterize and determine some properties of aromatic conjugated polymers containing diazo groups in their main chains. For this purpose, starting from dinitro derivatives of biphenyl, naphthalene and diphenyl ether, nitroamine derivatives were prepared by selective reduction except 4-amino-4'-nitrodiphenyl sulphide which is obtained commercially. Four nitroamine derivatives were reduced with Zn powder in basic condition to convert nitroamine compounds to monomers containing diazo group. And then, twelve fully conjugated aromatic polymers

containing azo groups in their main chain were synthesized from diazo containing monomers with triphenylamine (TPA), triphenylphosphine (TPP) and N-methyldiphenyl amine (N-MDPA) via diazocoupling reaction. Characterizations of the monomers and polymers were performed by ^1H -NMR, ^{31}P -NMR, FTIR, UV-VIS, DSC, TGA techniques. It was found that all polymers are dark brown or black solids since they have fully aromatic conjugated molecular structure. Polymers prepared from TPA and TPP are insoluble in most of organic solvents but polymers prepared from N-MDPA are soluble in most of organic solvents due to the formation of quite linear chains. It was determined that they have two maxima at around 280 and 380 nm in UV region. They are nonconductive in crude polymeric form. Because of their fully aromatic backbones they showed high thermal stability and resistant to heat up to the energy required to break azo bonds.

Keywords: Aromatic Backbone Diazo Polymers, Conjugated Polymers, Diazo Coupling, Light Sensitive Polymers

ÖZET

YENİ AROMATİK ANA ZİNCİR DİAZO POLİMERLERİNİN SENTEZİ VE TANIMLANMASI. BUNLARIN BAZI ÖZELLİKLERİ VE OLASI UYGULAMA ALANLARI

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Bu çalışmada, ana zincirinde diazo grubu içeren aromatik konjuge polimerlerin hazırlanması, karakterize edilmesi ve bazı özelliklerinin analizi amaçlanmıştır. Bu amaçla ticari olarak elde edilen 4-amin-4'nitrobifenil sülfid dışındaki diğer nitro amin türevleri; bifenil, naftalin ve difenil eter bileşiklerinin dinitro türevlerinin seçici indirgenmesiyle elde edilmiştir. Elde edilen dört nitroamin türevi çinko tozu ile bazik ortamda indirgenerek diazo grubu içeren monomerler sentezlenmiştir. Daha sonra, bu monomerler TPA (trifenilamin),

TPP (trifenilfosfin), ve N-MDPA (N-metildiamin) bileşikleri ile diazolama yöntemi kullanılarak 12 farklı azo grubu içeren tamamı konjuge aromatik polimerler sentezlenmiştir. Sentezlenen bu monomer ve polimerlerin karakterizasyonu ^1H -NMR, ^{31}P -NMR FTIR, UV-VIS, DSC, TGA teknikleri kullanılarak yapılmıştır. Elde edilen tüm polimerler tamamıyla aromatik konjuge yapısında olduğundan, bunlar koyu kahve veya siyah renkte katılardır. TPA ve TPP ile hazırlanan polimerler birçok organik çözücünde çözünmezken, N-MDPA ile hazırlanan bu polimerler lineer yapısına bağlı olarak birçok organik çözücünde çözünmektedir. UV bölgesinde 280 ve 380 nm aralığında iki tane maksimum saptanmıştır. Bu polimerler katı halde iletken değildir. Tam aromatik yapıları sebebiyle yüksek ısı kararlılığına göstermiştir ve azo bağlarının kırılması için gerekli enerjiye denk sıcaklığa kadar dirençlidir.

Anahtar Kelimeler: Aromatik Ana Zincir Diazo Polimerleri, Konjuge Polimerler, Diazo Kenetlenmesi, Işığa Duyarlı Polimerler

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CHAPTER I. INTRODUCTION

1. INTRODUCTION

In recent years, azo group containing polymers have great attention because of their unique properties and potential technological applications. These compounds became industrially very important after first azo dye synthesized [1]. Recently, not only synthetic uses but also their photochemical and thermal applications are well understood [2].

Azobenzene is a well-known photoresponsive chromophore which can exist in two geometric isomers, trans (E) and cis (Z) form. These configurations can be easily interconverted upon UV/visible light or heat as shown Figure 1.1. [3]. Due to versatility of these photoactive systems, azobenzene and derivatives can be selectively attached to side chain, main chain, chain ends of a wide class of polymer matrix [4]. When the azobenzenes are bound or doped to a polymer system, these rapid and reversible photoisomerization results in a series of motions, consequently these motions depending on which level at occur, enable it to use for different photonic applications [5].

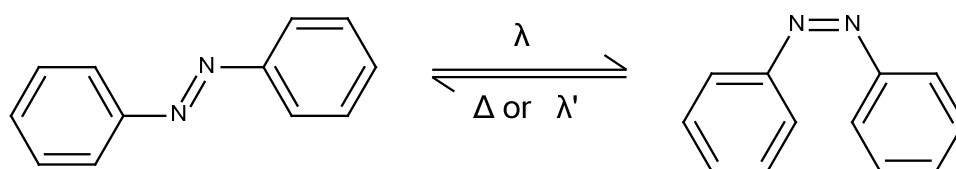


Figure 1. 1. Photoisomerization of azobenzene

The first studies of azobenzene containing polymers were azobenzene chromophore doped into polymer matrix, also known as guest-host-system. The low molecular weight azo dye and the polymer are dissolved together in the suitable solvents and film formed from the solution by spin coating onto glass sides. Later on, azobenzene functionalized polymers were studied in detail because of their better properties [4].

Although most of studies have focused on side chain azo containing polymers, main chain containing azo polymers have also been synthesized. One of the reason of main chain azo polymers being relatively rare is that azobenzene groups are attached the polymer chain ends so the mobility of polymer chain is restricted. Despite of this, the polymer backbone has still flexibility for the alignment of the main chain. Their photoinduced birefringence, surface relief gratings, second order non linear optical effects [6] and liquid crystalline properties [7] have been investigated.

Conjugated polymers have great attention because of their widespread applications such as light emitting diodes, non-linear optical devices, surface relief gratings, solar cell, chemo- and biosensors and so on [8]. These applications have motivated researchers to incorporate azo chromophores into the conjugated polymer structure [9]. For this purpose, recent studies

have focused on the synthesis of the conjugated polymers having azobenzene unit as the substituent. But, little attention has been paid to idea that azobenzene itself can be a part of conjugated polymer backbone. Poly (p-phenylene), poly (phenylene ethylene), poly (p-phenylene vinylene), such typical conjugated polymers, have synthesized with azobenzene as conjugative unit in the backbone by Izumi and co-workers [10]. Conjugated main chain azo polymers are exhibited excellent properties, for such optical, electrical and magnetic areas [11].

1.1. AZO POLYMERS

Azo polymers are the class of both aliphatic and aromatic polymers that have the azo group linkage (-N=N- bond) in the polymer matrix. [3] For various aspects, many different backbones have been used such as imides, esters, urethanes, ethers, organometallic ferrocene polymers, polycarbonates, polysilicones and conjugated polymers as polyacetylenes. But the most studied backbones are acrylates, methacrylates and isocyanates [12].

Due to the high thermal stability and photochemical isomerization of azobenzene chromophores, most of azo polymers contain aromatic azo group instead of aliphatic azo linkage. Even, the case of azo polymers maybe considered as azobenzene polymers.

Azobenzene containing polymers have been investigated for their special properties and potential technological applications such as display systems, telecommunication technologies, nonlinear optical devices, optical switching systems, holograms, surface relief gratings, optical information storage and

so on. Many of these applications are possible with azobenzene chromophore which has the efficient photoisomerization and photoinduced anisotropy. Eventough, photochemical reactions occur in such a small molecule, it can also be induced to occur in macromolecules. When this photoresponsive chromophore incorporated into the polymer backbone, changing of chromophore photoinduced configuration is expected to induce a conformation change of the polymer chain [13]. And also, low energy barrier between two excited states of azobenzene, makes its photoisomerization enable to study in the polymer backbone [14].

1.1.1. Aliphatic Azo Polymers

These polymers are commonly used for initiation step of free radical polymerization because of thermally unstable properties and decomposition into free radicals [15]. Decomposition mechanism of azo linkage occurs with homolytic cleavage of carbon-nitrogen bond. Reaction products are molecular nitrogen and radical species which may act as initiators for radical polymerization of vinyl monomers.

The other applications of aliphatic azo compounds are; to introduce thermosensitivity of polymers and obtain degradable materials. These materials keep their physical properties under one set of environmental conditions but decompose by changing conditions under control. This property is enable to produce networks for matrices or microcapsules that degrade on heating [16].

1.1.2. Aromatic Azo Polymers

Azobenzene-based chromophores doped or functionalized with polymers have received more and more attention in many research areas both fundamental and applied [17]. Aromatic azo polymers have high thermal resistant due to stability by resonance [15]. Azobenzene containing polymers in the side or main chain have been extensively studied as many different aspects in the past two decades [18].

1.1.2.1. Azobenzene Chemistry

Azobenzene is a chemical compound of two phenyl rings separated by azo -N=N- linkage. It was discovered by peter Griess at the beginning of modern organic chemistry, in 1858 [1].

Generally, azobenzene refer to the class of compounds that exhibit the core azobenzene structure with different ring substitution patterns also named as “diazenes”. All azobenzene molecules have nearly the same common properties. The strong electronic absorption of the conjugated π system is the most obvious of them. The absorption spectrum, lie anywhere from the UV to the visible red region, can be tailored via the ring substitution pattern. It allows chemical fine-tuning of color and use as dyes and colorants.

The rigid structure and large aspect ratio (r_a), which is the ratio of the length of the rigid portion to the average diameter of interest mainly to LC systems, of the azobenzene molecules make them ideal to organize into liquid crystalline (LC) media [12].

One of the most important characteristic property is the possibility of photochemically or thermally cis-trans isomerization of azobenzene. These properties enable it to improve physical and chemical properties such as viscosity, refractive index, conductivity, pH, solubility, wettability, mechanical properties, polymer morphology and so on [10].

Azobenzenes molecules can be separated mainly into three classes, according to their (n, π^*) and (π, π^*) relative energetic order, azobenzene-type molecules, aminoazobenzene-type molecules, pseudo stilbenes (Fig. 1.2).

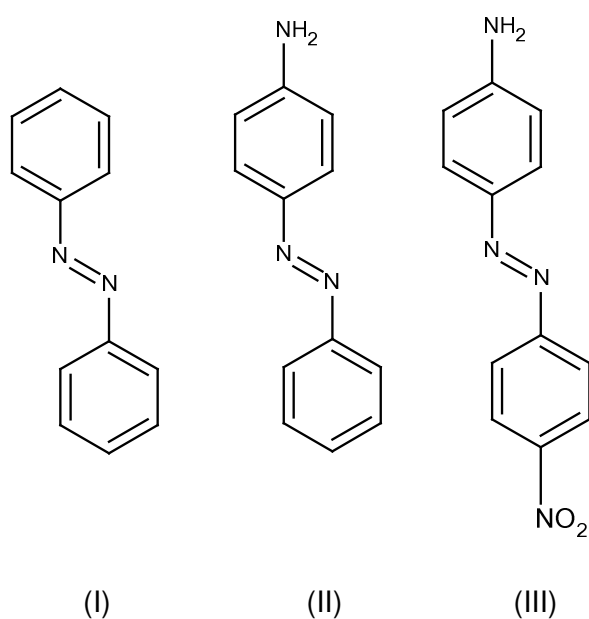


Figure 1.2. Examples of azo molecules classified as azobenzenes (I), aminoazobenzenes (II), and pseudo-stilbenes (III)

Spectroscopic character of molecule depends on substitution which is attached to azobenzene. The azobenzene type molecules, without any substituent, exhibit low intensity $n \rightarrow \pi^*$ band in the visible region of the spectrum and a higher intensity $\pi \rightarrow \pi^*$ in the UV. With adding an electron

donating group in para or ortho position (like aminoazobenzene-type molecules), the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are get closer to each other. Hence, even azobenzene type molecules don't sensitive to solvent polarity, aminoazobenzene type molecules can be sensitive. In this kind of molecules absorption bands shift to higher energy in nonpolar solvents and lower energy in polar solvents. Attaching with an electron-donor and electron-acceptor substituents to 4 and 4' position of azobenzene molecule, as pseudo-stilbene type molecules, exhibit asymmetric electron distribution referred as push/pull system. In this kind of system, $\pi \rightarrow \pi^*$ absorption band shifts to lower energy, toward the red and past the $n \rightarrow \pi^*$, are very sensitive to local environment, it allows use for some applications, such as nonlinear optical studies [12]. These significant differences between isomerization kinetics of different type of molecules, allow to design new kind of azo polymers with several properties [3].

1.1.2.2. Photochemistry of Azobenzene

Azobenzene is a well known photoresponsive chromophore and its photoinduced and thermal isomerizations have been extensively studied. Due to the azo group can exist in two geometrical isomers; the *trans* (*E*) and *cis* (*Z*) form. These two isomers converse each other by heat and light (Fig. 1.4). Between the ground state of *trans* isomer and *cis* isomer energy difference is 50 KJ/mol. Therefore, *trans* form is more stable than *cis* form. With exposed light or heat *trans* form isomerised to *cis* form, which can be converted back to the *trans* form again with photochemically and thermally.

According to Rau [19] these transformations are wholly reversible [3] (Fig.1.3.).

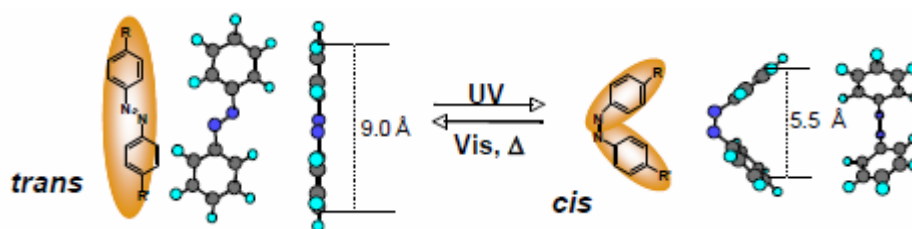


Figure 1.3. Photoisomerization of azobenzene chromophore [18]

When the azobenzene incorporated into polymer chain, series of motions occur in three levels as shown in Figure 1.4.

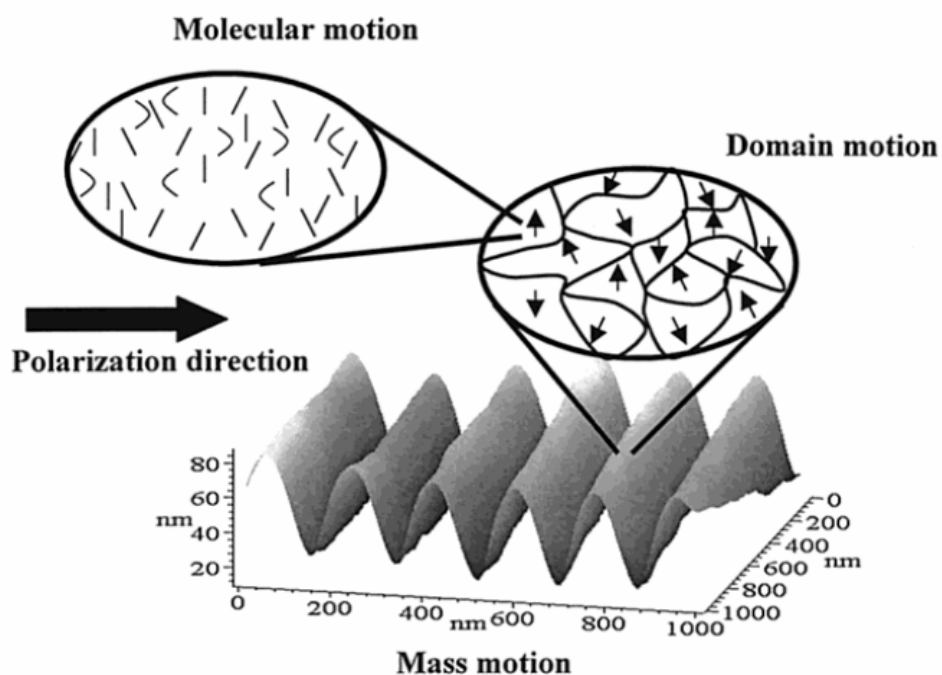


Figure 1.4. Types of photoinduced motions [20]

The first level is molecular motion which is a chromophore motion that influenced by linearly polarized light results with trans-cis-trans isomerization

cycle and reorientation of the chromophores. This behavior can be applied in the optical storage of information materials (Fig. 1.5).

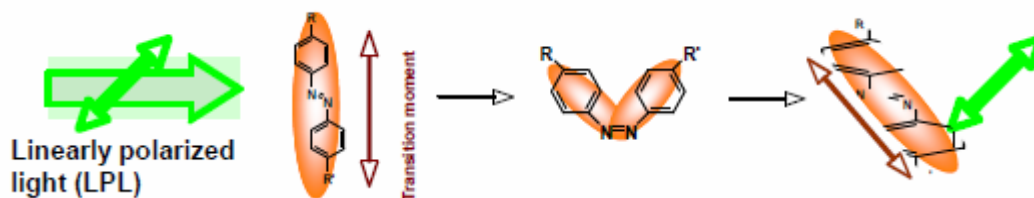


Figure 1.5. Reorientation of azobenzene chromophore. [18]

The second type of motion is domain motion which occurs at nanoscale level. At this level chromophore is part of liquid crystalline domain and when this structure is irradiated with polarized light results with whole LC domain reorientation to perpendicular direction to light polarization. The sizes of these domains are usually of the order of nanometers, the amount of moved material is greater than in the first level of motion (Fig. 1.6.).

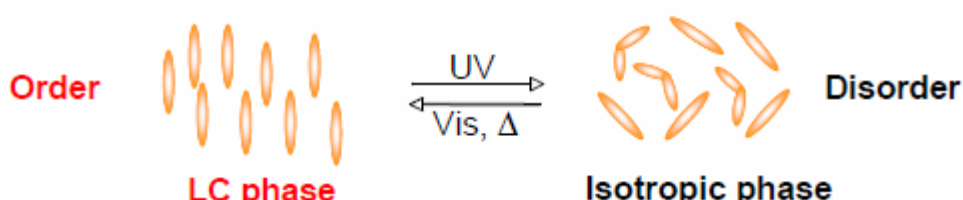


Figure 1.6. Photochemical phase transition [18]

The third type of motion is called macroscopic motion defines that the photoisomerization of azobenzenes accompany to movement of polymer material over long distances. This motion occurs not only on the mesogenic chromophore but also affect polymer chain. Consequence of this motion

occur patterns that visible with naked eye on the film surface. This behavior enables it to use in surface relief grating applications [5] (Fig. 1.7).

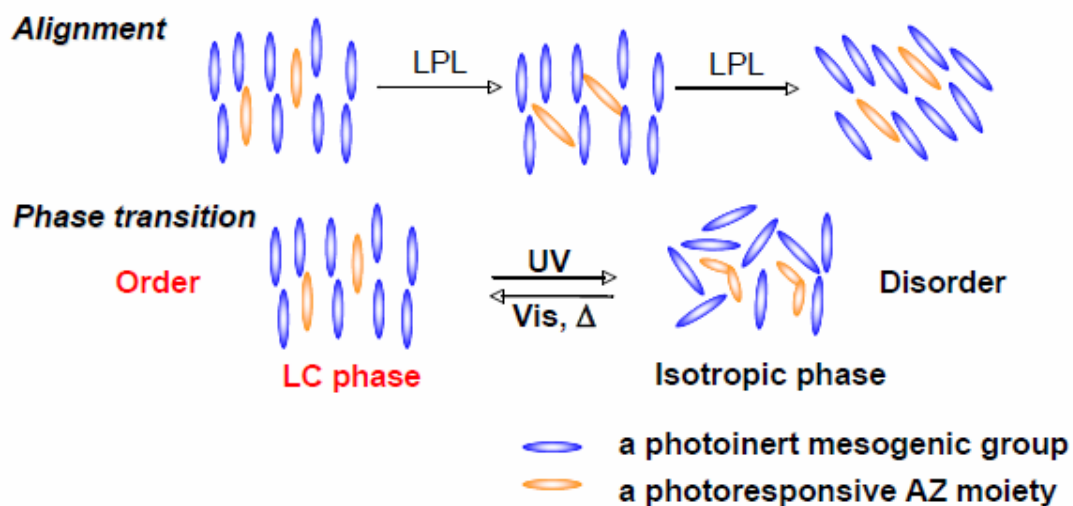


Figure 1.7. Photoinduced cooperative motion [18]

1.1.2.3. Side Chain Aromatic Azo Polymers

Polymers containing substituted azobenzene groups are named as side chain aromatic azo polymers. These polymers have great interest in the area of azo polymers as demonstrated by the huge amount of publications appeared in the literature [21]. Due to their potential applications in fields such as optical data storage, optical switching and non-linear optical materials many efforts have been made to design and synthesize new high- T_g aromatic azo polymers, such as polyacrylate containing fully aromatic azo side chains [22].

One of the other application area of this polymers are LC systems. For LC phases to be present the mobility is required. When the azobenzene attaches the polymer backbone less than 6 alkyl units long, the polymer will exhibit an

amorphous and isotropic solid-state phase as typical LC phases form [12] (Fig. 1.8).

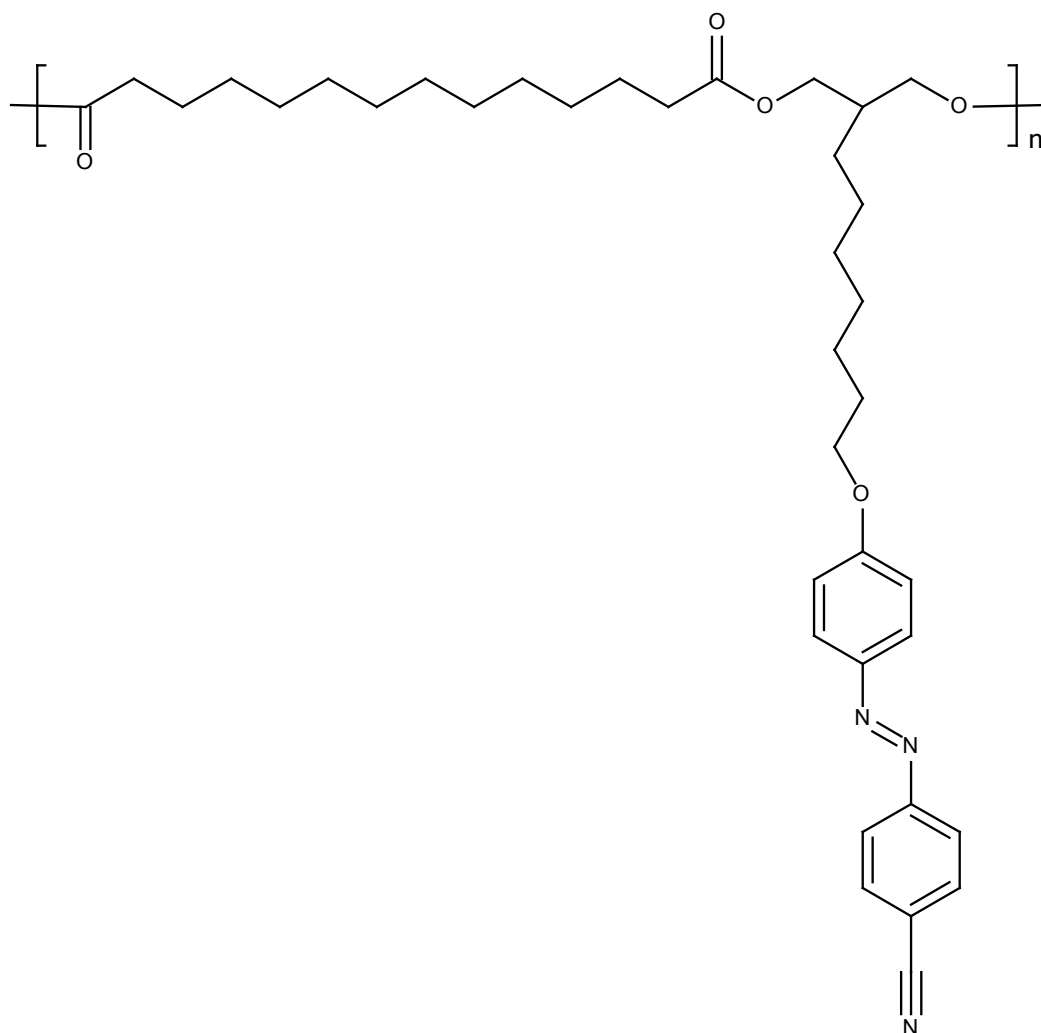


Figure 1.8. A typical liquid-crystalline side-chain azobenzene polymer

These kinds of polymers have much attention due to their tendency to make large optical birefringence by photoisomerism when irradiated by polarized light. This property enables it to use in the surface relief gratings (SRGs) films. By photoisomerization of the azobenzenes, electrons move from electron donating groups such as $-N=N-$, to electron acceptor groups like $-NO_2$, $-CN$, $-COOH$, $-CHO$ and $-SO_2H$, this electron transfer initiate SRGs. In

literature, most studies have focused on SRG applications of side chain azopolymers [23] (Fig. 1.9).

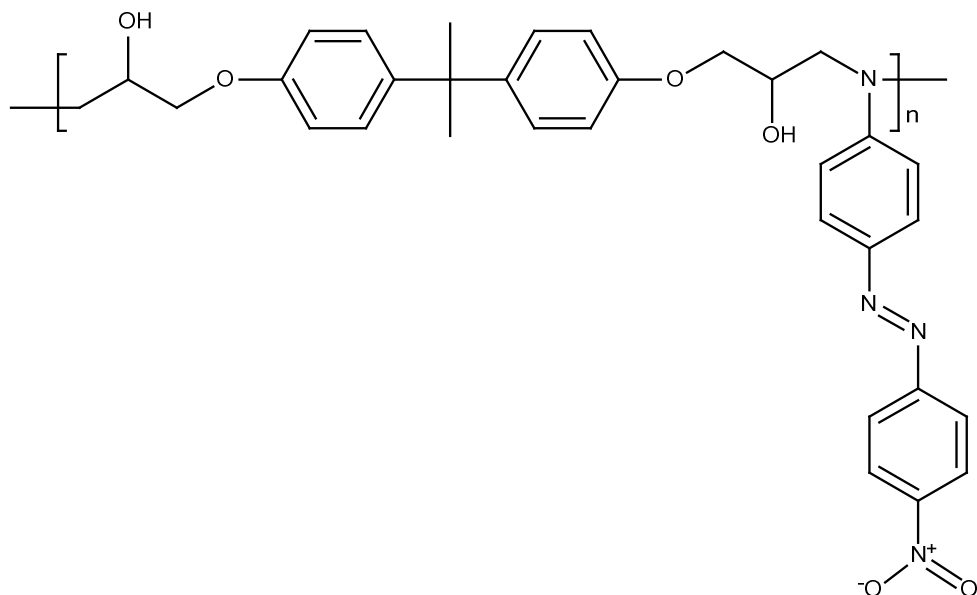


Figure 1.9: Aniline based side chain azo polymer for SRGs

1.1.2.4. Main Chain Azo Polymers

When the azobenzene groups are bound to the backbone at both end of the polymer named as main chain azo polymers. Between the excited trans and cis states of azobenzene separated by a low-energy barrier. Such a low value for the energy barrier between the trans and cis excited states of azobenzene makes the study of photoisomerization of azobenzene residues in the backbone of polymers [14].

There are a few example of azobenzene units containing polymers in the backbone apart from azobenzene substituted polymers [24]. These kinds of polymers have been investigated for the stability of photoinduced properties and third order NLO properties.

The formation of the surface grating in the main chain azo polymers has been investigated on the film of polyurea with azo aromatic chromophores (Fig. 1.10). Due to the rigid nature of main chain azo polymers, the mobility of the azobenzene chromophores are restricted, so they were showed slow formation on surface grating applications [25].

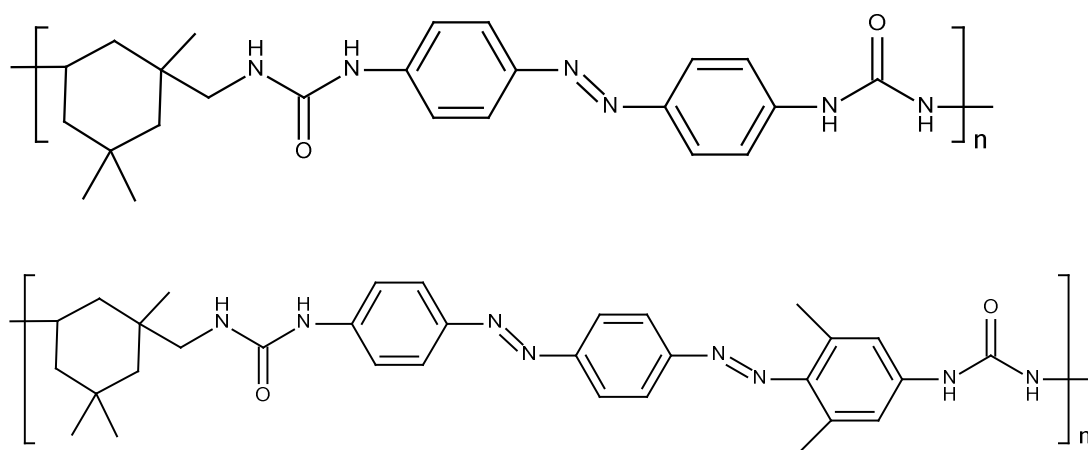


Figure 1.10. Chemical structures of the main chain azo functionalized polyurea

Introducing azobenzene linkages in the polymer backbone can improve thermal stability and allow broad application as an engineering plastic. In literature, flame-retardant polyamide containing azobenzene moieties in the main chain with high T_g was synthesized [26] (Fig. 1.11).

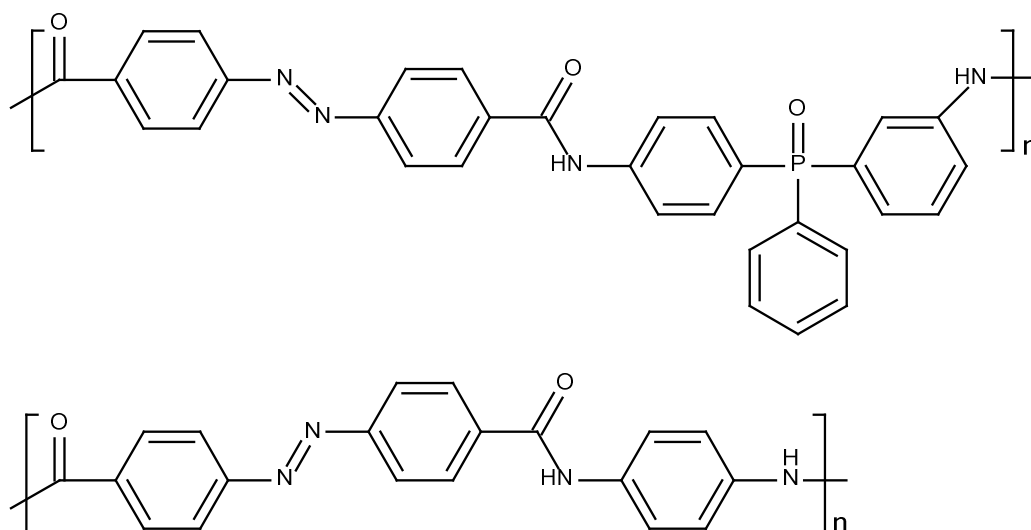


Figure 1.11. Chemical structures of the main chain azobenzene containing polyamide

Azo polyaramide main chain polymers were studied not only for their high thermal stability properties but also lyotropic liquid crystal (LC) behaviours. The advantages of rigid, regular and symmetrical main chain to enhancement of thermal stability, crystallinity and formation of LC phase. These kinds of polymers are candidates for potential optical techniques and were synthesized by researchers [27].

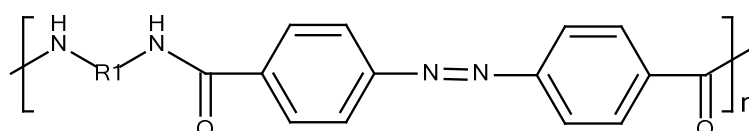


Figure 1.12. Chemical structures of the azo polyaramide

With different backbones main chain azo polymers have been also synthesized and their LC properties have been studied in literature [7].

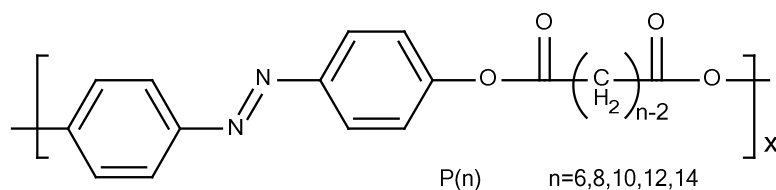


Figure 1.13. Chemical structures of the main chain segmented liquid crystalline polymers

Because of solubility problem of main chain azo polymers some researchers were focused on this issue and modified the insoluble main chain azo polymers by ionization method to increase solubility. As a result, they were succeeded these kinds of polymers to dissolve in common organic solvents and form polyions [28].

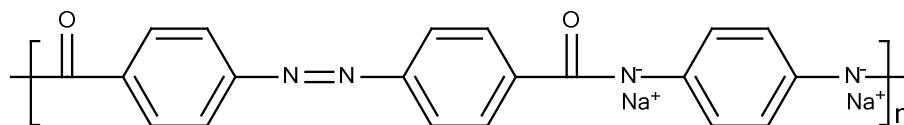


Figure 1.14. Chemical structures of the azo polyamide anion

1.1.2.4.1. Conjugated Azo Polymers

The term of conjugated azo polymer defines the polymer which has azo group in the polymer backbone is conjugated along the main chain. Conjugated polymers were intensively investigated in two decades of the last century because of their uncommon electrical conduction, as well as opto-electrical and electro-optical properties. Conjugated polymers are semiconductors that have unsaturated bonds along the chain have important

applications in modern science and daily life. Many types of conjugated polymers have been synthesized but the azobenzene itself has not been regarded as a conjugative building unit. However these kinds of polymers are candidates for functional materials with unexpected optical, electrical and magnetic properties [29].

Izumi and co-workers [10] have been synthesized different kinds of main chain azo conjugated polymers based on poly(phenylenevinylene) (PPV) and poly(p-phenylene) (PPP) backbone with different substituent (Fig. 1.15.).

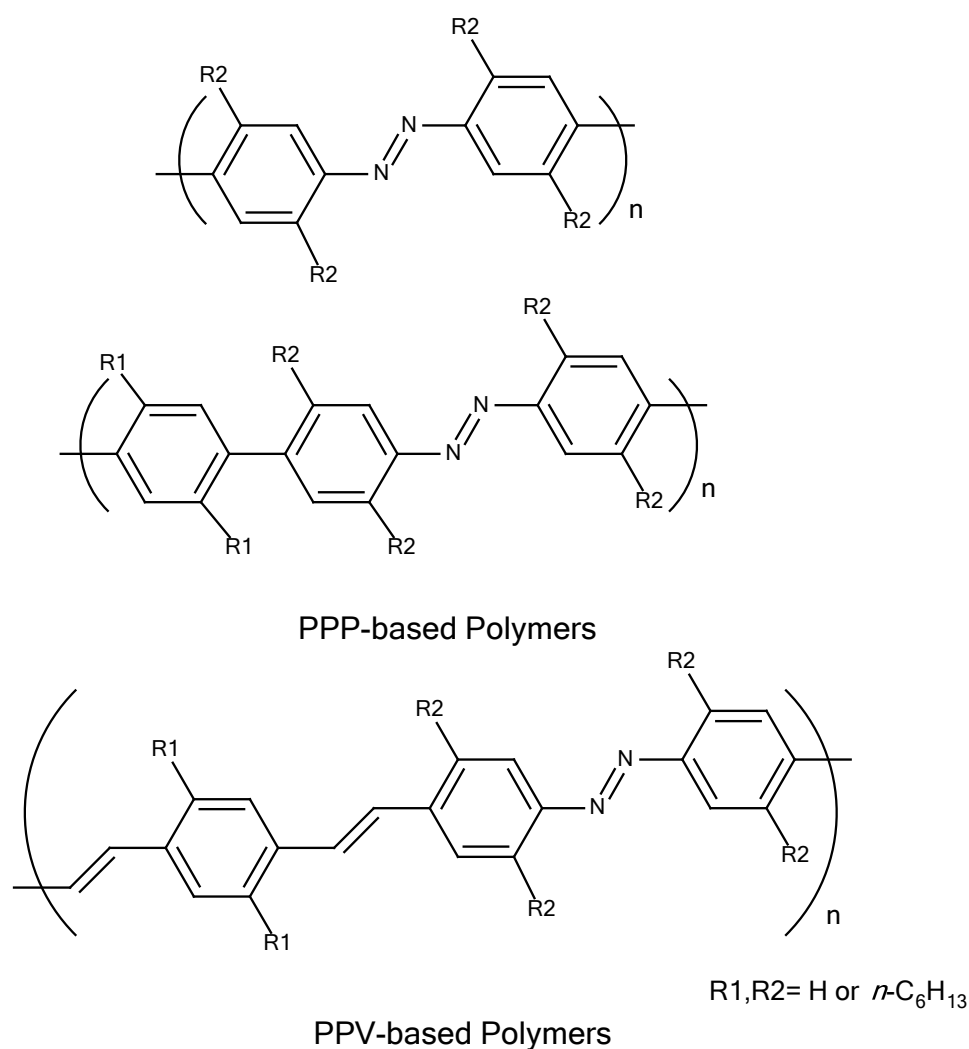


Figure 1.15. Chemical structures of the PPP and PPV based polymers

In 2000 two kinds of conjugated main chain azo polymer (Fig. 1.16.) have been synthesized by Timpu and co-workers [30] and reported that these polymers are real photoconductors between 350 and 600 nm.

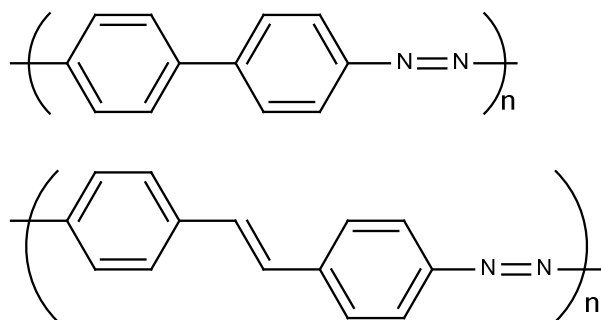


Figure 1.16. Chemical structures of the azo conjugated polymers

1.2. FORMATION OF AZO GROUP

Synthesis of aromatic azo compounds has great attention due to their widespread application area [31]. Azo group can be obtained by various synthesis methods. These methods are oxidation of primary amines, reduction of nitro group, diazotization as common methods [32], and deposition method which is based on decomposition of aromatic azides as new methods [30] (Fig. 1.17.).

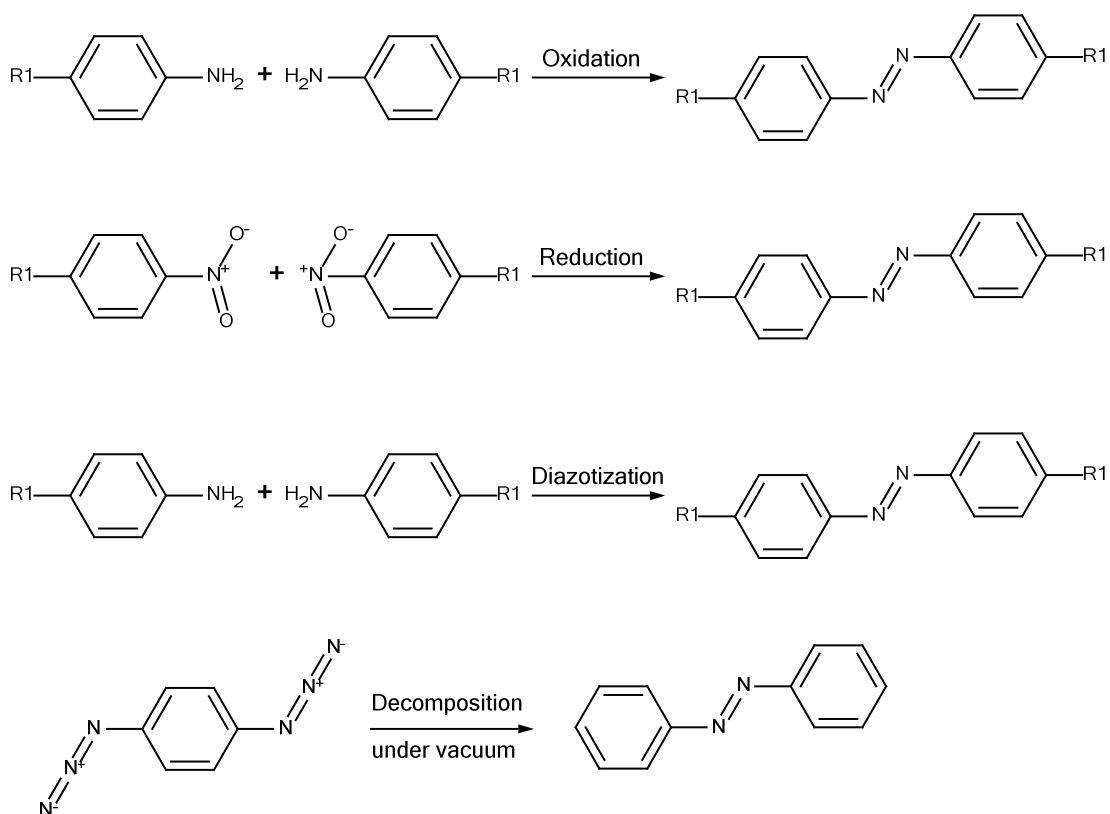


Figure 1.17. Synthesis methods of aromatic azo compounds

1.2.1. Oxidative Coupling

Oxidative coupling is a widely used method in the synthesis of azobenzenes. The oxidation of amines to azobenzene has been achieved with a wide variety of oxidizing reagents as manganese dioxide (MnO_2), permanganate ($KMnO_4$), sodium perborate and boric acid ($NaBO_3 / H_3BO_3$), lead tetracetate ($Pb(OAc)_4$), O_2 - Cu_2Cl_2 -pyridine and the other metal containing compounds [32].

1.2.1.1. O₂-Cu₂Cl₂-Pyridine

Primary aromatic amines such as aniline can be converted to azobenzenes by Cu⁺ catalyzed oxidation with oxygen and pyridine. This method has been utilized to synthesize azo polymers from aromatic diamines [9].

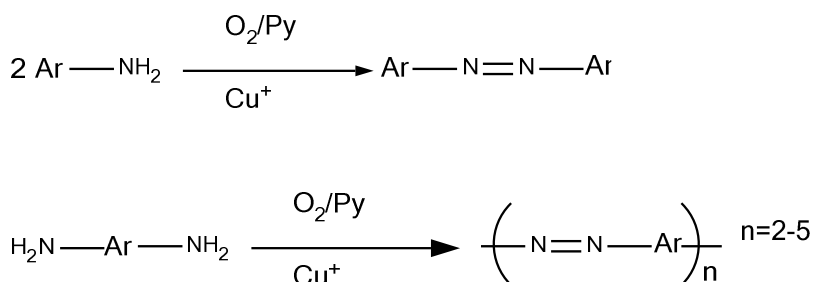


Figure 1.18. Catalyzed oxidative coupling of amines to azo derivatives

The active catalyst system can be obtained by oxidation of copper salt in presence of a nitrogen base or Cu₂Cl₂ or Cu₂(OAc)₄ can be also used. Possible mechanism is that copper ion complexed with amino group of the starting material then oxidizes them aids in the coupling of resulting species. During this reaction copper complex reoxidized by oxygen (or H₂O₂) [33].

1.2.1.2. NaBO₃/H₃BO₃

The synthesis of azobenzene derivatives from aromatic amines via the oxidation with sodium perborate has been reported [9]. In this method, coupling of aromatic diamines can also result in side reactions. Beside azobenzene, various amounts of azoxy compounds can be present at the end of reaction.

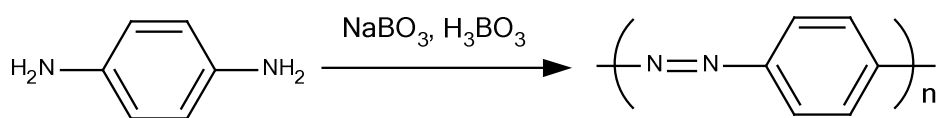


Figure 1.19. Polymerization of with perborate/boric acid oxidative coupling reaction

1.2.2. Diazotization

This method consists of two simple steps. The first one is preparing diazonium ion and the second one is coupling reaction. Usually, diazonium salts can be prepared from treatment of equivalent aqueous sodium nitrite solution with aromatic amine in mineral acid at 0 °C.

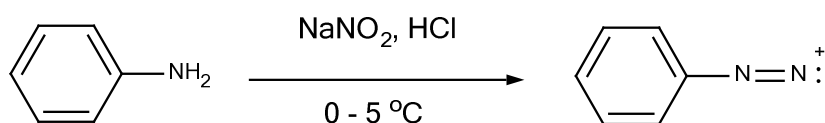


Figure 1.20. The formation of diazonium ion.

A low temperature is advantageous for good stability of diazonium compound. But, this advantageous outweigh the low rate of reaction and poor solubility of the starting material. In cases where the solubility is low higher temperatures such as 10-15 °C may be used or may be carried out in polar solvents such as dimethylformamide.

In second step, coupling component is attacked by the diazonium salt at a center with high electron density usually para position. Due to the attacking

species, substitution is mostly para to activating group. This method is based on reactivity of aromatic diazonium salts [34].

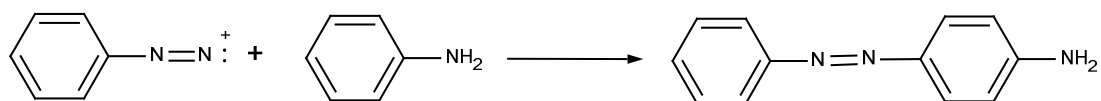


Figure 1.21. The azo coupling reaction.

1.2.3. Reduction of Nitro

1.2.3.1. Metal Free Coupling

This method is the alternative reduction method which is used glucose instead of metal compounds [32]. In literature, 4,4'-azodibenzoic acid has been synthesized from 4-nitrobenzoic in an aqueous solution of NaOH and treatment with an aqueous solution of glucose with high yields [26].

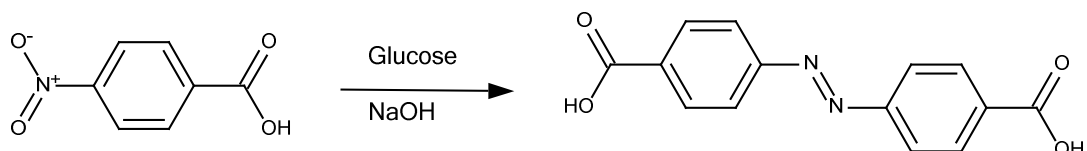


Figure 1.22. Synthesis of 4,4'-Azodibenzoic acid with metal free coupling

1.2.3.2. Coupling With Metals

1.2.3.2.1. Coupling with Lead (Pb) Powder

Srinivasa and co.workers [35] reported the synthesis of azo compounds by catalytic transfer hydrogenation of nitroarenes by using lead powder with

triethylammonium formate in methanol at room temperature (Fig. 1.23.). In this method, lead powder have been used for reduction of organic compounds and triethylammonium formate have been used as a hydrogen donor.

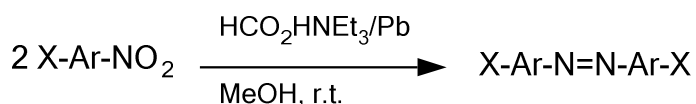


Figure 1.23. Formation of azo with Pb powder

1.2.3.2.2. Coupling with Zinc (Zn) Powder

Azobenzene derivatives have been synthesized from nitro compounds by reduction reaction using zinc in a basic medium. Sukwattanasinitt et al. [36] reported the synthesis of cyclic azobenzenes by reductive coupling reactions between two nitrobenzene groups with zinc in the presence of NaOH in isopropanol.

K. Maie et al. [37] synthesized 4,4'-hydroxymethyl azobenzene with reductive coupling of 4-nitrobenzyl alcohol under the basic conditions with Zn powder.

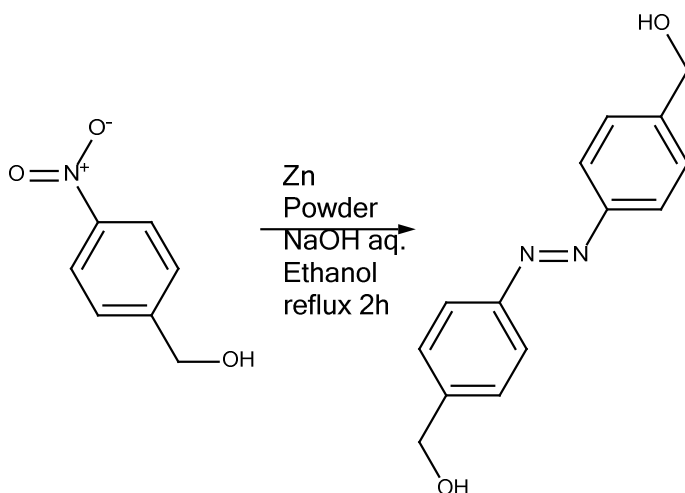


Figure 1.24. Synthesis 4,4'-hydroxymethyl azobenzene with Zn

1.2.4. Decomposition of Azides

In 2000, Timpu et al. [30] synthesized two different azo conjugated polymers using with deposition method which allows obtaining layers of azo-conjugated polymers by the thermal decomposition of aromatic diazides in vapor state. This method is mainly based on highly reactive intermediaries suffer recombination and reaction with nitrene radicals to form azo products in vacuum or inert atmosphere.

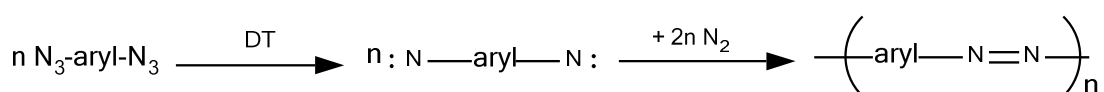


Figure 1.25. Expected thermolysis of aromatic diazides

4,4'-Diazidodiphenyl (DADP), 4,4'-diazidostilbene (DASB) and 1,5-diazidonaphthalene (DANP) were used as starting material in mentioned study (Fig. 1.27.). But only two azo-conjugated polymers resulted from DADP and DASB (Fig. 1.28.). This failure explained by the low decomposition temperature of DANP.

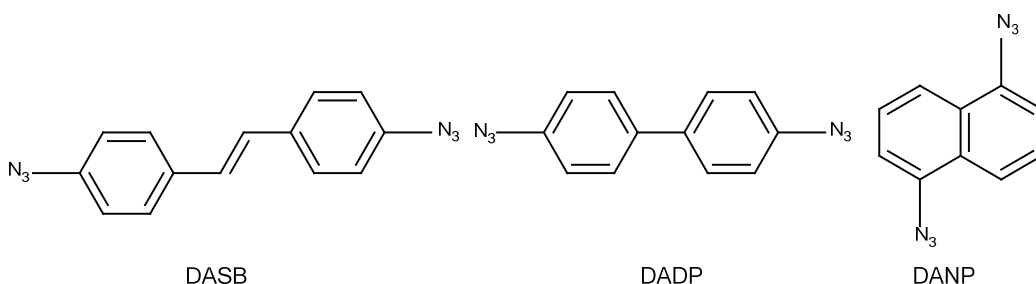


Figure 1.26. Chemical structure of starting materials

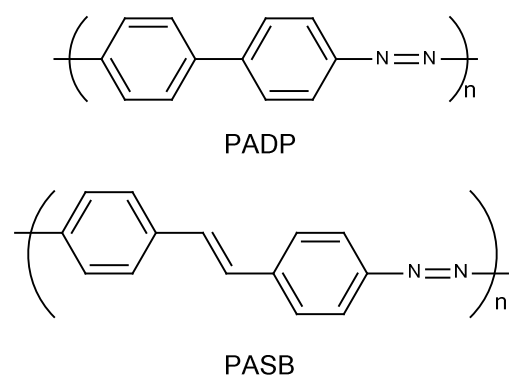


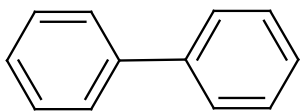
Figure 1.27. Chemical structure of resulted polymers

CHAPTER II. EXPERIMENTAL PART

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1. MATERIALS

1. Biphenyl



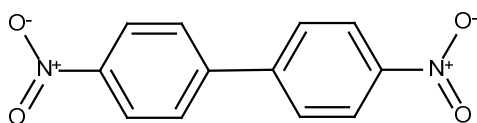
Molecular Weight: 154.21g/mol

Melting Point: 68-70 °C

Purification: Used as received from Sigma Aldrich (Purity: 99.5%).

2. 4,4'-Dinitrobiphenyl

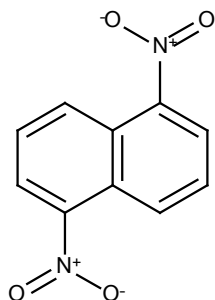
Synthesized from biphenyl as followed article [38].



Molecular Weight: 244.2 g/mol

Melting Point: 242 °C

3. 1,5'-dinitronaphthalene

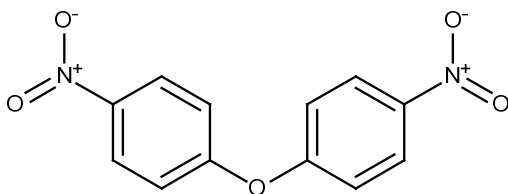


Molecular Weight: 218.17 g/mol

Melting Point: 214 °C

Purification: Used as received from Sigma Aldrich (Purity: $\geq 97\%$).

4. 4,4'-dinitrobiphenyl ether

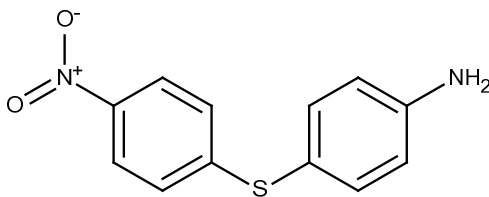


Molecular Weight: 260.2 g/mol

Melting Point: 140-145 °C

Purification: Used as received from Sigma Aldrich (Purity: 96%).

5. 4-amino-4'-nitro-biphenyl sulfide (ANBS)

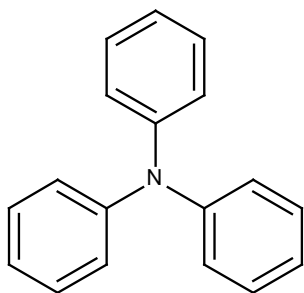


Molecular Weight: 246.29 g/mol

Melting Point: 143-145 °C

Purification: Used as received from Sigma Aldrich (Purity: 98%).

6. Triphenylamine (TPA)

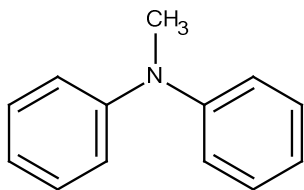


Molecular Weight: 245.32 g/mol

Melting Point: 127 °C

Purification: Used as received from Sigma Aldrich (Purity: 98%).

7. N-Methyl Diphenylamine (N-MDPA)

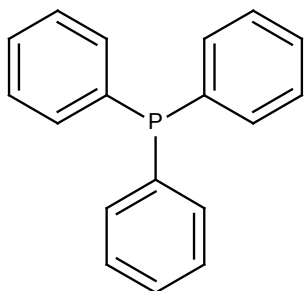


Molecular Weight: 183.25 g/mol

Boiling Point: 296-297 °C

Purification: Used as received from Sigma Aldrich (Purity: 96%).

8. Triphenylphosphine (TPP)



Molecular Weight: 262.29 g/mol

Boiling Point: 79-81 °C

Purification: Used as received from Sigma Aldrich (Purity: 99%).

9. Other Materials

Toluene, acetone, ethanol, hydrochloric acid 35% (HCl), iron (III) chloride (FeCl₃), activated charcoal, hydrazine monohydrate (N₂H₄), potassium carbonate (K₂CO₃), sodium hydroxide (NaOH), Zinc dust (Zn) are used in their commercial forms.

2.2. EXPERIMENTAL PROCEDURE

This study was carried out in three steps. The first step is the selective reduction of dinitro compounds to nitro-amine derivatives. 4,4'-dinitrobiphenyl, 1,5'-dinitronaphthalene, 4,4'-dinitrobiphenyl ether was reduced to 4-amino-4'-nitrobiphenyl (ANBP), 1-amino-5'-nitro-naphthalene (ANNP), 4-amino-4'-nitro-biphenyl ether (ANBE) respectively by modified selective reduction technique. Only 4-amino-4'-nitro-biphenyl sulfide (ANBS) was purchased.

The second step is the azo group formation from nitro-amine compounds by the metal catalyzed reduction of nitro groups, using Zn powder in aqueous hydroxide base.

The last step is the diazocoupling type polymerization of diaminoazobenzene monomers with triphenylamine (TPA), triphenylphosphine (TPP) and N-methyldiphenylamine (N-MDPA). The method used is a traditional method based on treatment of aromatic amines with nitrous acid and then with an activated aromatic ring. The resultant 12 different kinds of products characterized via $^1\text{H-NMR}$, FTIR, DSC, TGA techniques.

2.2.1. Synthesis of nitro amine derivatives

2.2.1.1. Synthesis of 4-amino-4'-nitrobiphenyl (ANBP)

In a 1 L three necked round-bottomed flask equipped with a reflux condenser. 4,4'-Dinitrobiphenyl (25 g, 0.1 mol) was dissolved in 500 mL boiling toluene and then 1 mol activated charcoal and 0.0011 mol of iron (III)

chloride were added. Hydrazine monohydrate (8.5 g, 0.17 mol) was added drop wise over 15-20 minutes, as reducing agent, under continuous refluxing. After the addition of hydrazine monohydrate was completed, the reaction mixture was stirred an additional 35 min. The hot reaction mixture was filtered through a hot funnel. The residual material on activated charcoal was extracted with a 150 mL of boiling acetone. Previous filtrate and acetone extract were combined and concentrated to $\frac{1}{3}$ of their original volume. Nitroamine was separated as an aqueous solution of amine hydrochloride salt by adding 50 mL of 35% HCl solution. The aqueous phase was separated and neutralized with 10% K_2CO_3 solution. The orange colored nitroamine solid was filtered and washed with 400 mL water. Crude product was purified by recrystallization from toluene [38]. Yield 65%, mp 202-204 °C. FTIR (KBr), ν (cm^{-1}): 3385(NH_2), 3489(NH_2), 1627, 1587, 1496, 1330(NO_2), 1278, 1207, 1112, 825. UV-VIS, λ_{max} (nm): 278, 400.

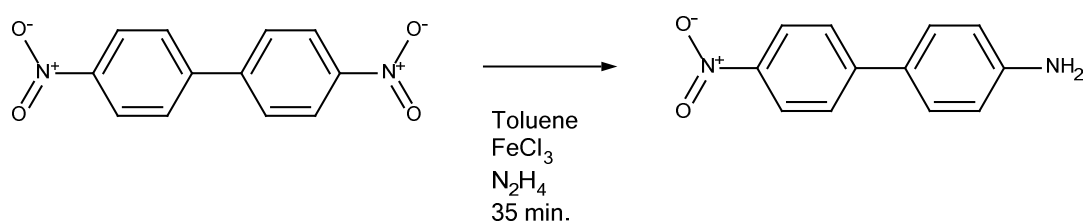


Figure 2.1. Synthesis of 4-amino-4'-nitrobiphenyl (ANBP)

2.2.1.2. Synthesis of 1-amino-5-nitronaphthalene (ANNP)

From 1,5'-dinitronaphthalene, ANNP was prepared by the same method as ANBP synthesis. Only for recrystallization 10% ethanol water solution was used different from toluene. The dark red colored nitroamine (ANNP) solid

was obtained with success. Yield 75%, mp 182 °C. FTIR (KBr), ν (cm^{-1}): 3414(NH_2), 3331(NH_2), 1629, 1570, 1512, 1321(NO_2), 1278, 1130, 777. UV-VIS, λ_{max} (nm): 280, 340, 440.

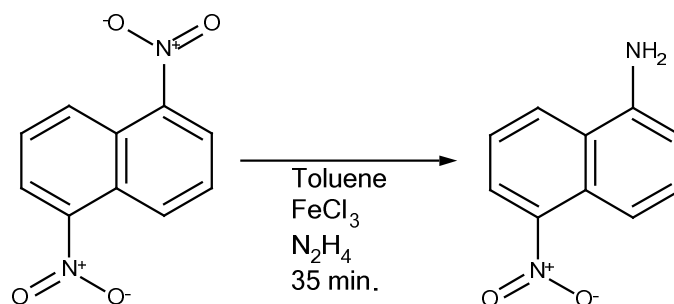


Figure 2.2. Synthesis of 1-amino-5'-nitronaphthalene (ANNP)

2.2.1.3. Synthesis of 4-amino-4'-nitro-biphenyl ether (ANBE)

4,4'-dinitro-biphenyl ether was selective reduced to obtain ANBE exactly the same method as synthesis ANBP. The yellow colored nitroamine solid was achieved. Yield 65%, mp 132 °C. FTIR (KBr), ν (cm^{-1}): 3444(NH_2), 3365(NH_2), 1627, 1585, 1500, 1340(NO_2), 1286, 1112, 875. UV-VIS, λ_{max} (nm): 308.

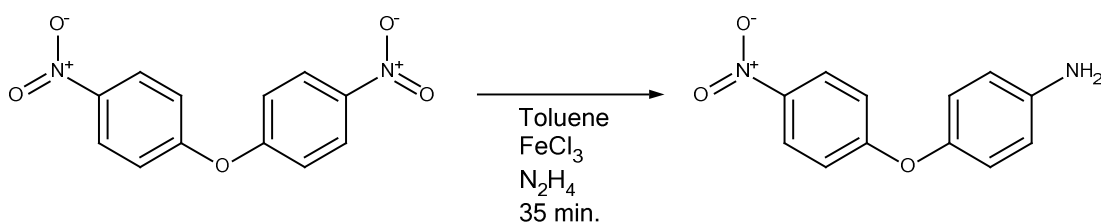


Figure 2.3. Synthesis of 4-amino-4'-nitro-biphenyl ether (ANBE)

2.2.2. Dimerization of nitro-amine compounds

This step is the synthesis of monomers. In our study, referenced method [39] was adapted to this work.

2.2.2.1. Synthesis of 4,4'-bis (p-aminophenyl) azobenzene (cANBP)

Three necked round bottomed flask with a reflux condenser was placed in a heating bath. 4-amino-4'-nitrobiphenyl (ANBP) (0.02 mol, 4.28 g) was dissolved in 200 ml ethanol. After all solid was dissolved in 4.2 g NaOH/30 ml water (3.5M) and Zn powder (0.02 mol, 1.7 g) added. Mixture was stirred 24 hours under reflux. 30% excess of initial amount of Zn dust was added to mixture at 20th hrs of reaction. At the end of 24 hours the mixture was filtered while hot to remove Zn dust. Solvent ethanol was removed in rotary evaporator. Residue solid in water was treated with 10% v/v HCl solution to remove zinc salts from crude product. The mixture was stirred for 2 hours. Solid was filtered and adjusted to 7.0-9.0 by adding 10% NaOH solution. Dark orange colored solid was filtered and washed plenty of water, dried under high vacuum at 50°C. Final purification was carried out in trace water free acetone to remove unreacted starting aminonitro compound. The resultant monomer was code as cANBP. Yield 86%, mp 267-269°C. FTIR (KBr), ν (cm⁻¹): 3427, 3338(NH₂), 3213(NH₂), 1593, 1489, 1273, 821. UV-VIS, λ_{max} (nm): 280, 426. ¹H-NMR (400 MHz, DMSO d-₆), δ_{H} (ppm): 5.5 (4H; N-H), 6.75 (4H; Ar-H), 7.6 (4H; Ar-H), 7.8 (4H; Ar-H), 8.3 (4H; Ar-H). RAMAN ν (cm⁻¹): 1138, 1239, 1394, 1441(-N=N-), 1589.

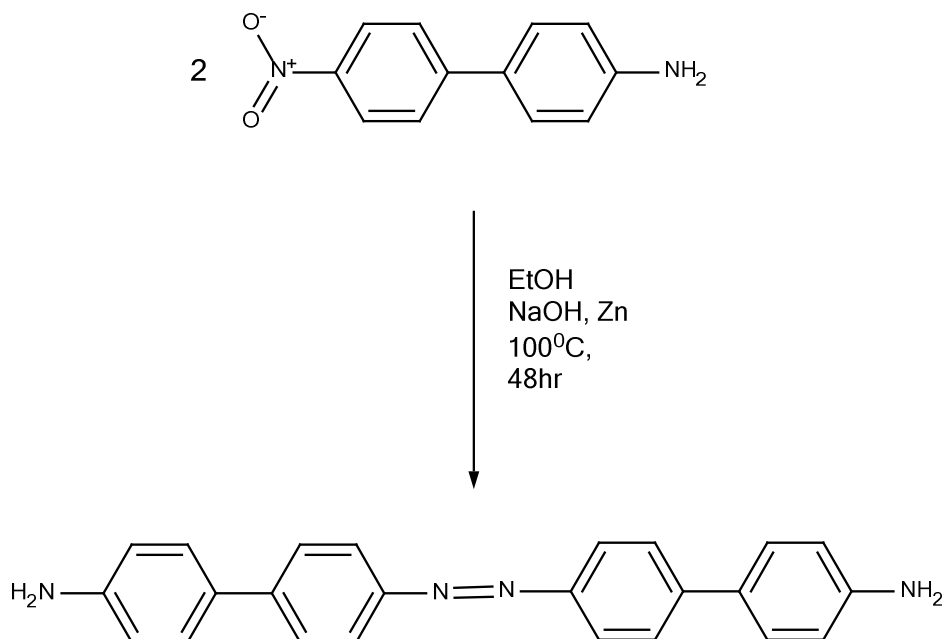


Figure 2.4. Synthesis of 4,4'-bis(p-aminophenyl) azobenzene (cANBP)

2.2.2.2. Synthesis of 5,5'-diamino-1,1'-azonaphtalane (cANNP)

Black colored solid was obtained by the same coupling method as the synthesis of cANBP. The resultant monomer was code as cANNP. Yield 50.2%, mp 222-236°C. FTIR (KBr), ν (cm^{-1}): 3462, 3354(NH_2), 3215(NH_2), 1620, 1593, 1510, 1433, 1408, 1282, 781. UV-VIS, λ_{max} (nm): 280, 348, 462. ^1H -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): 5.5 (2H; N-H), 4.8 (2H; N-H), 6.6-7.4 (12H; Ar-H).

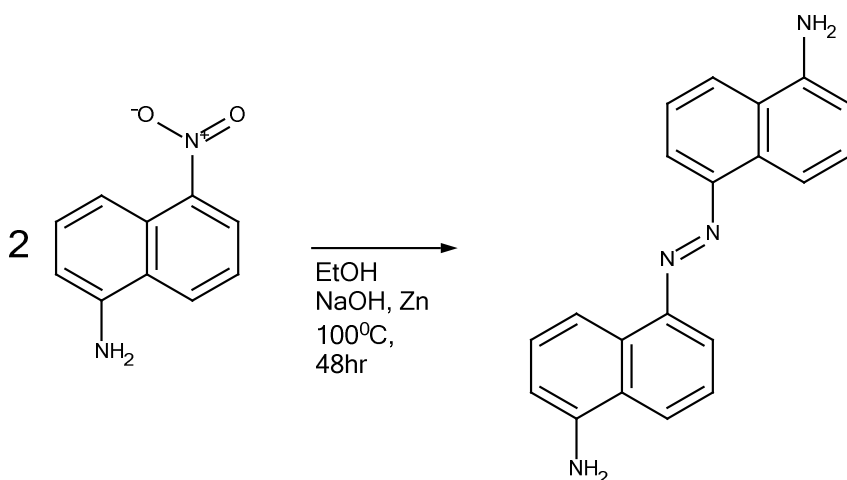


Figure 2.5. Synthesis of 5,5'-diamino-1,1'-azonaphtalene (cANNP)

2.2.2.3. Synthesis of 4,4'-bis (p-aminophenoxy) azobenzene (cANBE)

Dark green colored solid was obtained by the same coupling method as the synthesis of cANBP. The resultant monomer was code as cANBE. Yield 65.6%, mp 267-269 °C [33]. FTIR (KBr), ν (cm^{-1}): 3398, 3308(NH_2), 3209(NH_2), 1581, 1508, 1492, 1232, 1151, 840. UV-VIS, λ_{max} (nm): 362. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$), δ_{H} (ppm): 5.1 (4H; N-H), 6.6 (4H; Ar-H), 6.8 (4H; Ar-H), 7.0 (4H; Ar-H), 7.8 (4H; Ar-H).

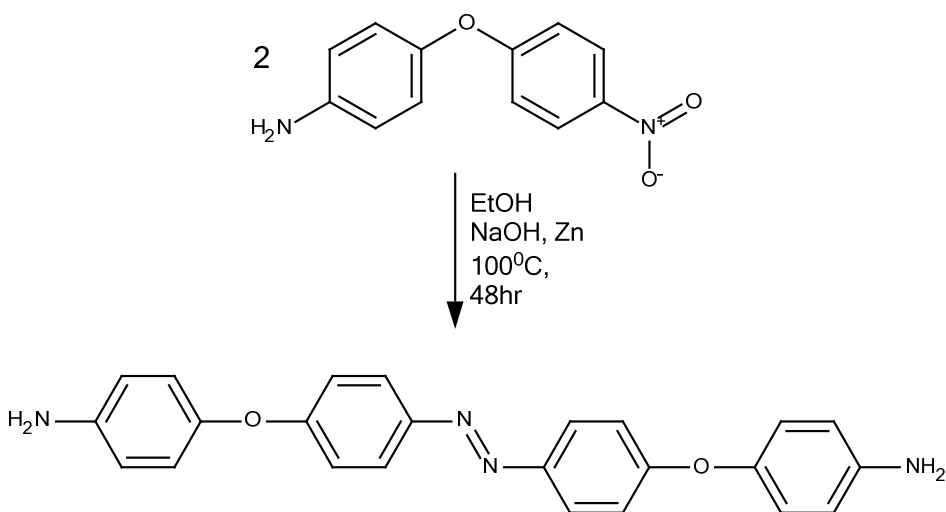


Figure 2.6. Synthesis of 4,4'-bis(p-aminophenoxy)azobenzene (cANBE)

2.2.2.4. Synthesis of 4,4'-bis (p-aminophenylthio) azobenzene (cANBS)

Orange solid was obtained by the same coupling method as synthesis of cANBP. The resultant monomer was code as cANBS. Yield 83.3%, mp 267-269 °C. FTIR (KBr), ν (cm^{-1}): 3446, 3340(NH_2), 3217(NH_2), 1631, 1595, 1577, 1496, 1303, 1182, 1078, 829. UV-VIS, λ_{max} (nm): 278, 396. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO } d_6$), δ_{H} (ppm): 5.6 (4H; N-H), 6.6 (4H; Ar-H), 7.1 (4H; Ar-H), 7.2 (4H; Ar-H), 7.7 (4H; Ar-H).

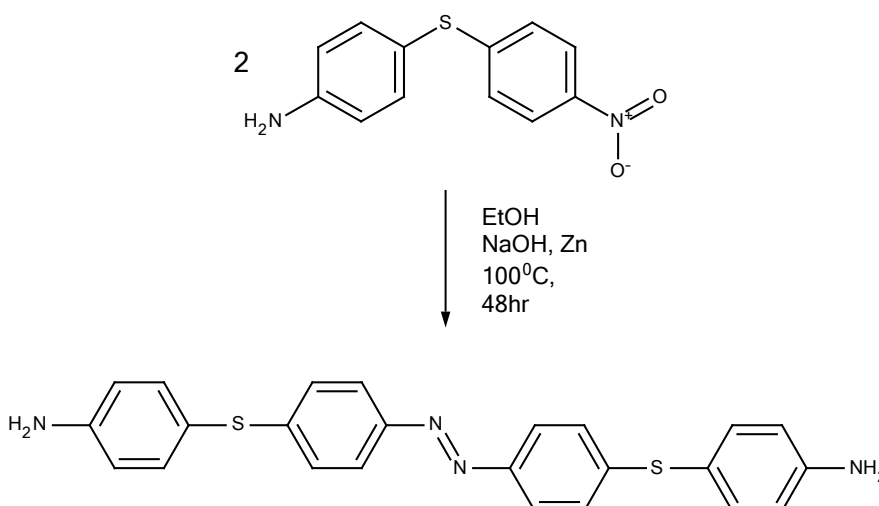


Figure 2.7. Synthesis of 4,4'-bis(p-aminophenylthio)azobenzene (cANBS)

2.2.3. Polymerization of Coupled Azo Monomers with TPA & TPP & N-MDPA

2.2.3.1. Polymerization of 4,4'-bis (4-aminophenyl) azobenzene with TPA [Poly(TPA-cANBP)]

4,4'-bis(4-aminophenyl) azobenzene (0.005 mol, 1.82 g) was dissolved in a homogenous mixture of 20 mL glacial acetic acid and 1.4 ml sulfuric acid.

Aqueous solution of sodium nitrite (0.015 mol) was prepared by adding 0.9 mL water. This solution was added dropwise into acid solution at 0°C to obtain diazonium salt. After adding nitrite aqueous solution, mixture was stirred additional one hour at 0°C. Diazonium salt was added drop wise into TPA (0.0025 mol) in 40 mL DMF solution. The diazotization reaction was carried out with stirring at room temperature for 48 hours. Then, the solution was poured into an excess of water to precipitate polymer. The precipitate was filtered and washed with water several times, and dried. The product was refluxed in 40 mL acetone to remove both low molecular weight polymer and unreacted starting material. After one hour stirring, the product was filtered, washed with acetone and dried at 50°C in a vacuum oven. The resultant polymer was code as Poly(TPA-cANBP). For the characterization FTIR, UV-VIS, RAMAN, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3421, 3032, 1658, 1597, 1518, 1483, 1452, 1396, 1342, 1396, 1342, 1157, 1078, 1003, 831. UV-VIS, λ_{max} (nm): 284, 392. RAMAN, ν (cm^{-1}): 1135, 1283, 1404(-N=N-), 1444(-N=N-), 1586. $^1\text{H-NMR}$ (400 MHz, DMSO d_6), δ_{H} (ppm): Failed because of solubility problem.

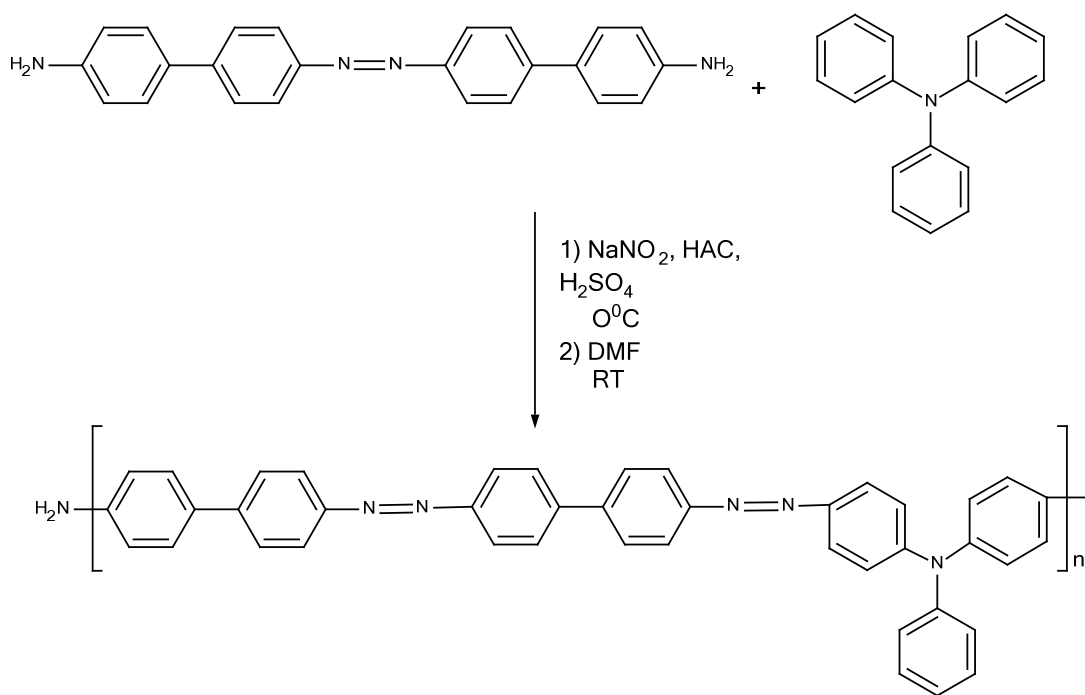


Figure 2.8. Synthesis of Poly(TPA-cANBP)

2.2.3.2. Polymerization of 5,5'-diamino-1,1'-azonaphtalane with TPA [Poly(TPA-cANNP)]

The polymerization of cANNP with TPA was achieved by the same method the synthesis of Poly(TPA-cANBP). The resultant polymer, Poly (TPA-cANNP), was black colored solid. For the characterization ^1H -NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3432, 1653, 1590, 1498, 1385, 1260, 1139. UV-VIS, λ_{max} (nm): Failed ^1H -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): Failed because of solubility problem.

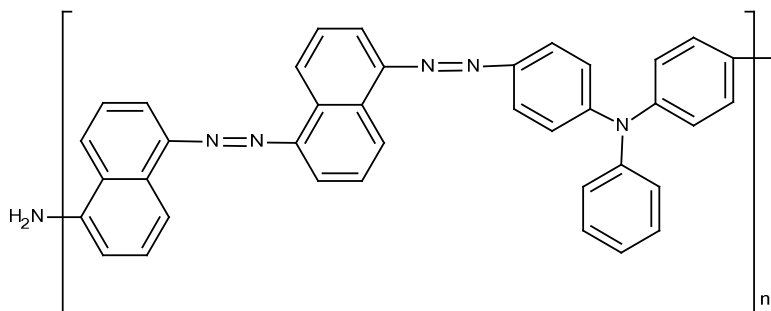


Figure 2.9. The chemical structure of Poly(TPA-cANNP)

2.2.3.3. Polymerization of 4,4'-bis (4-aminophenoxy) azobenzene with TPA [Poly(TPA-cANBE)]

The polymerization of cANBE with TPA was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (TPA-cANBE), was dark brown-black colored solid. For the characterization ¹H-NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm⁻¹): 3448, 3064, 1585, 1487, 1384, 1332, 1238, 1080, 837. UV-VIS, λ_{max} (nm): 290, 348. ¹H-NMR (400 MHz, DMSO d₆), δ_{H} (ppm): 7-8.2 (Ar-H).

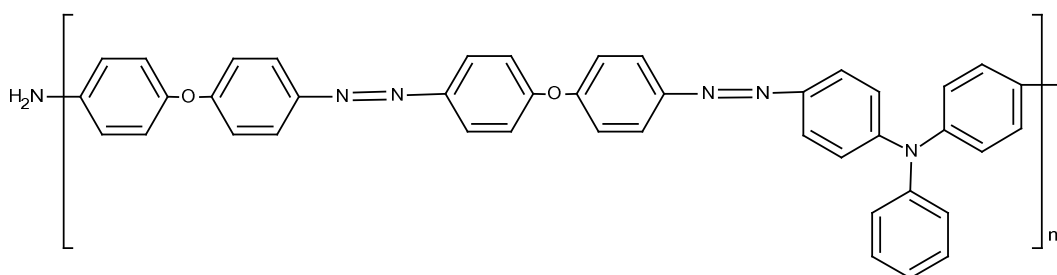


Figure 2.10. The chemical structure of Poly(TPA-cANBE)

2.2.3.4. Polymerization of 4,4'-bis (4-aminophenylthio) azobenzene with TPA [Poly(TPA-cANBS)]

The polymerization of cANBS with TPA was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (TPA-cANBS), was dark red colored solid. For the characterization ^1H -NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3452, 3057, 1664, 1577, 1477, 1450, 1388, 1078, 827. UV-VIS, λ_{max} (nm): 286, 386. ^1H -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): Failed because of solubility problem.

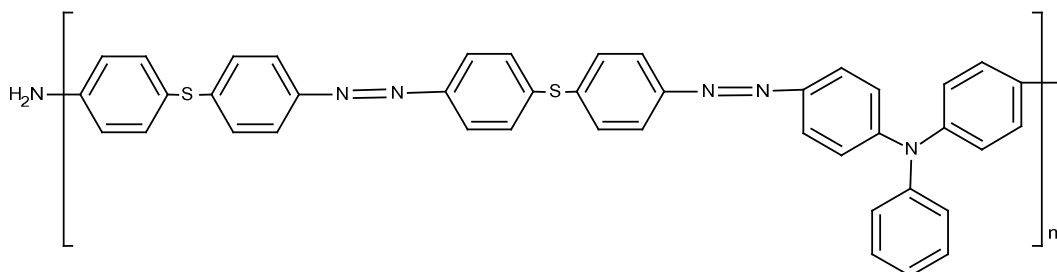


Figure 2.11. The chemical structure of Poly(TPA-cANBS)

2.2.3.5. Polymerization of 4,4'-bis (4-aminophenyl) azobenzene with TPP [Poly(TPP-cANBP)]

The polymerization of cANBP with TPP was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (TPP-cANBP), was dark brown colored solid. For the characterization FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3439, 3028, 1593, 1525, 1483, 1454, 1383, 1334, 1166, 1082, 1001, 827. UV-VIS, λ_{max} (nm): 286, 390. ^{31}P -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): 25.

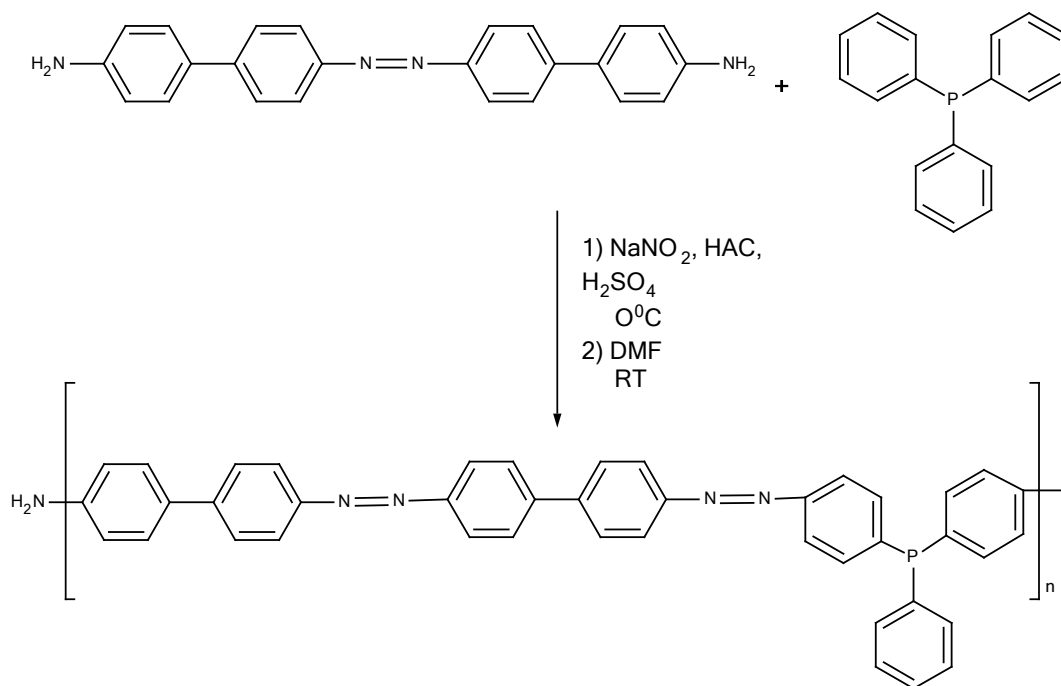


Figure 2.12. Synthesis of Poly(TPP-cANBP)

2.2.3.6. Polymerization of 5,5'-diamino-1,1'-azobiphenyl with TPP [Poly(TPP-cANBP)]

The polymerization of cANBP with TPP was achieved by the same method as the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (TPP-cANBP), was a black colored solid. For the characterization FTIR, UV-VIS, DSC, TGA techniques were used. FTIR (KBr), ν (cm^{-1}): 3454, 3190, 1572, 1408, 1342, 1111. UV-VIS, λ_{max} (nm): Failed ^{31}P -NMR (400 MHz, $\text{DMSO}-d_6$), δ_{H} (ppm): 25.

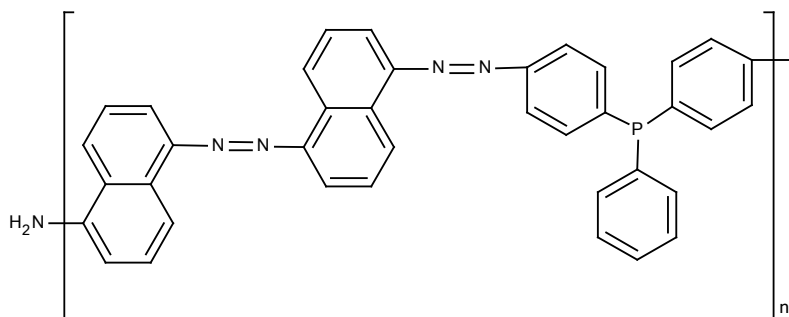


Figure 2.13: The chemical structure of Poly(TPP-cANNP)

2.2.3.7. Polymerization of 4,4'-bis (4-aminophenoxy) azobenzene with TPP [Poly(TPP-cANBE)]

The polymerization of cANBE with TPP was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (TPP-cANBE), was dark brown colored solid. For the characterization FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm⁻¹): 3470, 3059, 1587, 1533, 1491, 1238, 1143, 837. UV-VIS, λ_{max} (nm): 288, 358. ³¹P-NMR (400 MHz, DMSO d₆), δ_{H} (ppm): 25.

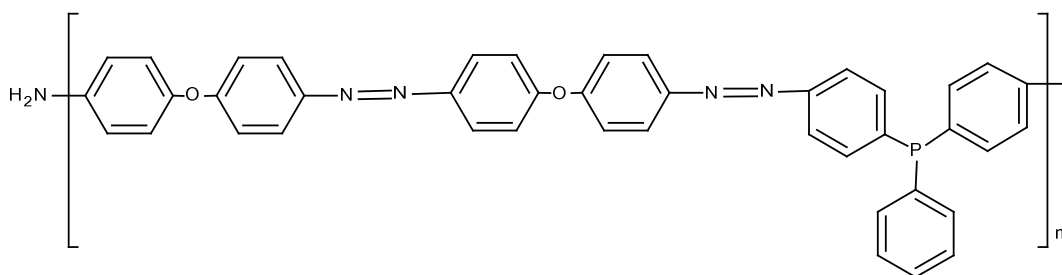


Figure 2.14. The chemical structure of Poly(TPP-cANBE)

2.2.3.8. Polymerization of 4,4'-bis (4-aminophenylthio) azobenzene with TPP [Poly(TPP-cANBS)]

The polymerization of cANBS with TPP was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (TPP-cANBS), was dark red colored solid. For the characterization FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3057, 1674, 1583, 1492, 1452, 1346, 1078, 821. UV-VIS, λ_{max} (nm): 286, 386. ^{31}P -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): 25.

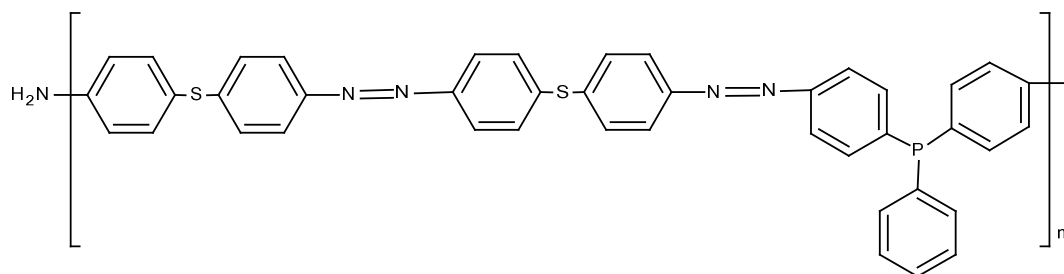


Figure 2.15. The chemical structure of Poly(TPP-cANBS)

2.2.3.9. Polymerization of 4,4'-bis (4-aminophenyl) azobenzene with N-MDPA [Poly(N-MDPA-cANBP)]

The polymerization of cANBP with N-MDPA was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (N-MDPA -cANBP), was dark brown-black colored solid. For the characterization ^1H -NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3460, 3030, 2875, 1664, 1591, 1487, 1448, 1392, 1338, 1124, 1111, 823. UV-VIS, λ_{max} (nm): 286, 372. ^1H -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): 2.5-3 (C-H); 7.5-8.5 (Ar-H).

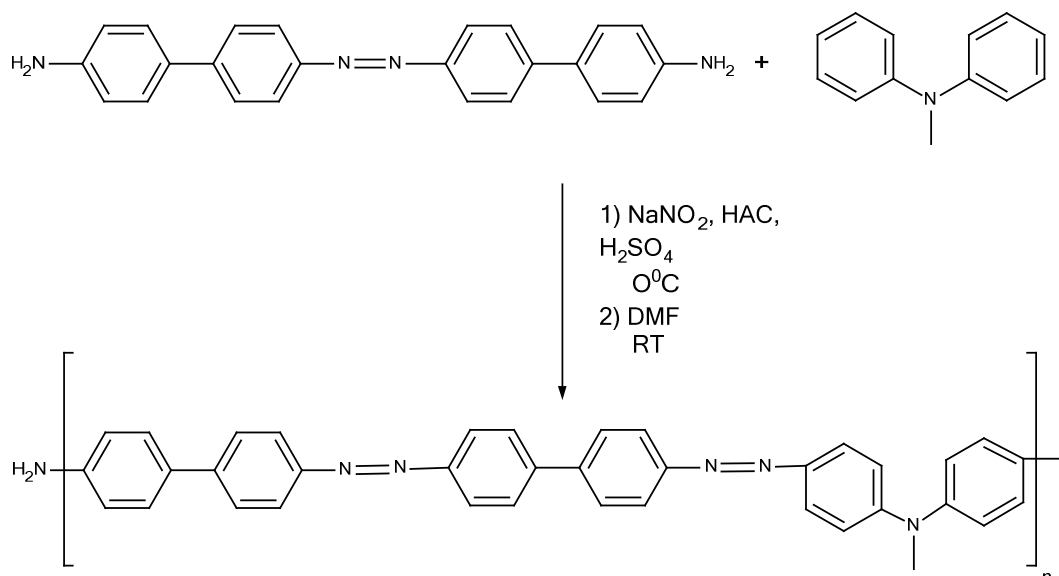


Figure 2.16. Synthesis of Poly(N-MDPA-cANBP)

2.2.3.10. Polymerization of 5,5'-diamino-1,1'-azonaphtalane with N-MDPA [Poly(N-MDPA-cANNP)]

The polymerization of cANNP with N-MDPA was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (N-MDPA -cANNP) , was black colored solid. For the characterization ¹H-NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm⁻¹): 3392, 3057, 1591, 1492, 1384, 1342, 1112, 819. UV-VIS, λ_{max} (nm): Failed. ¹H-NMR (400 MHz, DMSO d-₆), δ_{H} (ppm): Failed.

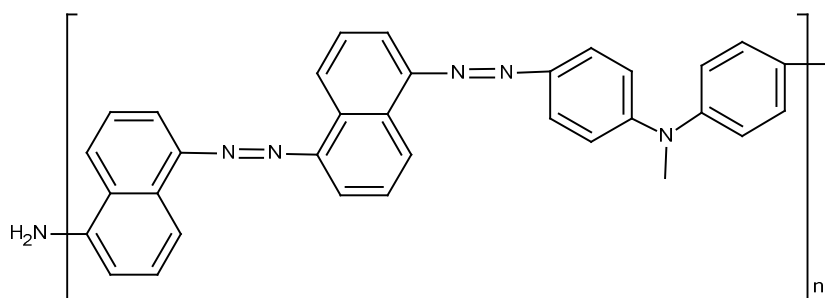


Figure 2.17. The chemical structure of Poly(N-MDPA-cANNP)

2.2.3.11. Polymerization of 4,4'-bis (4-aminophenoxy) azobenzene with N-MDPA [Poly(N-MDPA-cANBE)]

The polymerization of cANBE with N-MDPA was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (N-MDPA -cANBE), was dark brown colored solid. For the characterization ^1H -NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3059, 2874, 2816, 1587, 1492, 1348, 1236, 1145, 837. UV-VIS, λ_{max} (nm): 280, 356, 456. ^1H -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): 2.5-3 (C-H); 6.9-8.2 (Ar-H).

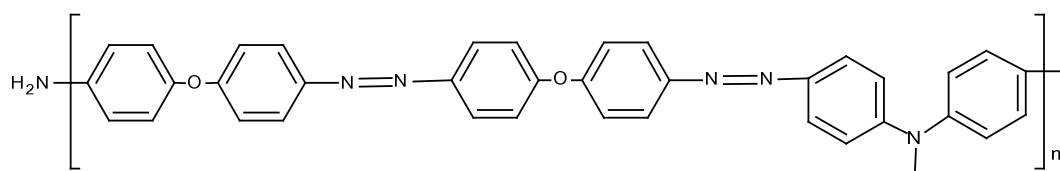


Figure 2.18. The chemical structure of Poly (N-MDPA-cANBE)

2.2.3.12. Polymerization of 4,4'-bis(4-aminophenylthio) azobenzene with N-MDPA [Poly(N-MDPA-cANBS)]

The polymerization of cANBS with N-MDPA was achieved by the same method the synthesis of Poly (TPA-cANBP). The resultant polymer, Poly (N-MDPA-cANBS), was dark red colored solid. For the characterization ^1H -NMR, FTIR, UV-VIS, DSC, TGA techniques was used. FTIR (KBr), ν (cm^{-1}): 3056, 2927, 2810, 1585, 1494, 1452, 1346, 1080, 837. UV-VIS, λ_{max} (nm): 286, 386, 468. ^1H -NMR (400 MHz, DMSO d_6), δ_{H} (ppm): 2.5-3 (C-H); 6.9-8.2 (Ar-H).

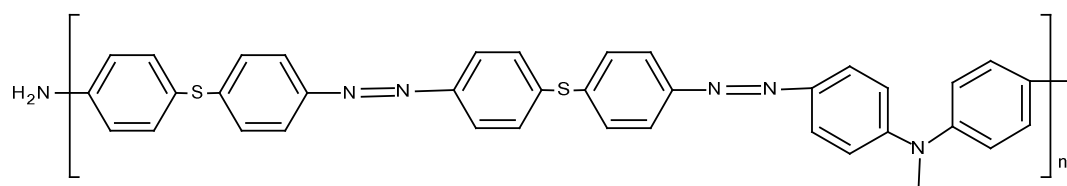


Figure 2.19. The chemical structure of Poly(N-MDPA-cANBS)

2.3. MEASUREMENTS

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of synthesized molecules were recorded using KBr discs on a Shimadzu FTIR Spectrometer in the range of 400-4000 cm^{-1} frequency.

2.3.2. Raman Spectroscopy

Raman Spectra were recorded Homemade Confocal RAMAN Setup installed at material instrumentation, as a He-Ne laser sources 633 nm line width with a power of 20 mV was used.

2.3.3. ^1H -NMR Spectroscopy

^1H -NMR spectra of monomers and polymers were recorded using Bruker 400 MHz in 10 M in DMSO- d_6 solution.

2.3.4. ^{31}P -NMR Spectroscopy

^{31}P -NMR spectroscopy of polymers made from TPP were recorded with using Varian 600 MHz in DMSO- d_6 solution.

2.3.5. UV/VIS Spectroscopy

UV spectra were recorded with JASCO V-530 UV/VIS spectrophotometer using DMF as a solvent.

2.3.6. Thermogravimetric Analysis

TGA thermograms of monomers and polymers were recorded in nitrogen atmosphere at a heating rate of 20 °C/min using Perkin Elmer Pyris 1 model TGA.

2.3.7. Differential Scanning Calorimetry (DSC)

DSC thermograms of monomers and polymers were recorded in the range of 20-350 °C under N₂ atmosphere using Perkin Elmer Pyris 1 DSC. Scans were run at a heating rate of 10 °C/min.

CHAPTER III. RESULTS AND DISCUSSION

3. CHARACTERIZATION

3.1. CHARACTERIZATION BY FTIR SPECTRA

In this study, FTIR spectroscopy was used to determine the existence of specific functional groups in nitro amine derivatives and coupled of these compounds (azo monomers) and finally synthesized polymers and also to compare to each other.

The most informative bands in the infrared spectrum of aromatic compounds occur in the low frequency between the ranges 675-900 cm^{-1} due to the ring C-H out of plane bending bands. In plane bending of the ring C-H bands occur in the 1000-1300 cm^{-1} region. C-H stretching bands appear in the region of 3000-3100 cm^{-1} with low frequency. Aromatic C=C stretching vibration absorb in the 1585-1600 cm^{-1} and 1400-1500 cm^{-1} regions. Aromatic nitro compound, which is the starting material of this study, characteristic bands occur in the region of 1500-1550 cm^{-1} and 1360-1290 cm^{-1} corresponding to asymmetrical and symmetrical NO_2 stretching band, respectively. Primary amines shows two absorption bands; one near 3500 cm^{-1} due to the asymmetrical N-H stretching vibration and the other one near

3400 cm^{-1} due to the symmetrical N-H stretching vibration. And also shows strong N-H bending band in the region of 1650-1580 cm^{-1} . Aromatic amines display strong C-N stretching absorption in the 1266-1342 cm^{-1} region. Tertiary aromatic amines characteristic strong C-N stretching band occurs in the 1310-1360 cm^{-1} . The most characteristic absorption band of ethers in the infrared is a strong band in the region of 1000-1260 cm^{-1} due to the asymmetrical C-O-C stretching. Sulfides characteristic band occur in the region of 600-700 cm^{-1} assigned to the C-S linkage but due to the weakness of absorption and variability of position, this band has little value to determine structure. Aliphatic C-H stretching absorption peaks occur in the general region of 2840-3000 cm^{-1} . The N=N stretching vibration band can only observe unsymmetrical para substituted azobenzenes in the infrared spectrum at around 1429 cm^{-1} . Symmetrical azo compounds N=N stretching band is forbidden in the infrared [40].

ANBP FTIR spectrum is shown in the Fig. 3.1. Presence of the following bands at 3385 cm^{-1} and 3489 cm^{-1} (symmetric and unsymmetric N-H stretching, respectively), 1627 cm^{-1} (N-H bending), 1587 cm^{-1} - 1496 cm^{-1} (aromatic C=C, C-C ring stretching), 1330 cm^{-1} (symmetric N-O stretching), 1278-1207 cm^{-1} (C-N stretching), 1112 cm^{-1} (in plane C-H bending), 825 cm^{-1} (out of plane C-H bending) confirmed ANBP structure. FTIR spectrum of cANBP is shown in Fig. 3.1. Formation of azo was confirmed by disappearance of band at 1330 cm^{-1} . With the increase of azo content the intensities of -NH_2 bands are obviously decreased. Due the symmetrical structure of synthesized azo monomer, N=N stretching band couldn't indicated in ir spectrum data. Poly(TPA-cANBP) FTIR spectrum (Fig. 3.1.)

showed the characteristic peaks of monomer. A broad peak at around 1664 was due to polyconjugation. The new peak at 1342 was indicated tertiary C-N stretching band. And also intensity of in plane C-H bending at 1078 cm^{-1} and out of plane C-H bending at 831 cm^{-1} was obviously increased due to the wholly aromatic structure of TPA-cANBP polymer. N-MDPA-cANBP polymer FTIR spectrum (Fig. 3.1.) showed the characteristic peaks of TPA-cANBP polymer. Only the new peak at around 2900 was due to the aliphatic C-H stretching. FTIR spectrum of Poly(TPP-cANBP) represented in Fig. 3.2., showed as the same peaks as Poly(TPA-cANBP). Although the polymers were dried before the analysis, a broad peak at around 3400 cm^{-1} seen in FTIR spectrum of all polymers due to the absorbed water.

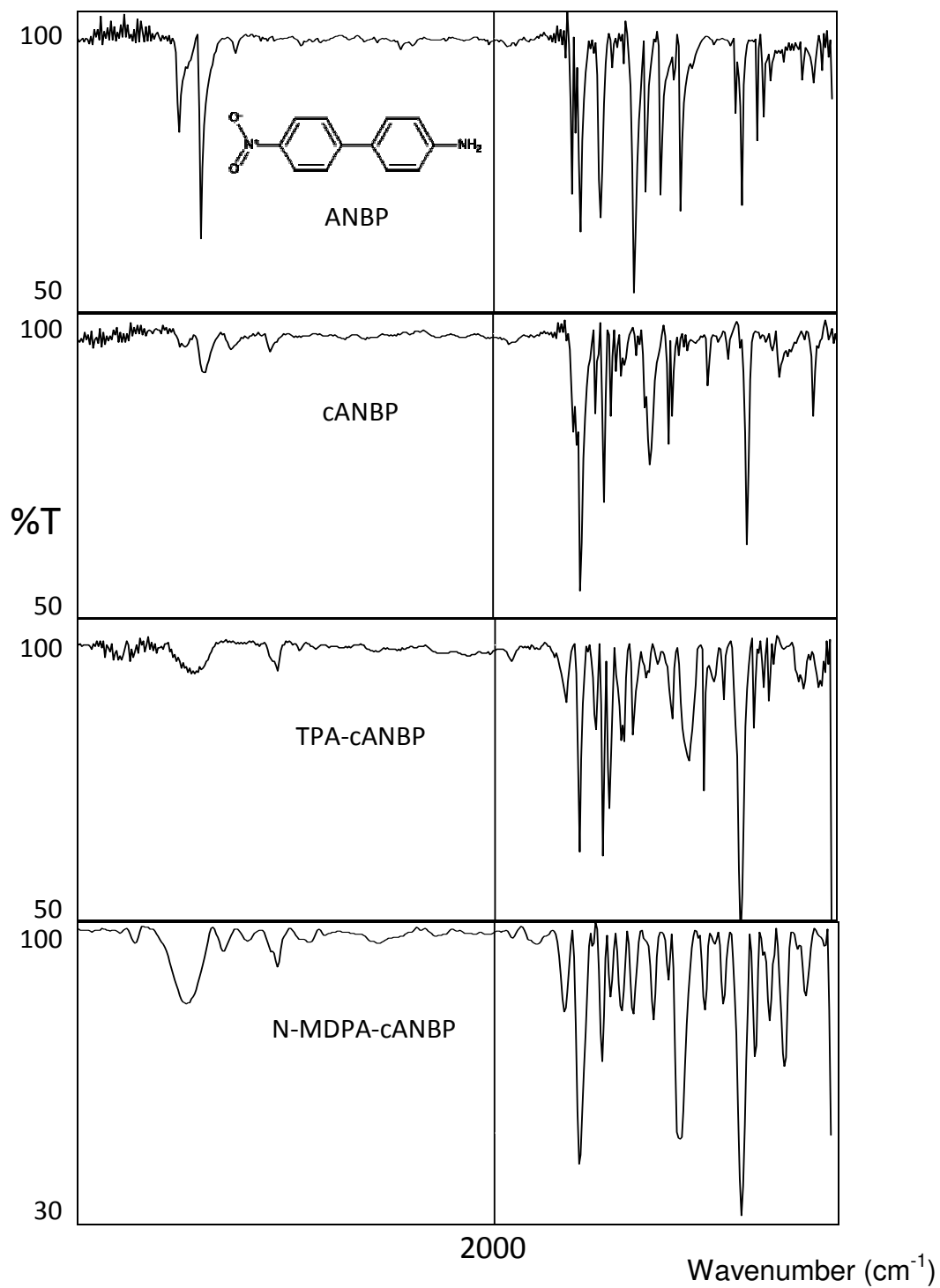


Figure 3.1. FTIR Spectra of ANBP, cANBP, TPA-cANBP and N-MDPA-cANBP polymer

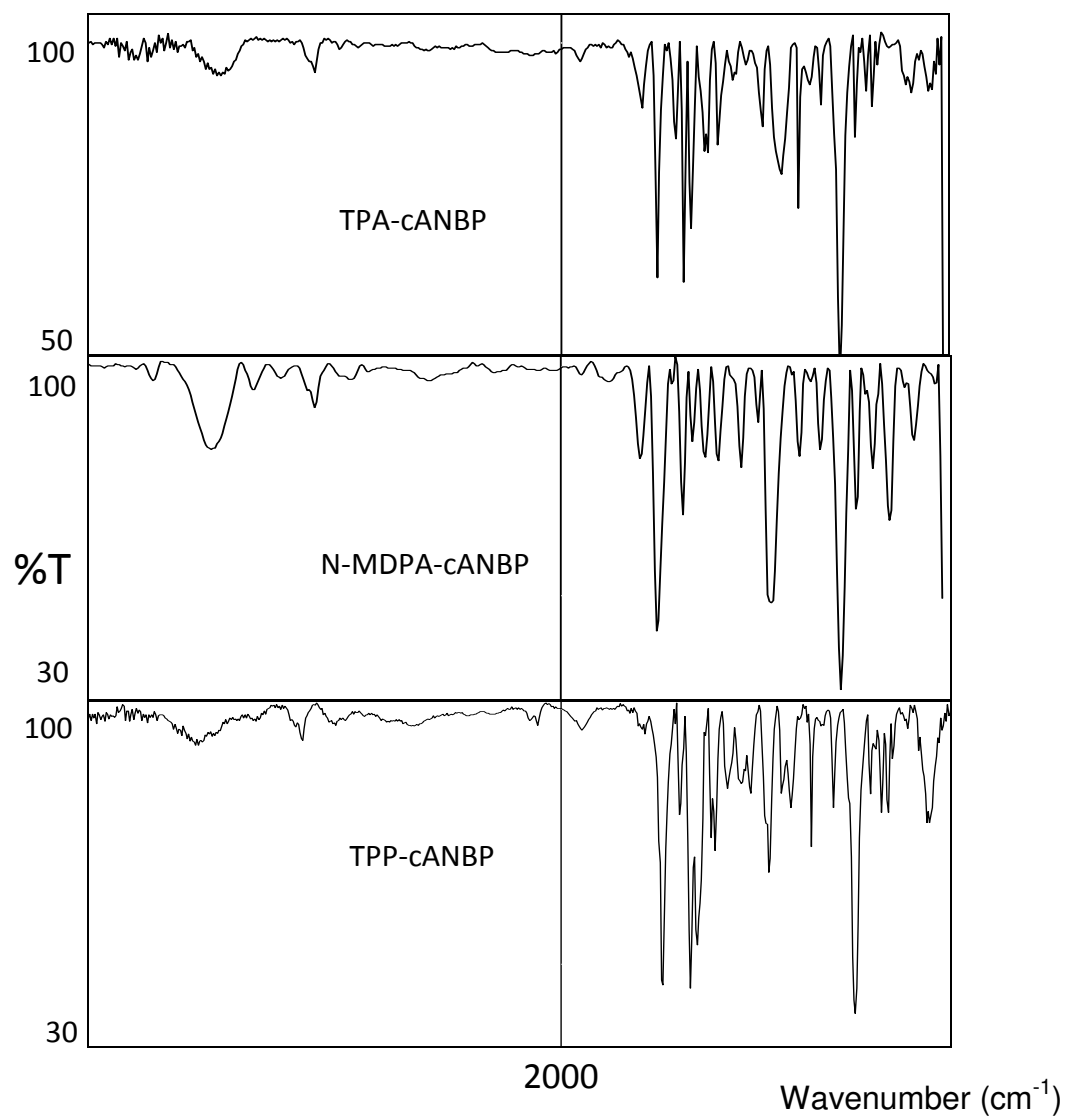


Figure 3.2. FTIR Spectra of TPA-cANBP, N-MDPA-cANBP and TPP-cANBP polymer

The representative FTIR spectrum of ANNP is shown in the Fig. 3.3. Presence of the following bands at 3414 cm^{-1} and 3331 cm^{-1} (symmetric and unsymmetric N-H stretching, respectively), 1629 cm^{-1} (N-H bending), 1570 cm^{-1} - 1512 cm^{-1} (aromatic C=C, C-C ring stretching), 1321 cm^{-1} (symmetric N-O stretching), 1278 cm^{-1} (C-N stretching), 1130 cm^{-1} (in plane C-H bending), 777 cm^{-1} (out of plane C-H bending) confirmed ANNP structure.

FTIR spectrum of cANNP is shown in Fig. 3.3. disappearing of the band at 1321 cm^{-1} due to the N-O stretching is evidence of the monomer is coupled from nitro moiety. As seen Fig. 3.3. -NH_2 bands are obviously decreased due to the coupled of structure. The intensity of the band at 1620 cm^{-1} increased because of the conjugation on the synthesized monomer.

As shown FTIR spectrum of Poly (TPA-cANNP) in Fig. 3.3. the strong absorption peak at 1384 cm^{-1} which is the responsible for tertiary C-N stretching could be the evidence of polymerization of monomer with TPA. Because of the low content of -NH_2 group related absorption peak wasn't indicated.

In the IR spectra of Poly (N-MDPA-cANNP), beside seen the peak at 1384 cm^{-1} the new peak at around 2900 cm^{-1} arising from aliphatic C-H stretching might be the evidence of polymerization of cANNP with N-MDPA. The spectra of Poly (TPP-cANNP) isn't so informative as represented at Fig. 3.4., seen only aromatic ring stretching at around $1500\text{-}1600\text{ cm}^{-1}$ and C-N stretching band at around 1400 cm^{-1} .

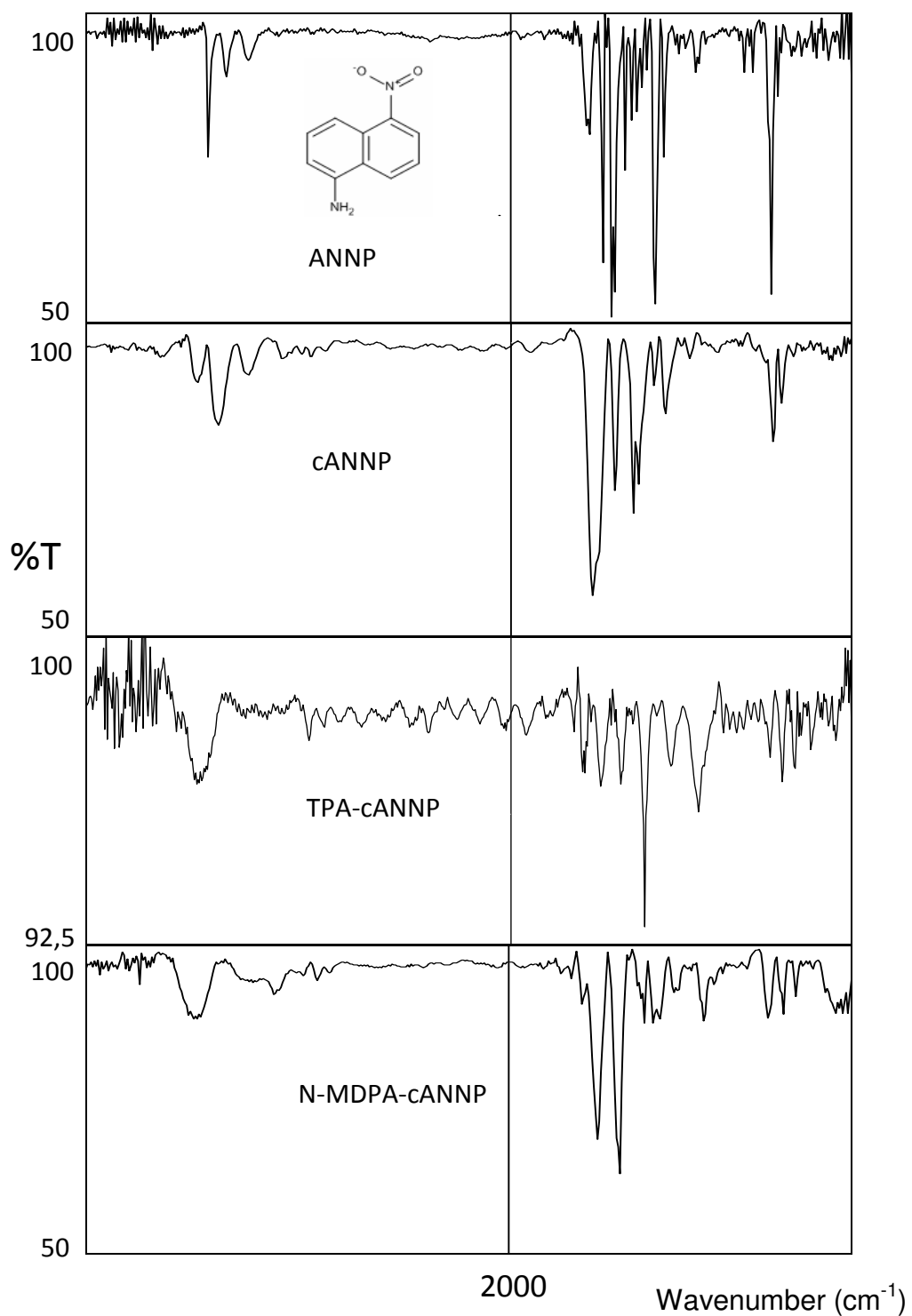


Figure 3.3. FTIR Spectra of ANNP, cANNP, TPA-cANNP and N-MDPA-cANNP polymer

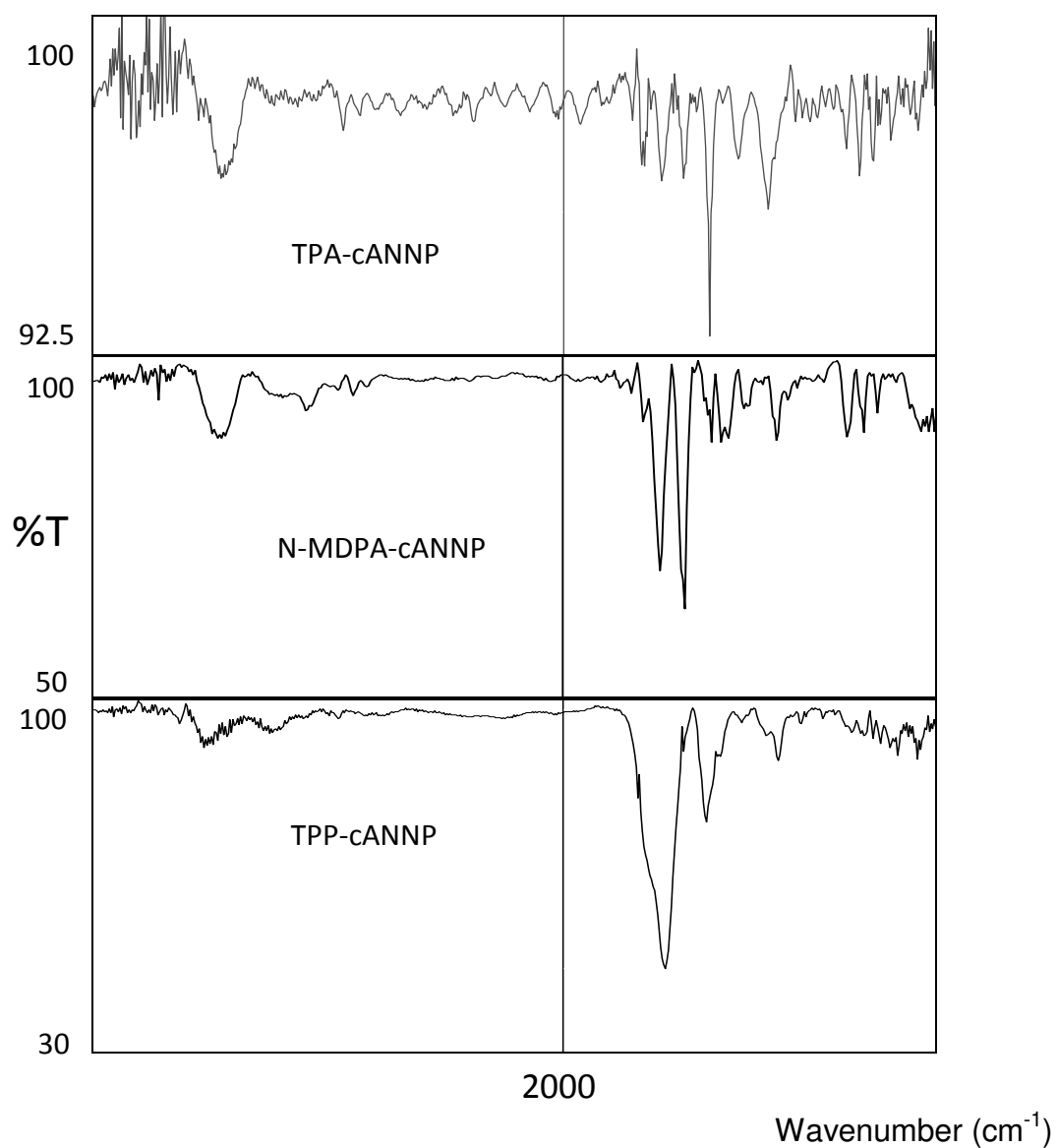


Figure 3.4. FTIR Spectra of TPA-cANNP, N-MDPA-cANNP and TPP-cANNP polymer

ANBS showed the same characteristic band as other nitro amines in the FTIR spectrum as shown Fig. 3.5. [(3466 cm^{-1} and 3379 cm^{-1} (symmetric and unsymmetric N-H stretching, respectively), 1629 cm^{-1} (N-H bending), 1573 cm^{-1} - 1495 cm^{-1} (aromatic C=C, C-C ring stretching), 1332 cm^{-1} (symmetric N-O stretching), 1294 cm^{-1} (C-N stretching), 1118 cm^{-1} (in plane C-H bending), 742 cm^{-1} (out of plane C-H bending)] ANBS showed also other characteristic peak at 682 cm^{-1} assigned to the C-S linkage.

As shown in Fig. 3. 5. cANBS structure was confirmed by disappearance of band at 1332 cm^{-1} in the FTIR spectra.

The new peak at 1338 cm^{-1} in the FTIR spectrum of TPA-cANBS related to tertiary C-N stretching is the evidence of polymerization.

N-MDPA-cANBS polymer structure was confirmed by aliphatic C-H stretching absorption peak at around 2900 cm^{-1} . The strong absorption band also indicated at 1346 cm^{-1} related to tertiary C-N stretching as well as other polymers. FTIR spectrum of all cANBS polymers are the parallel to each other is shown in Fig. 3.6.

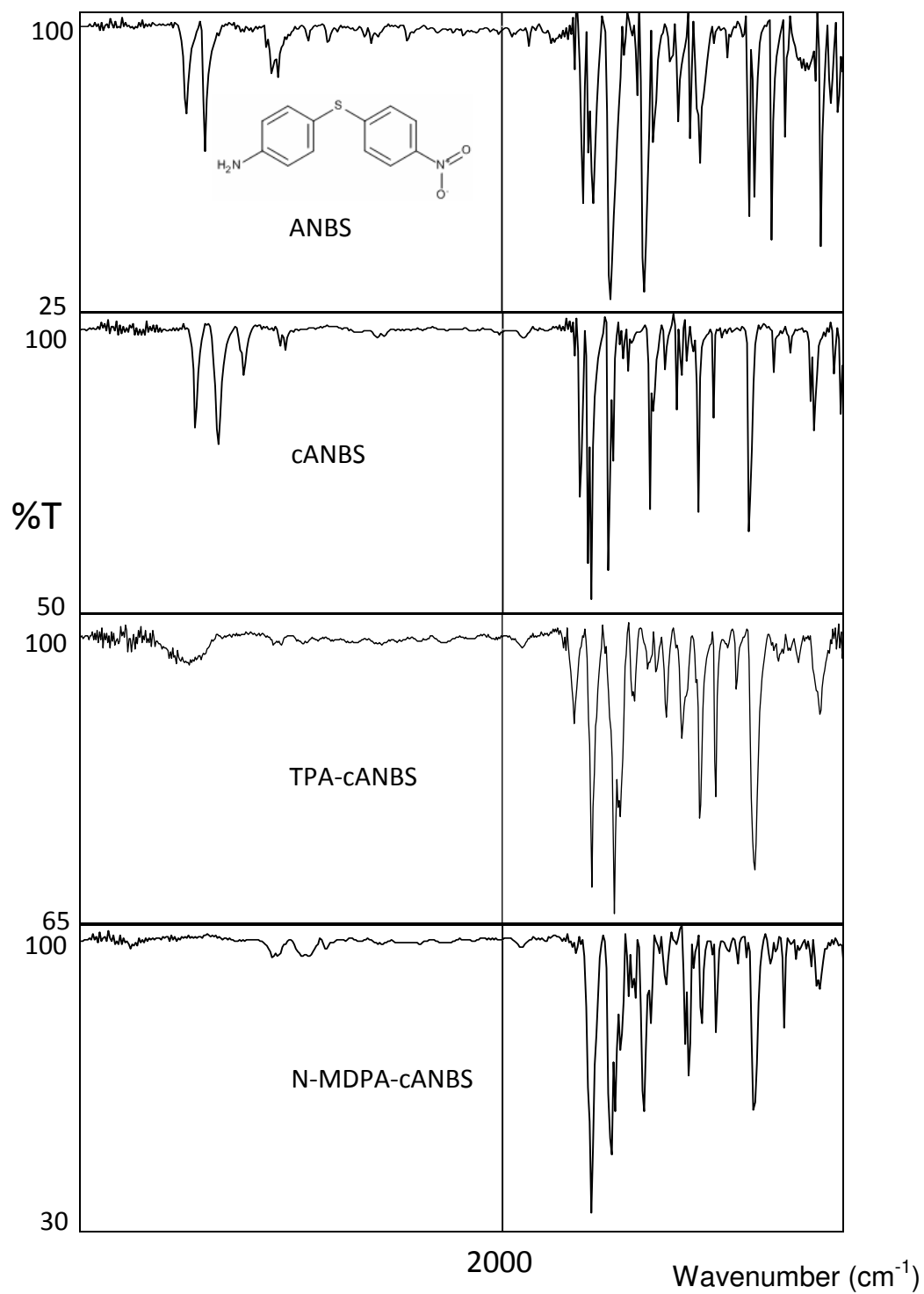


Figure 3.5. FTIR Spectra of ANBS, cANBS, TPA-cANBS and N-MDPA-cANBS polymer

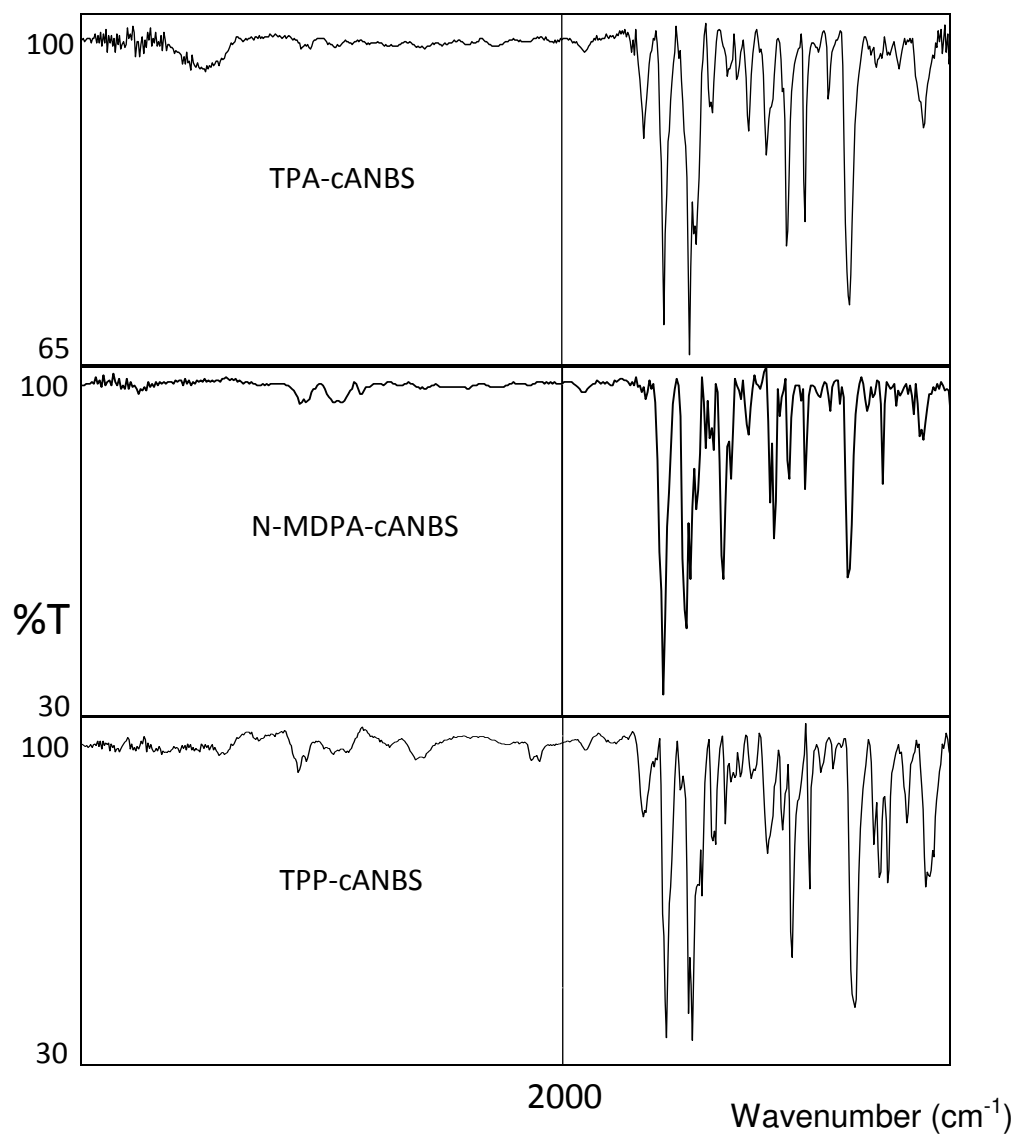


Figure 3.6. FTIR Spectra of TPA-cANBS, N-MDPA-cANBS and TPP-cANBS polymer

ANBE showed the same characteristic band as other nitro amines in the FTIR spectrum as shown in Fig. 3.7. [(3444 cm^{-1} and 3365 cm^{-1} (symmetric and unsymmetric N-H stretching, respectively), 1627 cm^{-1} (N-H bending), 1585 cm^{-1} - 1500 cm^{-1} (aromatic C=C, C-C ring stretching), 1340 cm^{-1} (symmetric N-O stretching), 1286 cm^{-1} (C-N stretching), 1112 cm^{-1} (in plane C-H bending), 875 cm^{-1} (out of plane C-H bending)] And also, ANBE showed the strong absorption band at 1240 cm^{-1} which is the most characteristic band of ethers in the infrared, due to the asymmetrical C-O-C stretching.

The FTIR spectra of cANBE is shown in Fig. 3.7. As well as other coupled compounds FTIR spectra, the band at 1340 cm^{-1} due to the N-O stretching was disappeared.

The representative FTIR spectra of TPA-cANBE polymer is showed fig. Due to the polyconjugation the absorption peak at around 1500 cm^{-1} was increased and the peak at 1384 cm^{-1} due to the tertiary C-N stretching was indicated.

With the results of the FTIR spectrum of N-MDPA-cANBE polymer as shown in Fig. 3.7. polymer structure was confirmed. Increasing the intensity in the region 2900 cm^{-1} related to aliphatic C-H stretching and the strong absorption peak at 1348 cm^{-1} due to the tertiary C-N stretching is the evidence of polymerization. FTIR spectrum of all cANBE polymers are the parallel to each other is shown in Fig. 3.8.

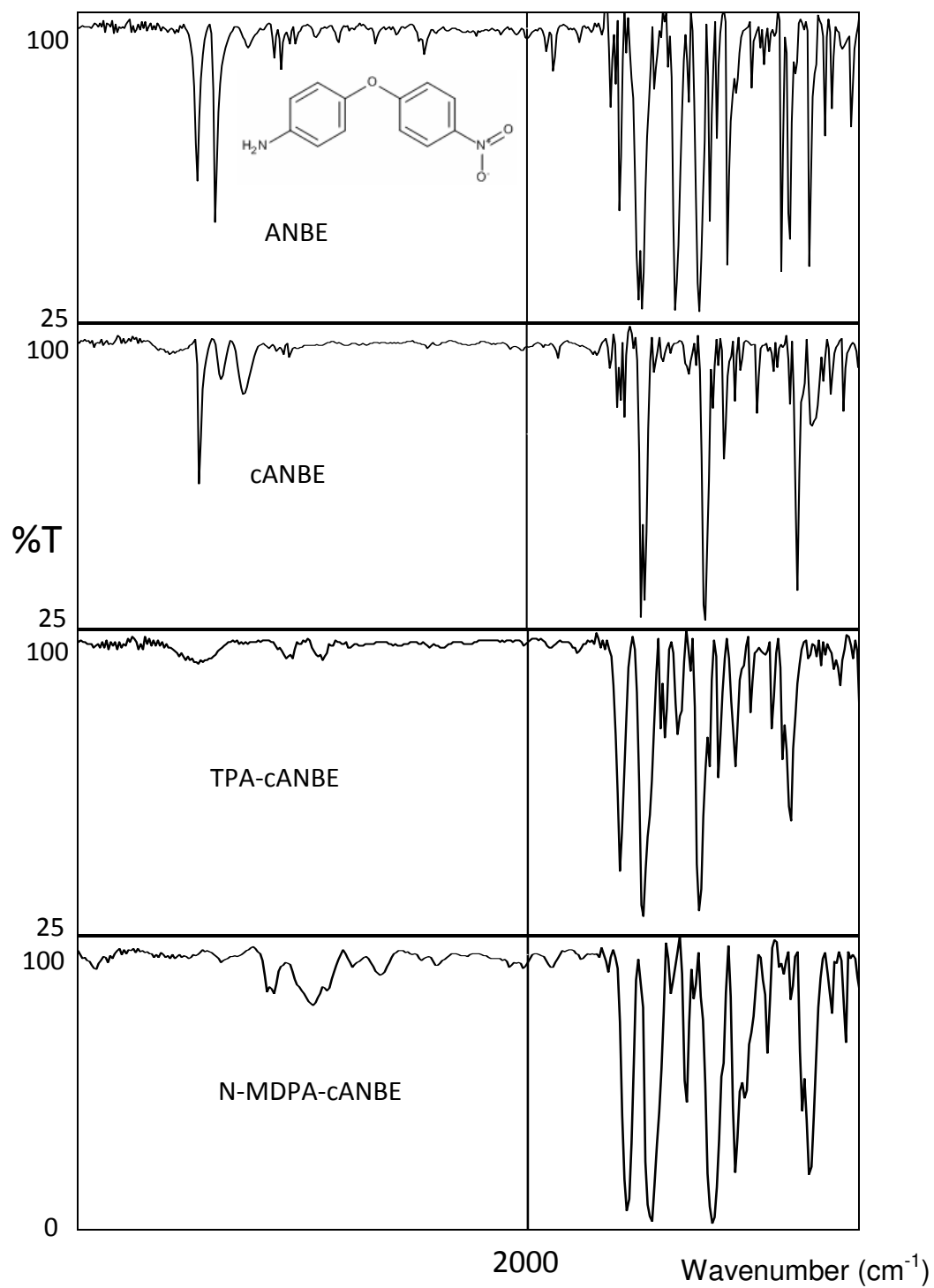


Figure 3.7. FTIR Spectra of ANBE, cANBE, TPA-cANBE and N-MDPA-cANBE polymer

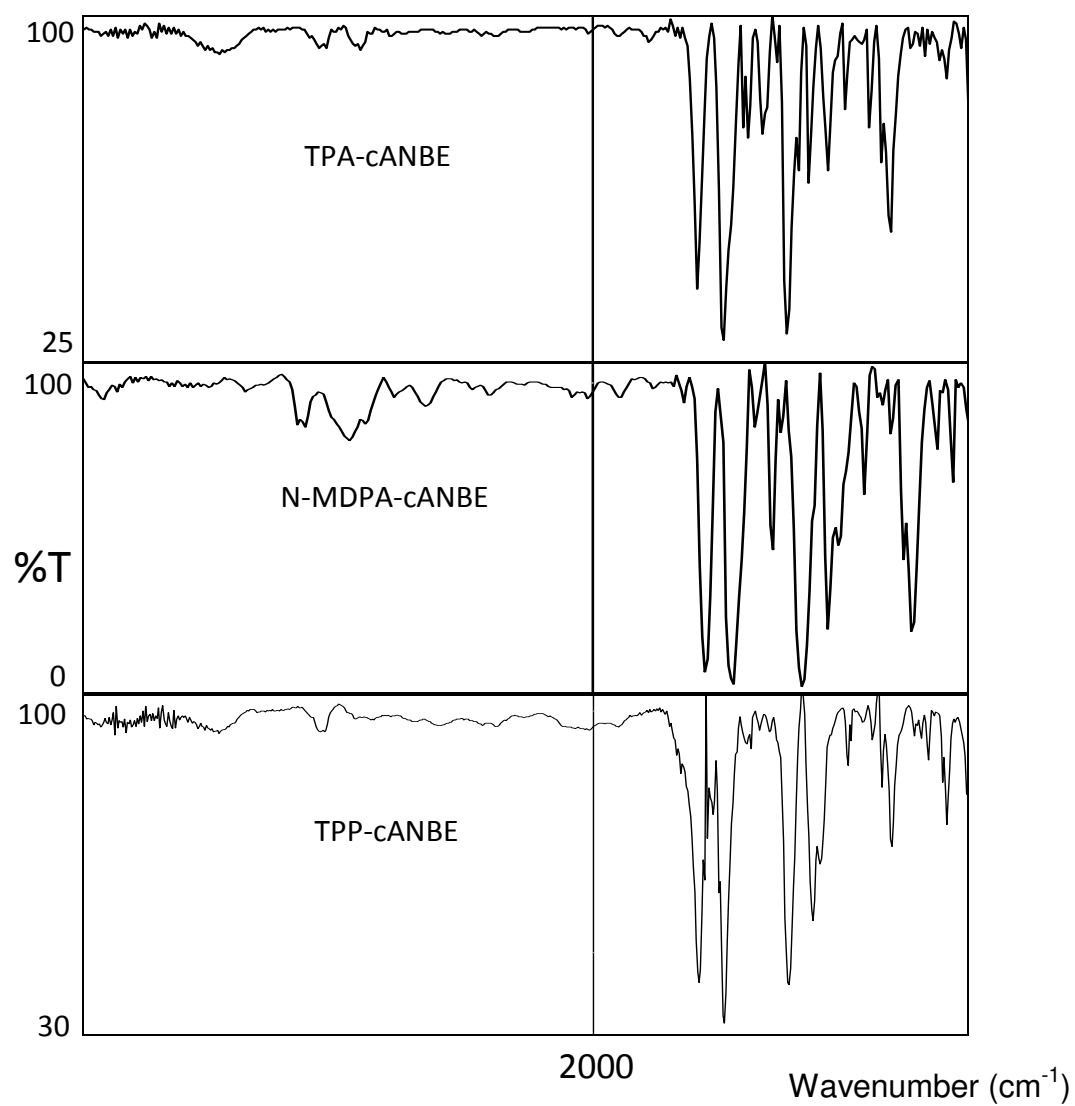


Figure 3.8. FTIR Spectra of TPA-cANBE, N-MDPA-cANBE and TPP-cANBE polymer

3.2. CHARACTERIZATION BY RAMAN SPECTRA

The formation of azo group was confirmed by using Raman spectroscopy. Due to the symmetric nature of monomers, corresponding -N=N- group peak wasn't observed in the infrared spectrum [40]. In the Raman spectrum, aromatic -N=N- stretching band occurs between the ranges $1410\text{--}1440\text{ cm}^{-1}$.

The peak at 1441 cm^{-1} and 1444 cm^{-1} in the Raman spectrum of cANBP and TPA-cANBP, respectively, is the evidence of azo group occurrence (See Fig. 3.9. and Fig. 3.10.).

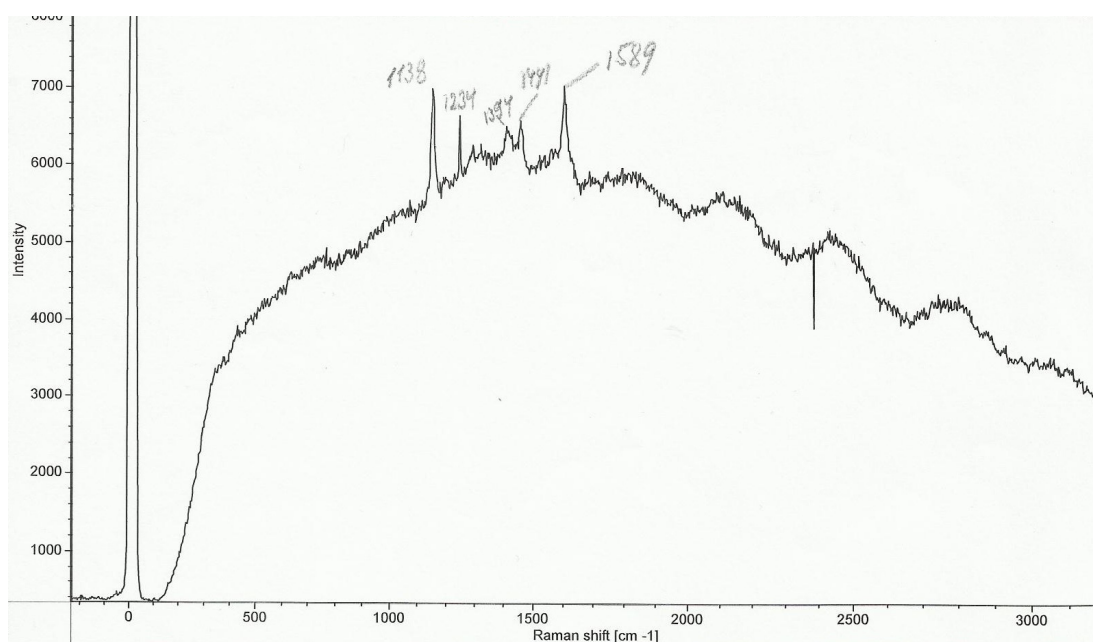


Figure 3.9. Representative raman spectra of cANBP monomer

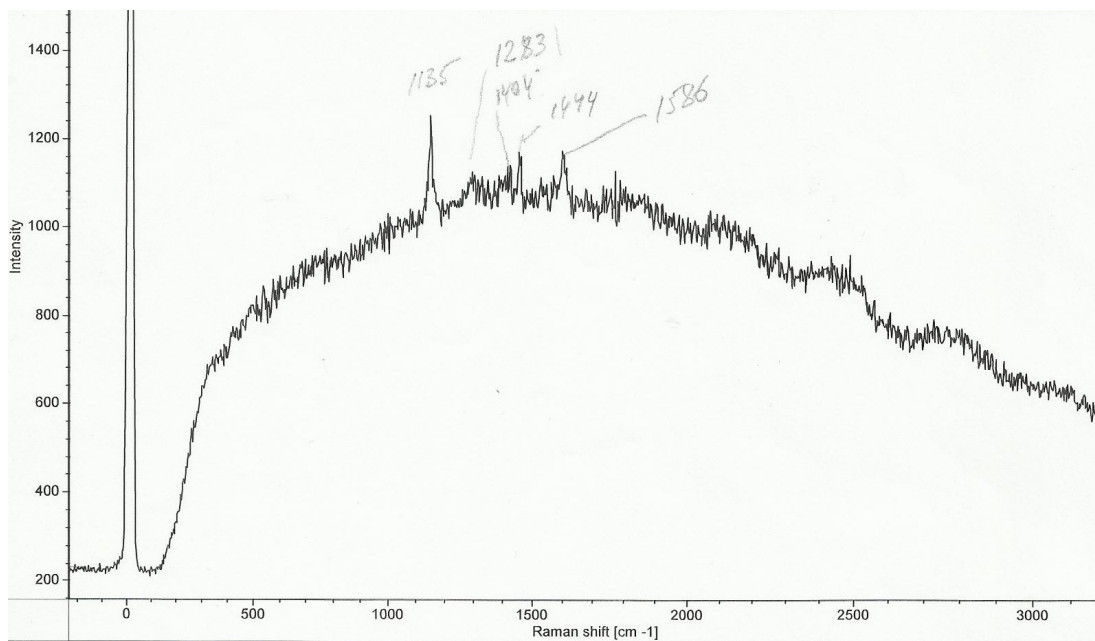


Figure 3.10. Representative raman spectra of TPA-cANBP polymer

3.3. CHARACTERIZATION BY ^1H -NMR SPECTROSCOPY

In the ^1H -NMR spectra of monomers all magnetic resonance signals were clearly assigned according to the chemical shifts of hydrogen atoms. ^1H -NMR spectra of cANBP, cANNP, cANBE and cANBS are given in Fig. 3.11., Fig. 3.12., Fig. 3.13., and Fig. 3.14. respectively. These spectra of monomers possess characteristic signals as similar. Peaks around 6.5-8.5 ppm are related to the aromatic hydrogens and the peak appearing at 5-5.5 ppm displays amine hydrogen. ^1H -NMR spectrum of cANNP monomer is different from other monomers that might be related to rotational barrier of naphthenic structure as represented at Fig. 3.13.

Due to the rigid structure of main chain aromatic azo polymers, it was a challenge to dissolve them in common organic solvents, therefore it is difficult to analyze with ^1H -NMR. Only Poly (TPA-cANBE) chemical shifts assigned in ^1H -NMR spectrum due to its better solubility in DMSO solvent (See Fig. 3.15.).

In ^1H -NMR spectra of cANBE monomer the peak at 5.1 ppm corresponds to the resonance of the protons of the amino groups (H_e) was disappeared completely due to the polymerization as shown in Fig. 3.15. The other evidence of polymerization of cANBE with TPA is increasing in the intensity of H_a , H_b , H_c , H_d because of the increase of conjugated chain length.

N-MDPA polymers have better solubility in common organic solvents because of their quite linearity in chain. Thus their characterization was easier than TPA polymers in ^1H -NMR spectrum due to its better solubility in DMSO solvent. All polymers made from N-MDPA except Poly(N-MDPA-cANNP) chemical shifts assigned in ^1H -NMR spectrum (See Appendix A).

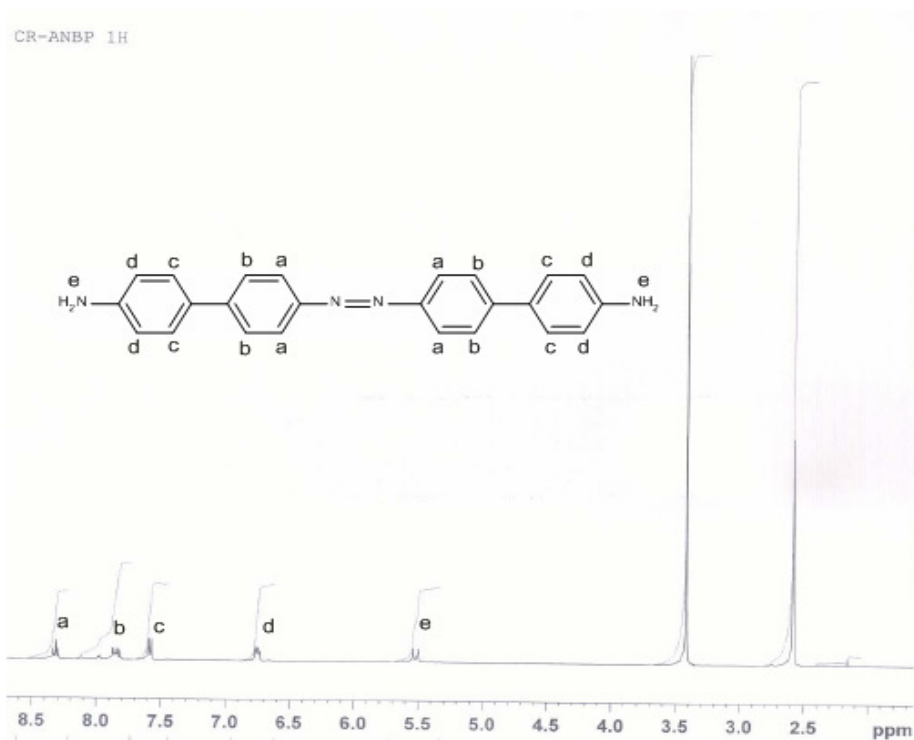


Figure 3.11. ¹H-NMR spectrum of cANBP monomer

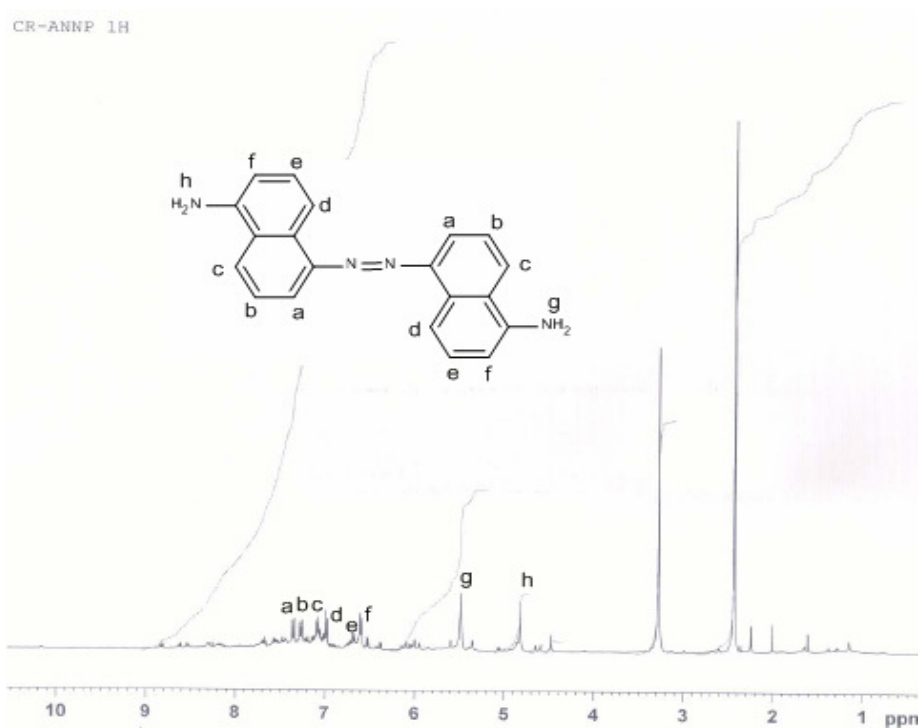


Figure 3.12. ¹H-NMR spectrum of cANNP monomer

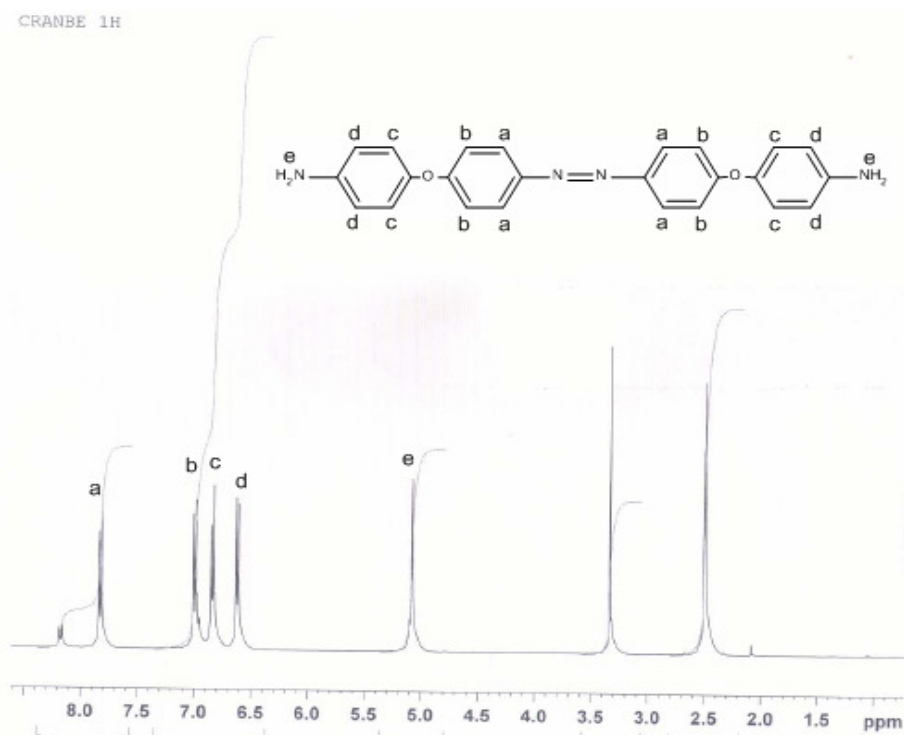


Figure 3.13. ¹H-NMR spectrum of cANBE monomer

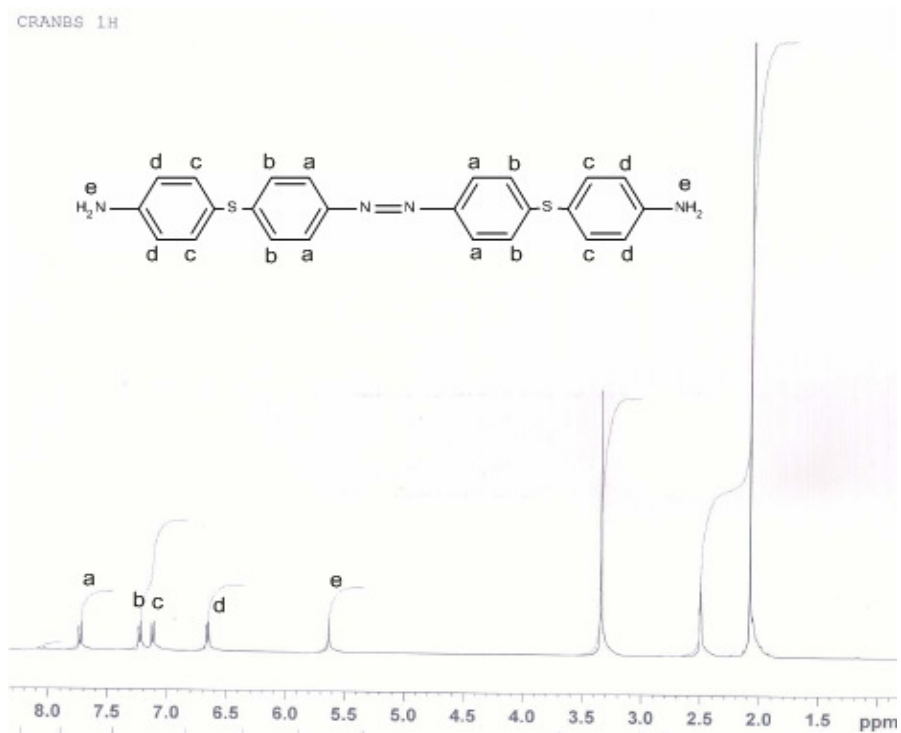


Figure 3.14. ¹H-NMR spectrum of cANBS monomer

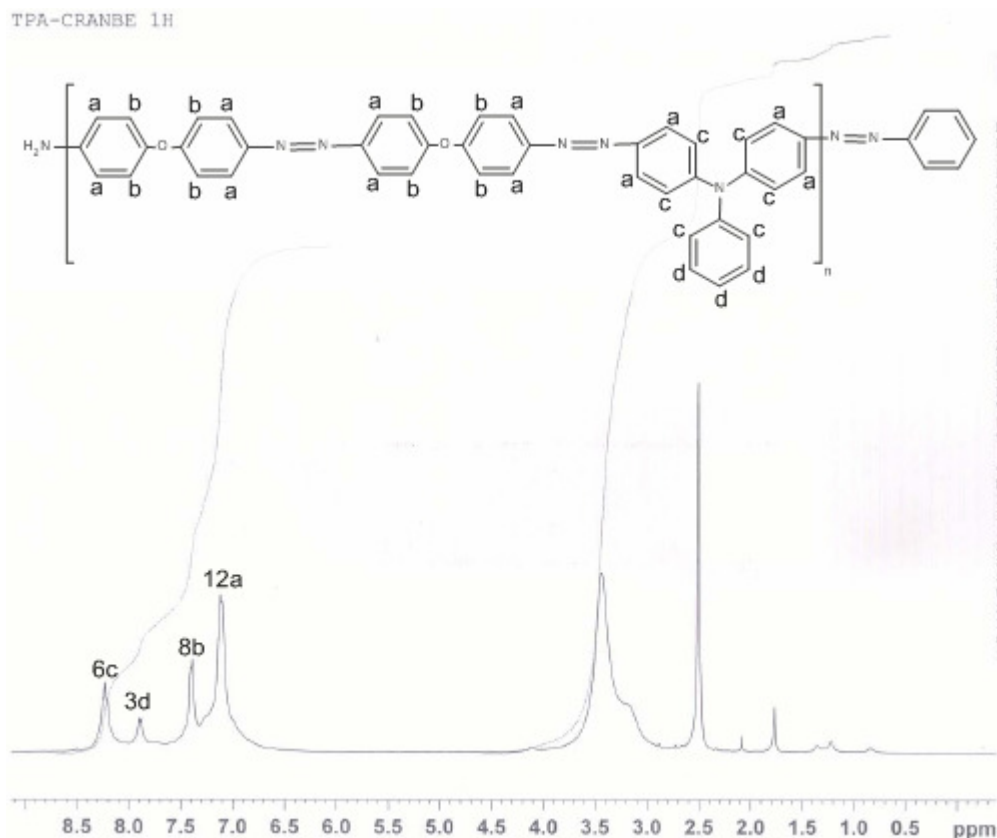


Figure 3.15. ¹H-NMR spectrum of Poly(TPA-cANBE)

3.4. CHARACTERIZATION BY ³¹P-NMR SPECTROSCOPY

Phosphorus occurs predominantly as the isotope ³¹P which has the nuclear spin value of ½ and make it visible in nuclear magnetic resonance (NMR) spectrometry [41] therefore to determine the structure of TPP polymers, ³¹P-NMR Spectroscopy was used in this study. Chemical shift ranges of P-PH₃ compounds are referenced to 0-10 ppm [41]. But chemical shifts also depend on the electronegativity of substituents, therefore were required some corrections. TPP bounds to monomer with azo linkage and this makes the nuclei tend to be deshielded. Therefore chemical shift value of phosphorus in TPP polymers were observed at 25 ppm (See Appendix B).

3.5. CHARACTERIZATION BY UV/VIS SPECTRUM

Due to conjugated system of synthesized molecules, characteristic electronic transitions could determine with UV/VIS Spectroscopy. The wavelengths of the peaks are summarized in Table 3.1. At around 280 nm absorption peak is benzenoid band characteristic of aromatic molecules $\pi \rightarrow \pi^*$ transition is seen all uv spectrum. Only at uv spectra of ANBE this peak couldn't seen because of overlapping.

The maximum wavelength of ANBP is observed at 400 nm which is the longest wavelength among aromatic nitro amine derivatives. Because one of para substitute is electron withdrawing (nitro) and the other para substitute is electron releasing group (amine) and the molecule have no spacer to destroy conjugation. Molecule with spacer like ANBS and ANBE, were showed max. absorption at shorter wavelengths, 346 nm and 308 nm, respectively. ANNP spectrum data results are kind of different. The wavelengths of absorption max in the UV/VIS spectra of ANNP in DMF were at three points; 280 nm, 340 nm and 440 nm. The first one is coming from $\pi \rightarrow \pi^*$ transition of benzenoid band. The absorption max at 340 nm is due to the conjugated p system. Even $n \rightarrow \pi^*$ is forbidden transition were seen in only ANNP at 440 nm. In cANNP these two peaks shifted to red due to increasing of conjugated system. While in spectrum of cANNP polymers, absorption peak wasn't observed. It may require a special treatment before studying in UV-Vis absorption spectroscopy.

All monomers were obviously red-shifted compared to those of the corresponding amino nitro derivatives. Even disappearing of nitro group,

which is responsible for red-shifted, max. absorption peaks were observed longer wavelengths. This clearly reveals that synthesized monomers have conjugation along the main chain, and this is only possible with azo linkage.

The UV/VIS Spectra of polymers qualitatively independent of the length of flexible segment along the chain and only depend on the active azo containing unit which is the same for all polymers and monomers. So all synthesized polymers showed typical spectral characteristics in the UV/VIS spectrum. Monomers obviously red-shifted compared to those of the corresponding amino nitro derivatives due to the increasing of conjugation. However, polymers are expected to shift to longer wave-length, they were blue-shifted. One of possible explanation is that auxochrome red-shifted effect is disappeared in polymers due to the coupling of amine groups. The other possible explanation is branching in polymer chain.

Different from other polymers, Poly (N-MDPA-ANBE) and Poly (N-MDPA-ANBS) polymers showed absorption peak at 456 nm and 468 nm, respectively, due to the $n \rightarrow \pi^*$ forbidden transition.

The Name of Sample	Max. Absorption		
	$\pi \rightarrow \pi^*$ (Benzenoid Band)	$\pi \rightarrow \pi^*$ (Conjugation)	$n \rightarrow \pi^*$
ANBP	278	400	-
ANBS	274	346	-
ANBE	-	308	-
ANNP	280	340	440
cANBP	280	426	-
cANBS	278	396	-
cANBE	-	362	-
cANNP	280	348	462
Poly(TPA-cANBP)	284	392	-
Poly(TPA-cANBS)	286	386	-
Poly(TPA-cANBE)	290	348	-
Poly(TPA-cANNP)	284	-	-
Poly(TPP-cANBP)	286	390	-
Poly(TPP-cANBS)	286	386	-
Poly(TPP-cANBE)	288	358	-
Poly(TPP-cANNP)	286	-	-
Poly(N-MDPA-cANBP)	286	372	-
Poly(N-MDPA-cANBS)	286	386	468
Poly(N-MDPA-cANBE)	280	356	456
Poly(N-MDPA-cANNP)	276	-	-

Table 3.1. Max. Absorption spectra (nm) of the molecules in DMF

3.6. CHARACTERIZATION BY TGA

The thermal stability of polymers was characterized by the thermogravimetric analysis (TGA). Onset of 5% and 10% weight loss and char yields at 900°C for these samples are given Table 3.2. Polymers are not thermally so stable due to the breakage of azo bonds at a lower temperature. Extrusion of molecular nitrogen facilitates the easy decomposition of polymers. Besides that the fully aromatic nature of polymers causes to produce high char yield. It is remarkable that N-MDPA polymers char yields are lower than corresponding to TPA and TPP polymers due to the higher hydrogen index of N-MDPA polymers. With these high char yield and nitrogen evolution at a temperature higher than 200 °C, these oligomeric molecules can be used in high technologic applications as a flame retardant additive.

Sample	5% Weight Loss (°C)	10% Weight Loss (°C)	Residue (%) at 900 °C
TPA-cANBP	237	331	54.7
TPA-cANNP	180	305	69.8
TPA-cANBS	231	320	49.1
TPA-cANBE	220	275	50.3
N-MDPA-cANBP	190	265	47.9
N-MDPA-cANNP	120	225	60.8
N-MDPA-cANBS	260	310	40.8
N-MDPA-cANBE	250	290	46.4
TPP-cANBP	265	320	54.8
TPP-cANNP	60	100	48.5
TPP-cANBS	245	320	49.1
TPP-cANBE	240	340	47.0

Table 3.2. Thermal behaviors of polymers

3.7. CHARACTERIZATION BY DSC

The phase transition behaviors of monomers and polymers were studied by using the differential scanning calorimetry (DSC). The glass transition temperature (T_g) wasn't detected for any products. The melting point (T_m) was determined only for cANBP, cANBE and cANBS monomers. The others probably either decomposed before the melt or could not give any reliable data. The DSC thermogram data were summarized in Table 3.3. Decomposition temperature was observed for all monomers and polymers. An exothermic peak was exhibited at a lower temperature by the all monomers. It was estimated that it belongs to the breakage of an azo bond. While a second exothermic peak obtained at a lower temperature for the polymers is probably because of the presence of a second azo group in a different environment. In short the observation of two decomposition temperature can be explained by the existence of two kinds of azo groups in polymers. This clearly indicated that polymerization have successfully achieved. Only cANNP polymers didn't show the secondary decomposition temperature. Rigidity of naphthalene structure was likely producing problem in synthesis.

Sample	T _m (°C)	T _{d1} (°C)	T _{d2} (°C)	T _g (°C)
cANBP	273	291	-	Undefined
cANNP	-*	250	-	Undefined
cANBS	209	252	-	Undefined
cANBE	213	260	-	Undefined
TPA-cANBP	-	123	236	Undefined
TPA-cANNP	-	<50	-	Undefined
TPA-cANBS	-	128	252	Undefined
TPA-cANBE	-	138	224	Undefined
TPP-cANBP	-	175	242	Undefined
TPP-cANNP	35	100	-	Undefined
TPP-cANBS	-	105	185	Undefined
TPP-cANBE	-	100	240	Undefined
N-MDPA-cANBP	-	182	252	Undefined
N-MDPA-cANNP	32	187	-	Undefined
N-MDPA-cANBS	-	235	289	Undefined
N-MDPA-cANBE	120	143	264	Undefined

Table 3.3. Thermal properties of products.

* cANNP doesn't show melting point before the decomposition.

3.8. ELECTRICAL CONDUCTIVITY OF POLYMERS

Undoped conjugated polymers are semiconductors or insulators. Despite intensive research, the relationship between morphology, chain structure and conductivity is still poorly understood. Generally, it is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains, however this could not be confirmed for PEDOT and polyaniline, which are largely amorphous. The conductivity measurement of polymers were performed by four point measurement method. And It was found that the polymers were nonconductive in their crude or unprocessed forms.

CHAPTER IV. CONCLUSION

In this study twelve different main chain conjugated azo polymers have been synthesized corresponding to four different monomers. All are newly synthesized. Polymerization step was carried out in dimethylformamide (DMF) solution because of good solubility of monomers in DMF. Long reaction time (2 days) was preferred to obtain polymers with high yields and it is also defined that TPA, TPP and N-MDPA molecules have low reactivity in azo coupling reactions because of their lower nucleophilic character. It was expected that this low reactivity of aromatic nucleophilic monomers is the reason of lower molecular weight in polymers. Synthesized polymers were characterized with ^1H -NMR, ^{31}P -NMR, FTIR, UV-VIS, DSC, TGA techniques. Due to the rigid structure of main chain aromatic azo polymers, it was a challenge to dissolve them in common organic solvents, therefore it was difficult to characterize. Accordingly, ^1H -NMR spectrum of synthesized polymers couldn't be obtained in general. The only ^1H -NMR spectrum of Poly (TPA-ANBE) and polymers made from N-NMDPA was observed due to the better solubility in DMSO. FTIR spectroscopy was also used to determine the existence of specific functional groups. Even the FTIR spectroscopy was used to determine the existence of specific functional groups, it wasn't so

informative in the characterization of polymers owing to structural similarity between monomers and polymers. TGA and DSC techniques were used for thermal analysis. The existence of second azo bond on the polymer chain which is the evidence of polymerization was detected in DSC. All polymers, except polymers made from cANNP, showed two decomposition temperatures on DSC. The possible explanation is the presence of two kind of azo bonds in polymers. The first one is azo bond formed in polymerization and the second one is azo bond on the starting monomer structure. TGA analysis also confirmed the existence of two kind of azo bonds in polymer chain. The weight loss was observed at the same temperature range with the exotherms identified due to N_2 evolution on DSC diagram.

It's hard to say that polymers made from cANNP monomer, Poly (TPA-cANNP), Poly (TPP-cANNP), Poly (N-MDPA-cANNP) were obtained with good quality or it was failed. Because, all cANNP polymers didn't show any absorption maximum at UV/VIS spectrum, and DSC curves didn't show secondary decomposition temperature which is the evidence of the polymerization. And also as seen in TGA data these polymers are not thermally as stable as others. The possible explanation for this failure; the monomer, cANNP, starts to decompose before the polymerization reaction. The DSC data of cANNP confirms the decision that the monomer decomposes before the melting.

According to TGA data, polymers produce high char due to their fully aromatic structures. These oligomeric molecules can be used in high technology applications as a flame retardant additive.

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APPENDIX A: ^1H -NMR

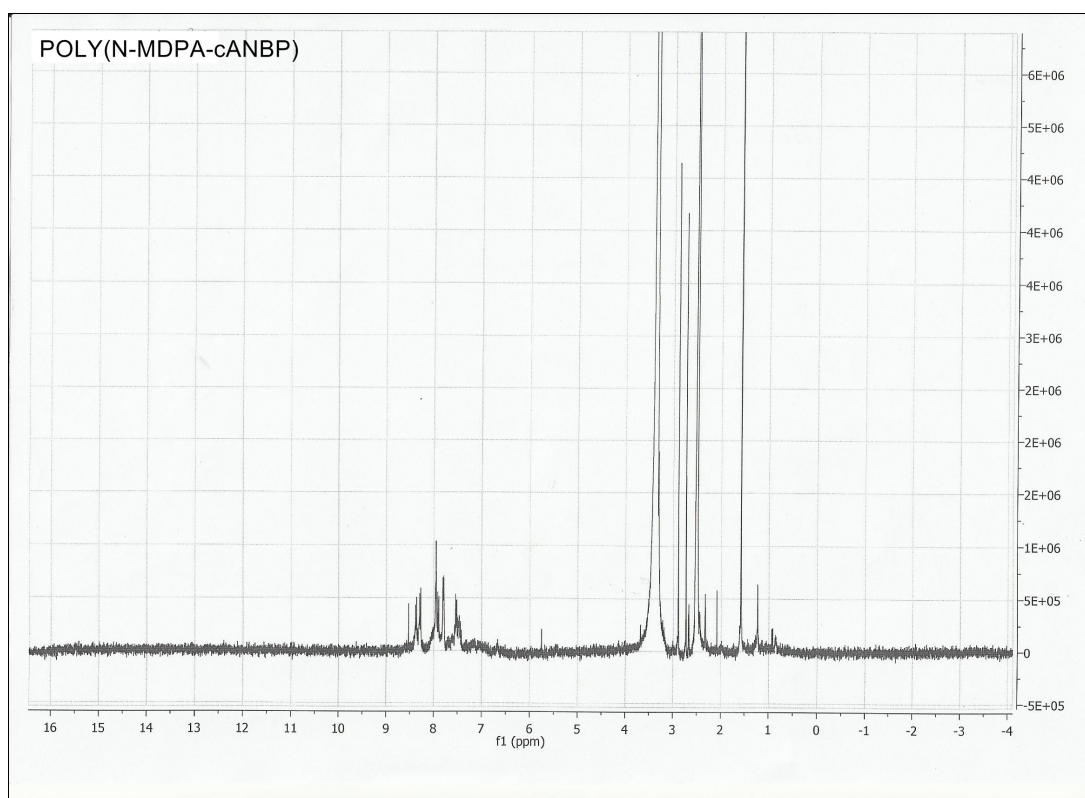


Figure A.1. ^1H -NMR of Poly(N-MDPA-cANBP)

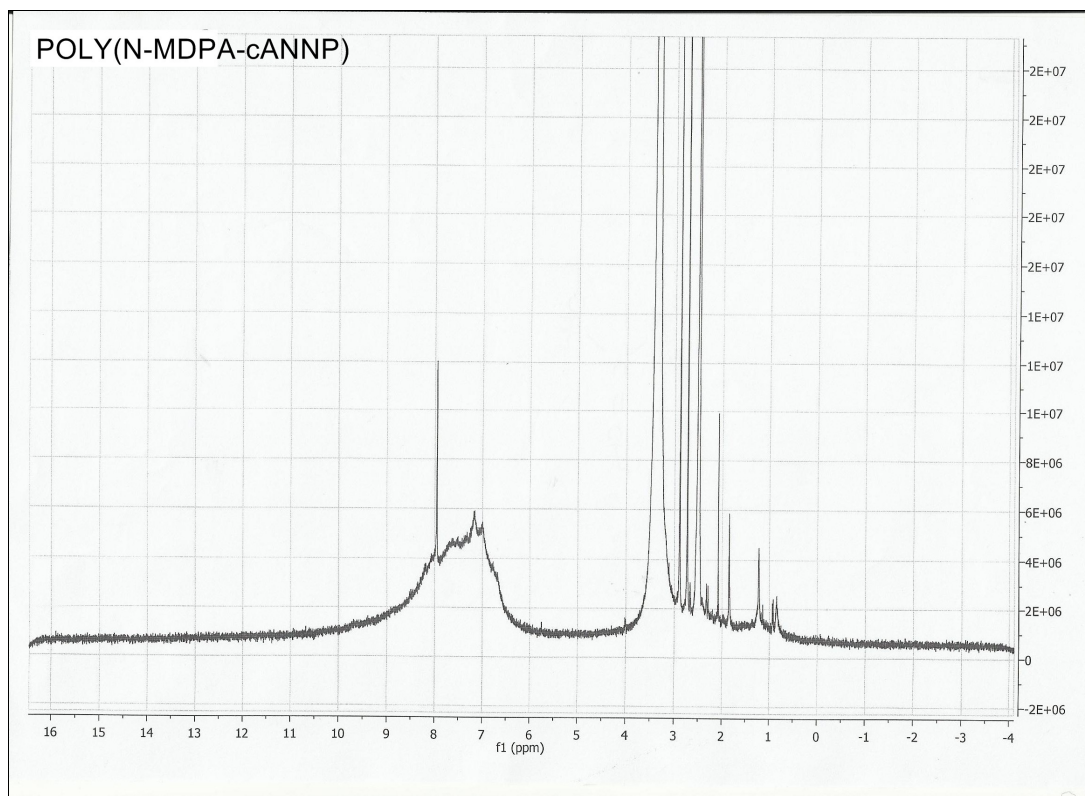


Figure A.2. ^1H -NMR of Poly(N-MDPA-cANNP)

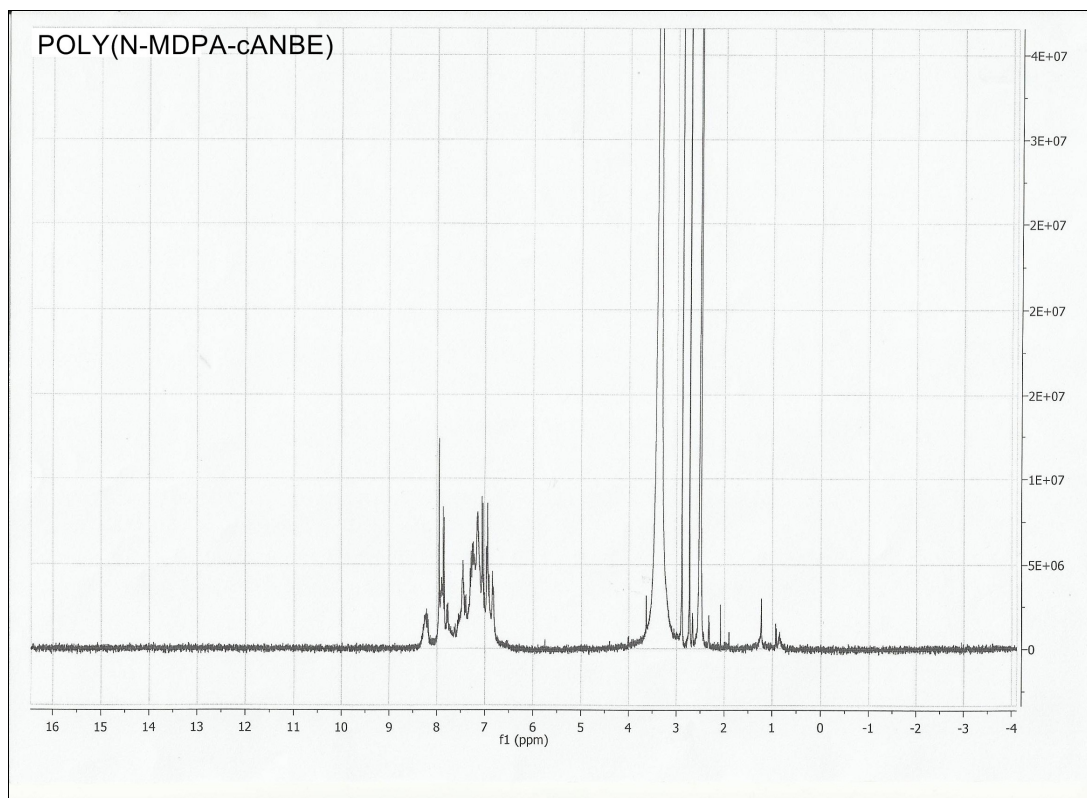


Figure A.3. ¹H-NMR of Poly(N-MDPA-cANBE)

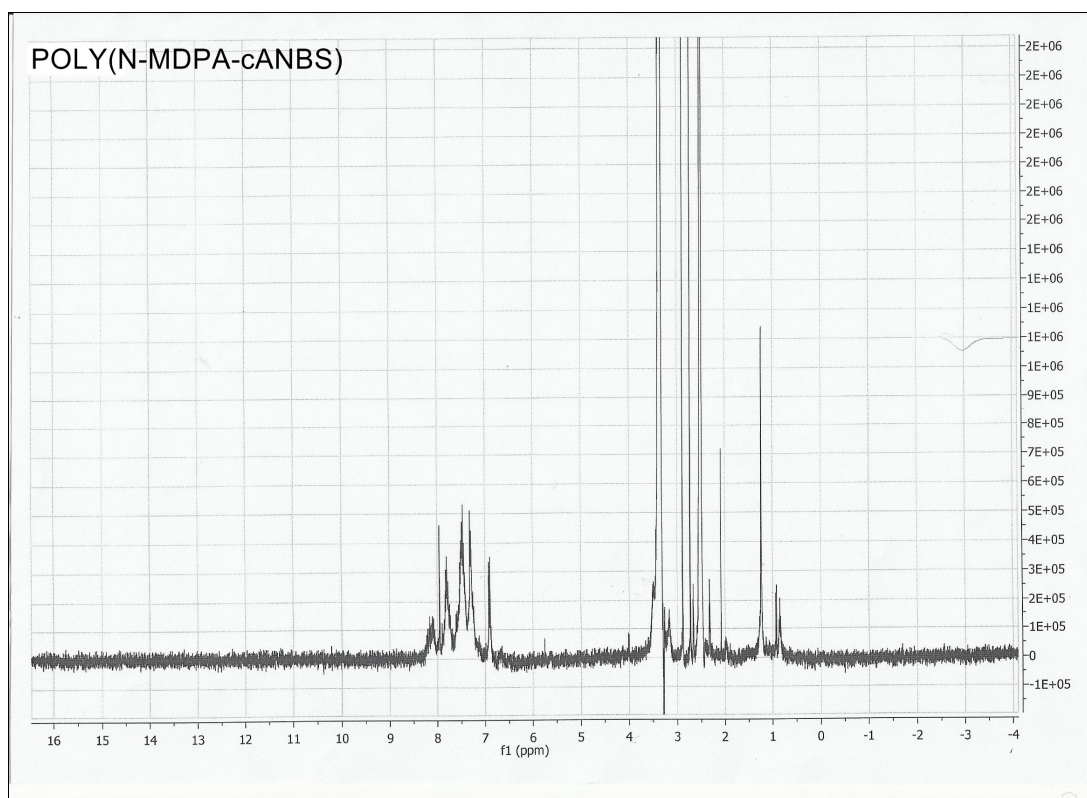


Figure A.4. ¹H-NMR of Poly(N-MDPA-cANBS)

APPENDIX B: ^{31}P -NMR

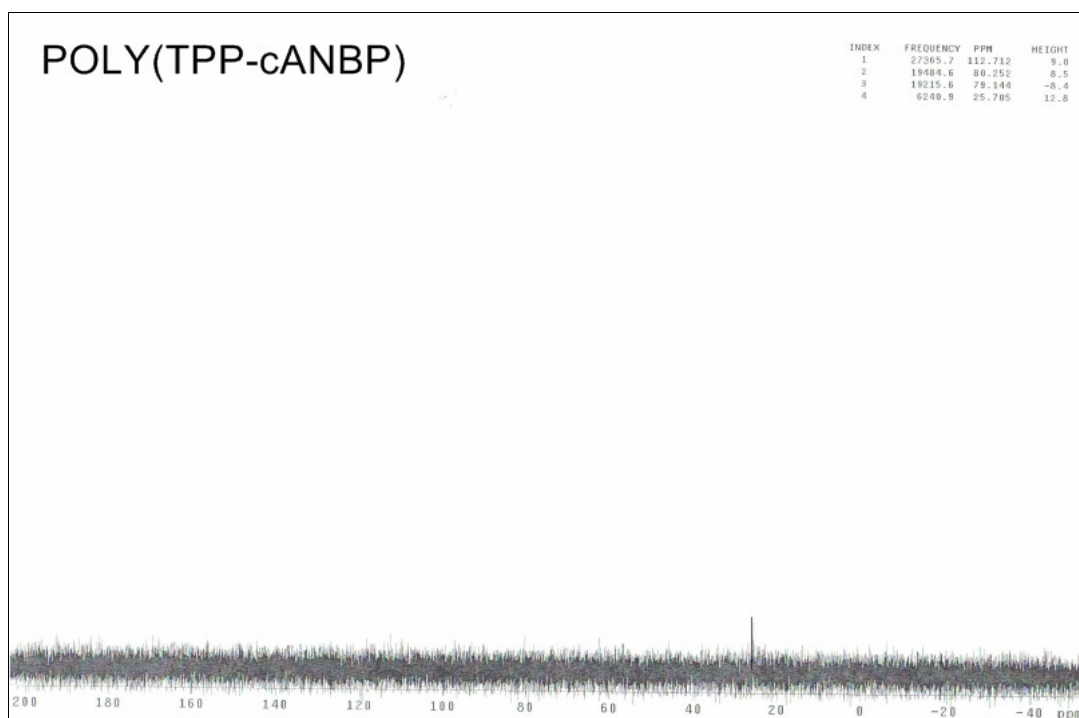


Figure B.1. ^{31}P -NMR of Poly(TPP-cANBP)

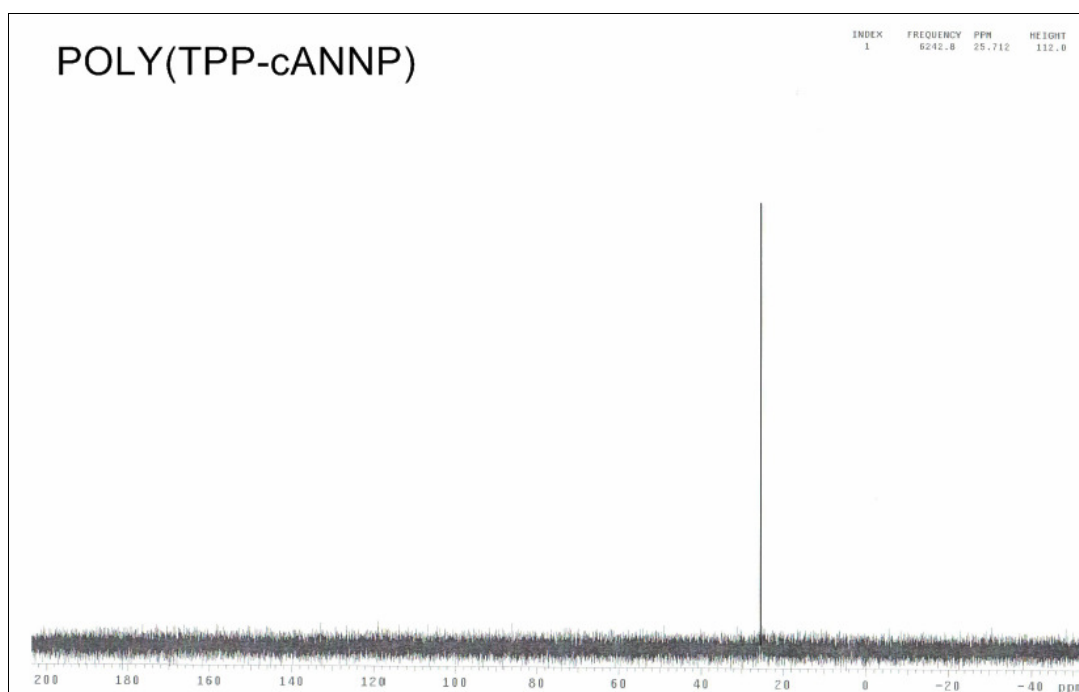


Figure B.2. ^{31}P -NMR of Poly(TPP-cANNP)

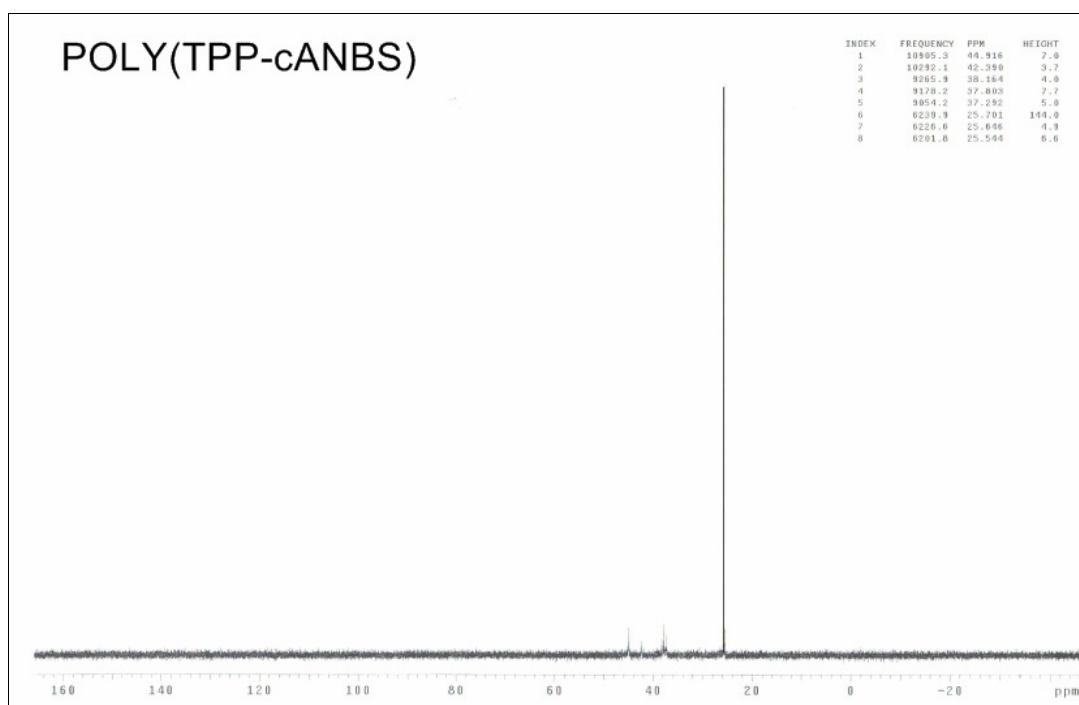


Figure B.3. ^{31}P -NMR of Poly(TPP-cANBS)

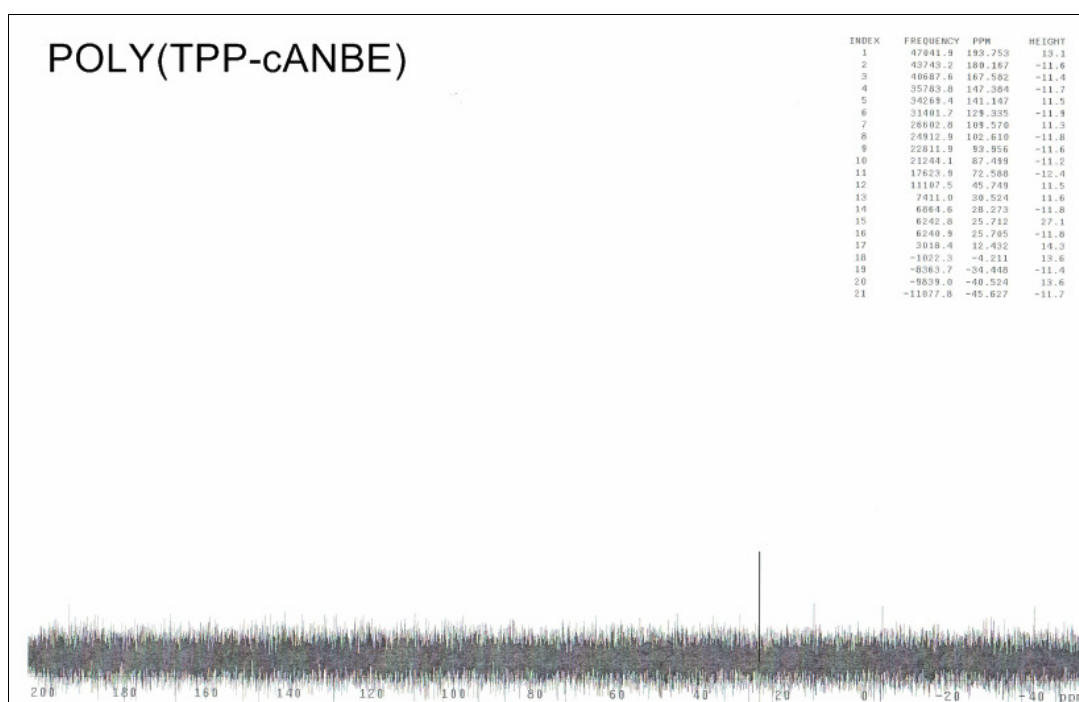


Figure B.4. ^{31}P -NMR of Poly(TPP-cANBE)

APPENDIX C: DSC&TGA

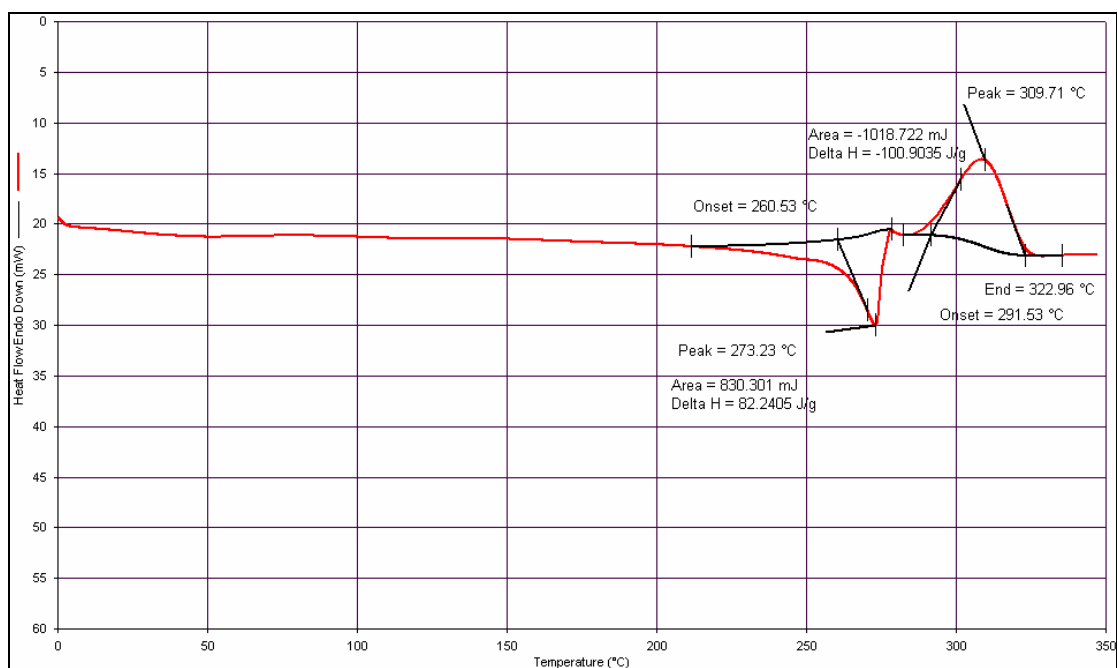


Figure C.1. DSC thermogram of cANBP

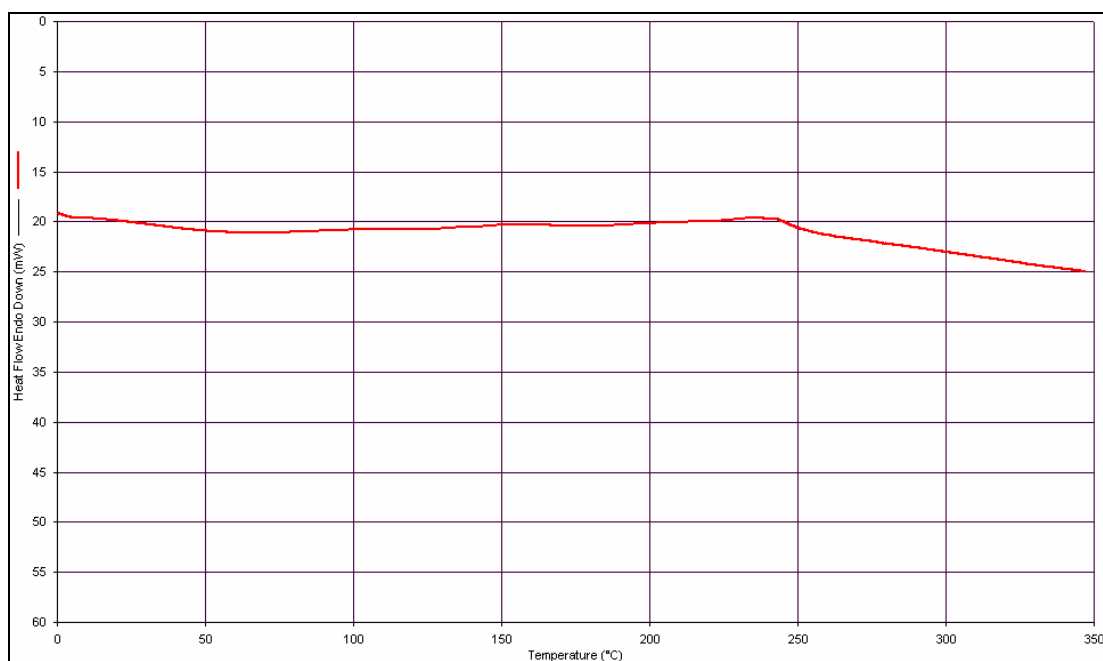


Figure C.2. DSC thermogram of cANNP

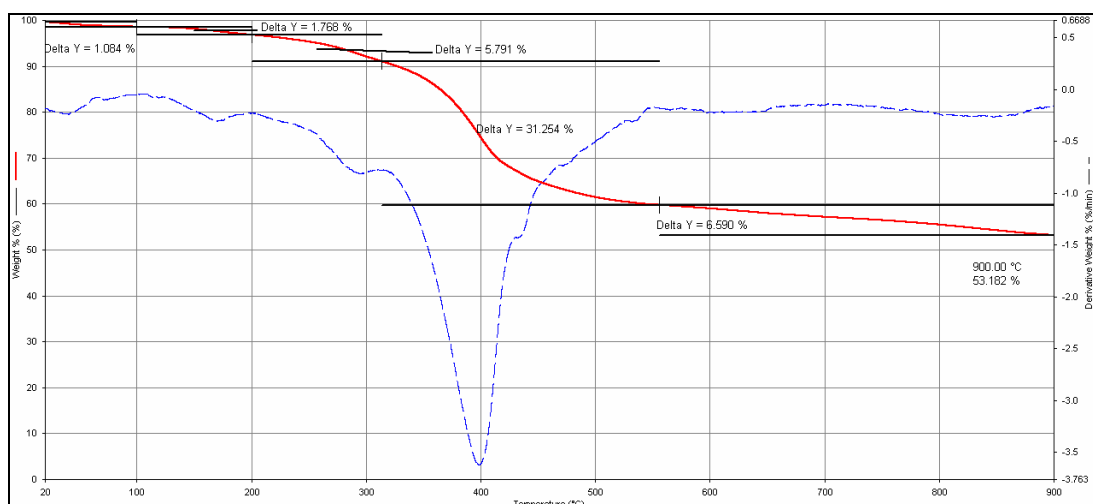


Figure C.3. TGA thermogram of cANNP

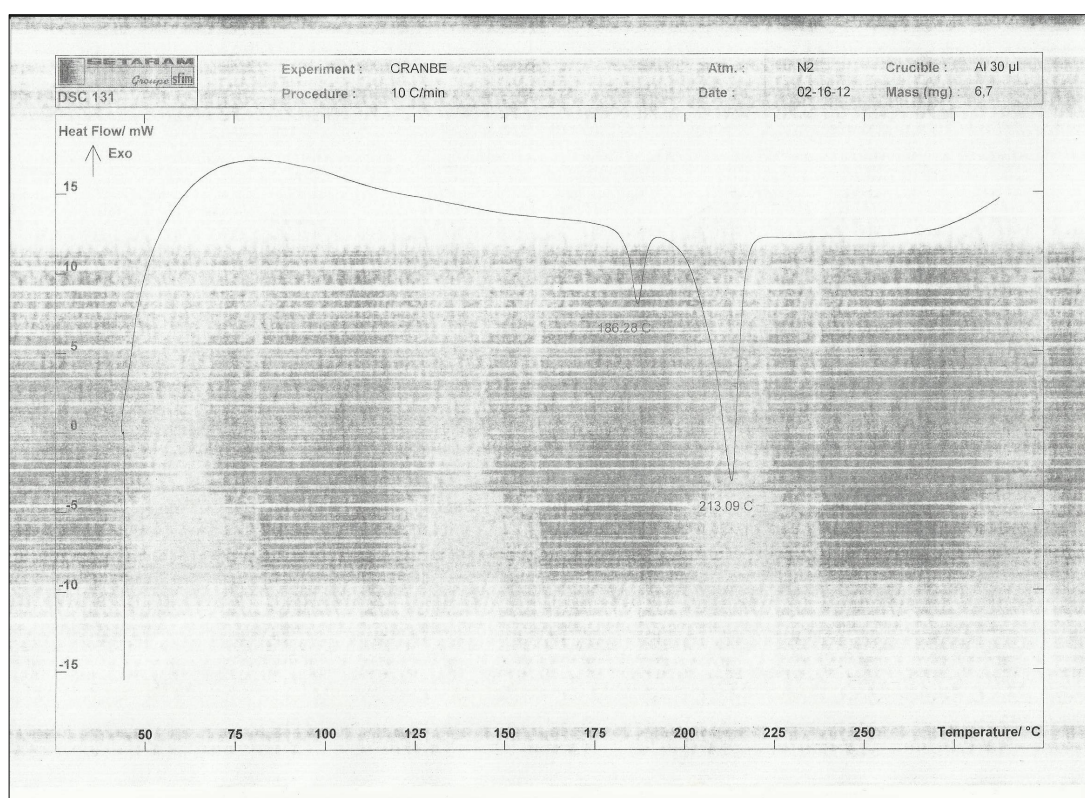


Figure C.4. DSC thermogram of cANBE

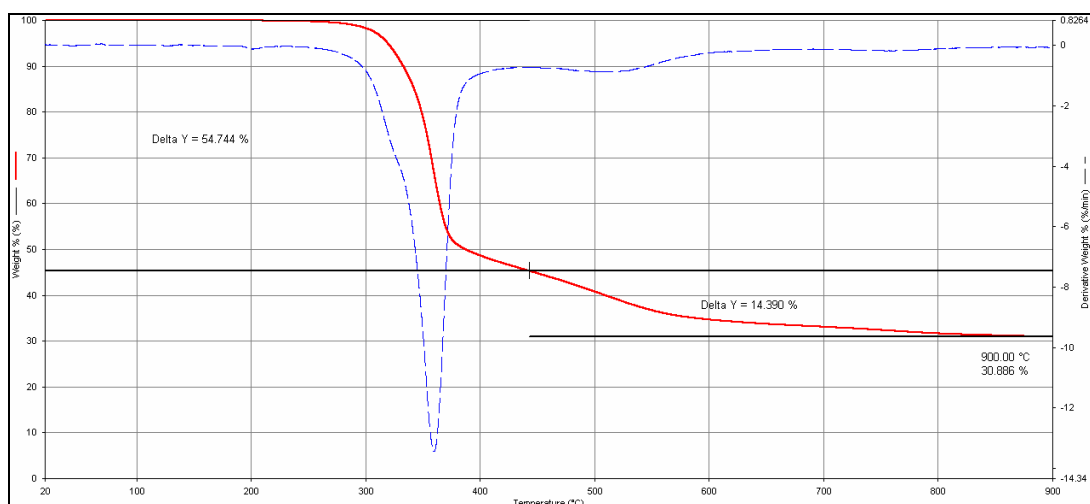


Figure C.5. TGA thermogram of cANBE

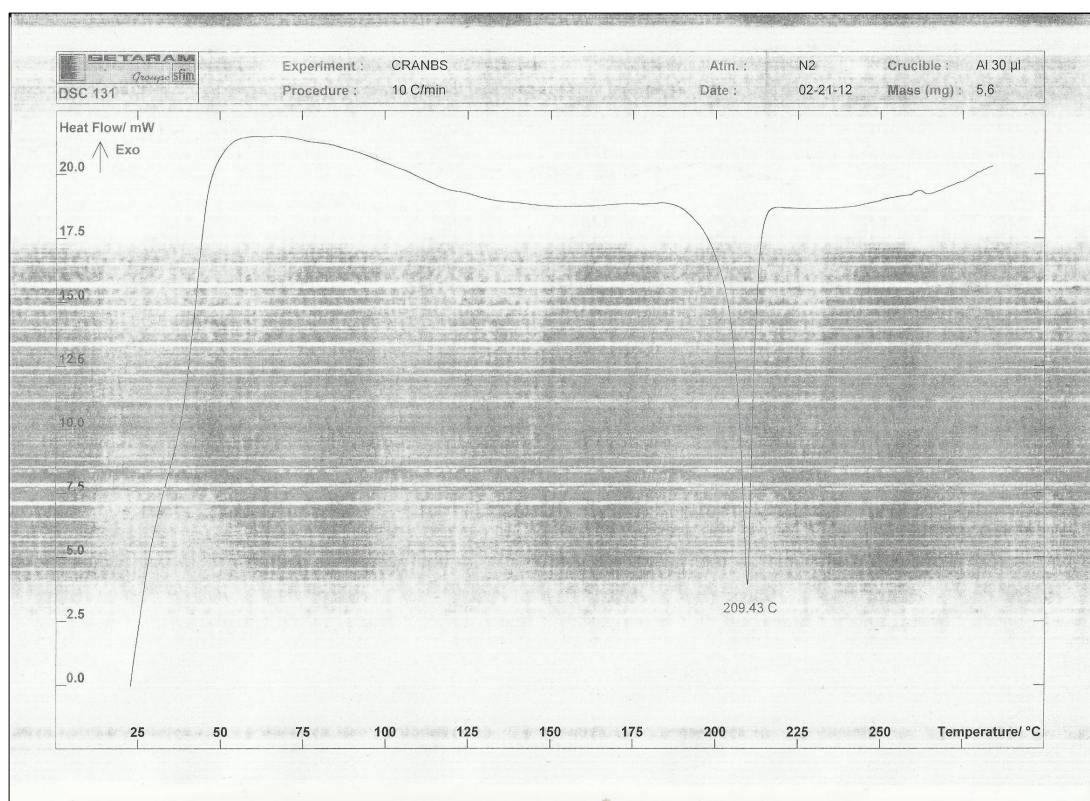


Figure C.6. DSC thermogram of cANBS

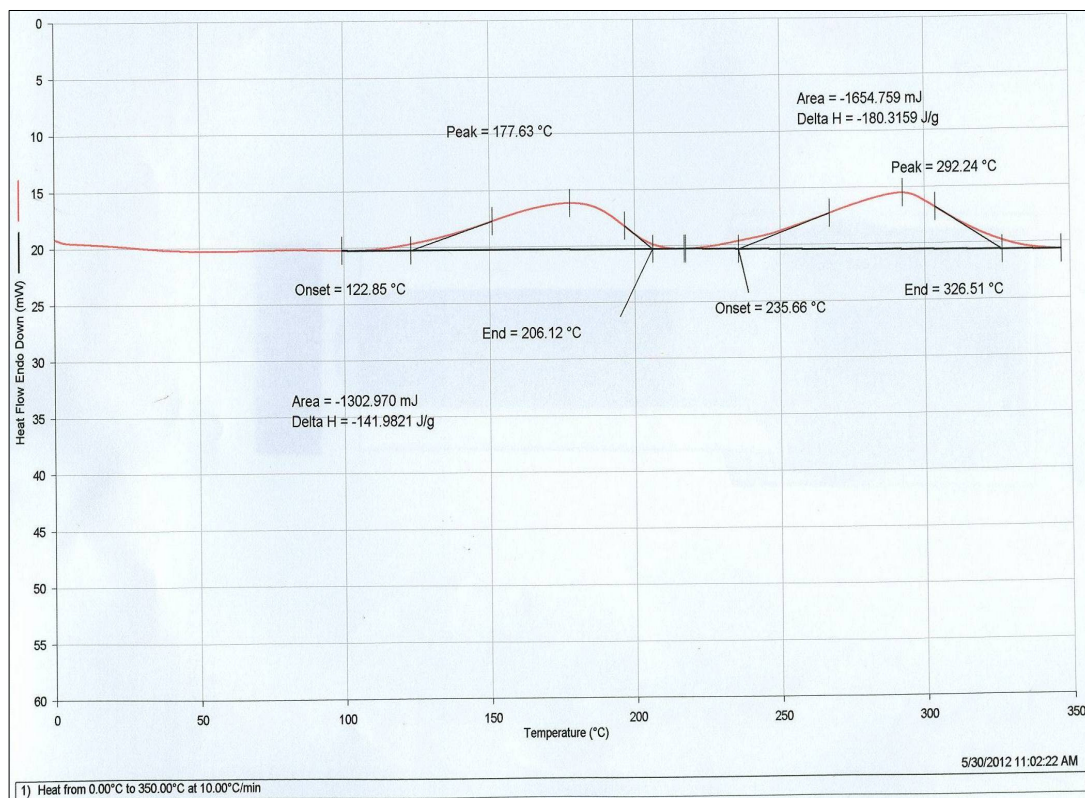


Figure C.7. DSC thermogram of Poly(TPA-cANBP)

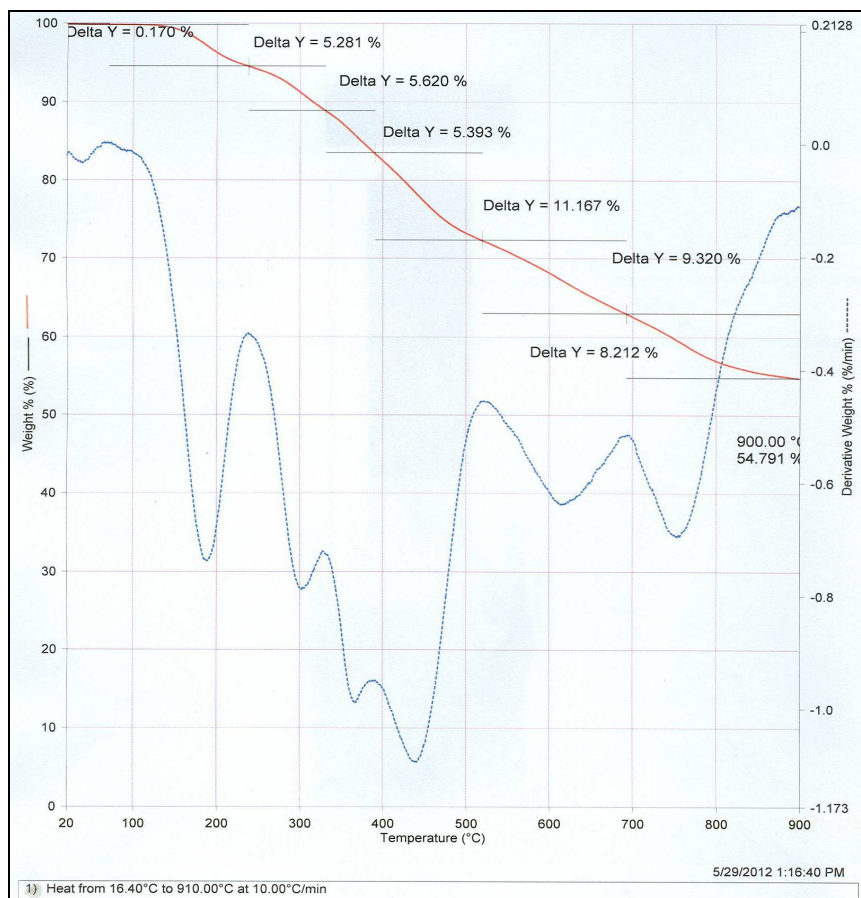


Figure C.8. TGA thermogram of Poly(TPA-cANBP)

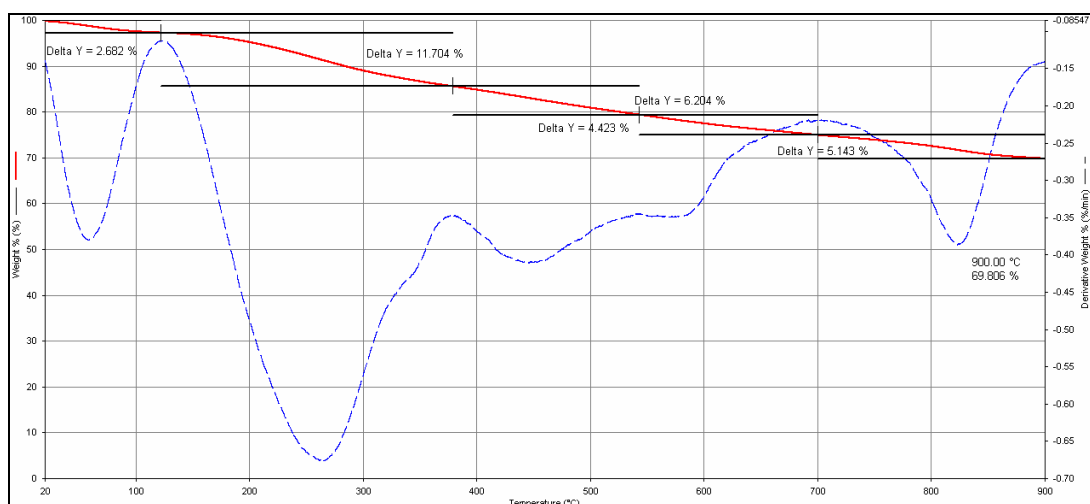


Figure C.9. TGA thermogram of Poly(TPA-cANNP)

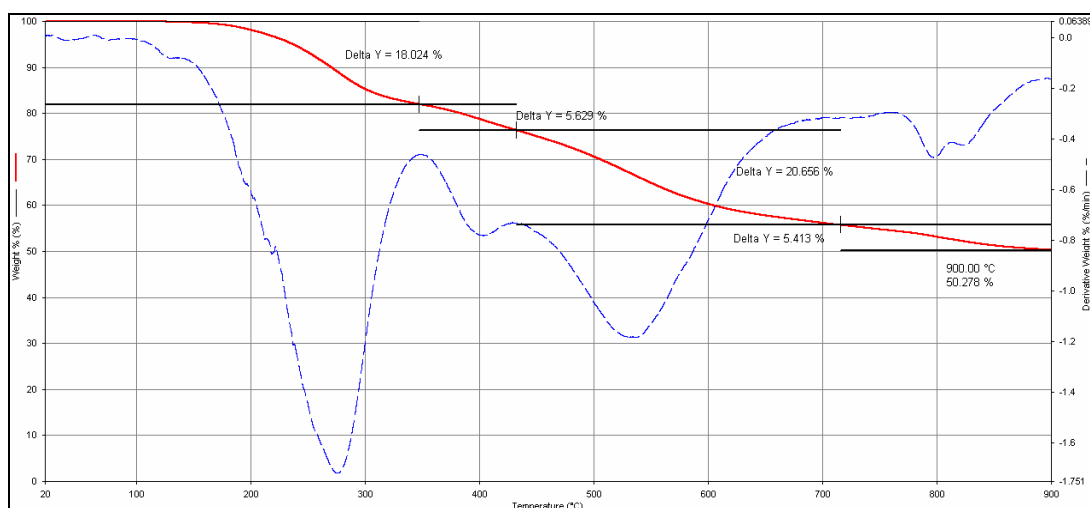


Figure C.10. TGA thermogram of Poly(TPA-cANBE)

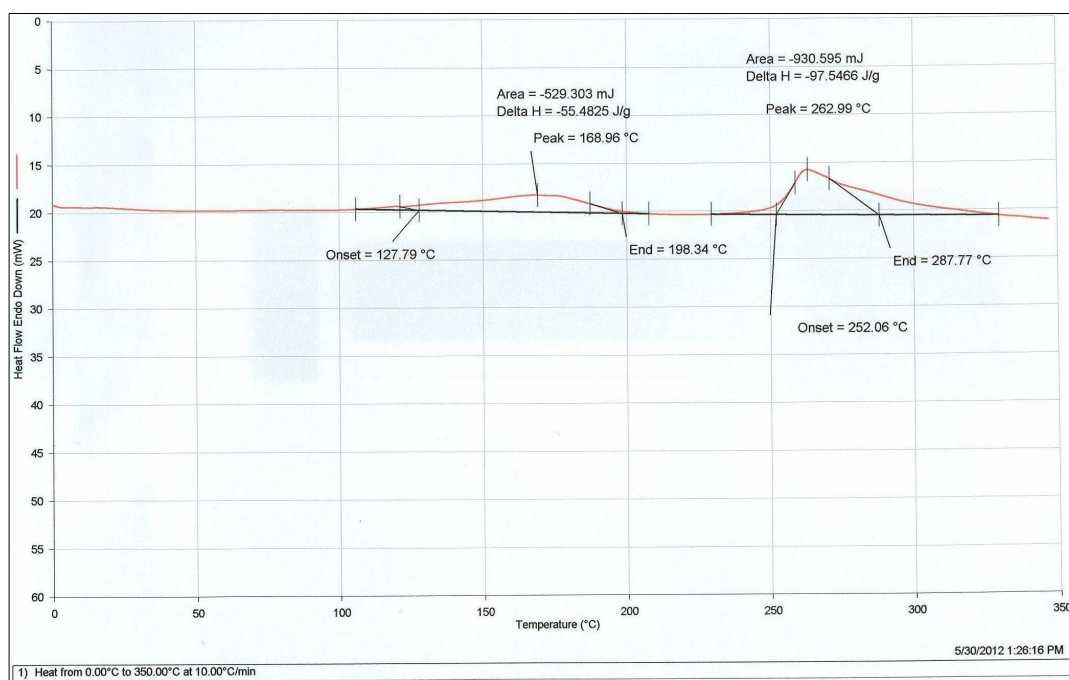


Figure C.11: DSC thermogram of Poly(TPA-cANBS)

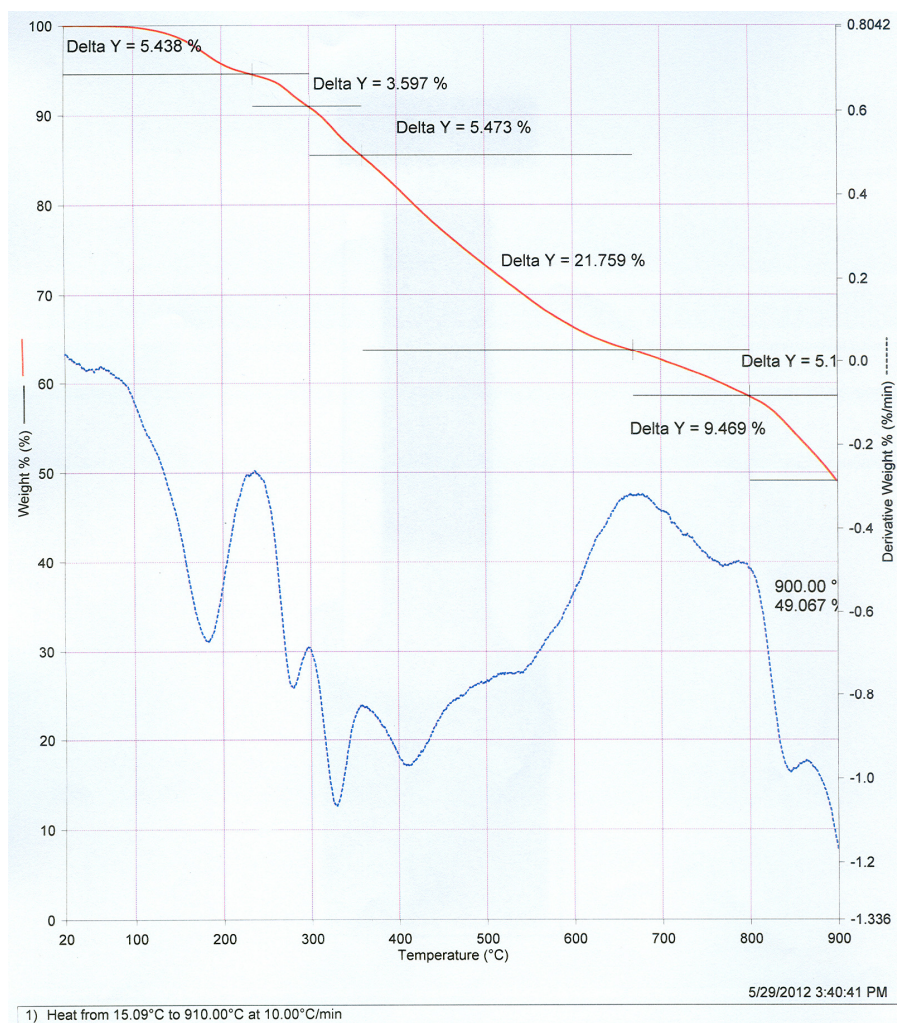


Figure C.12. TGA thermogram of Poly(TPA-cANBS)

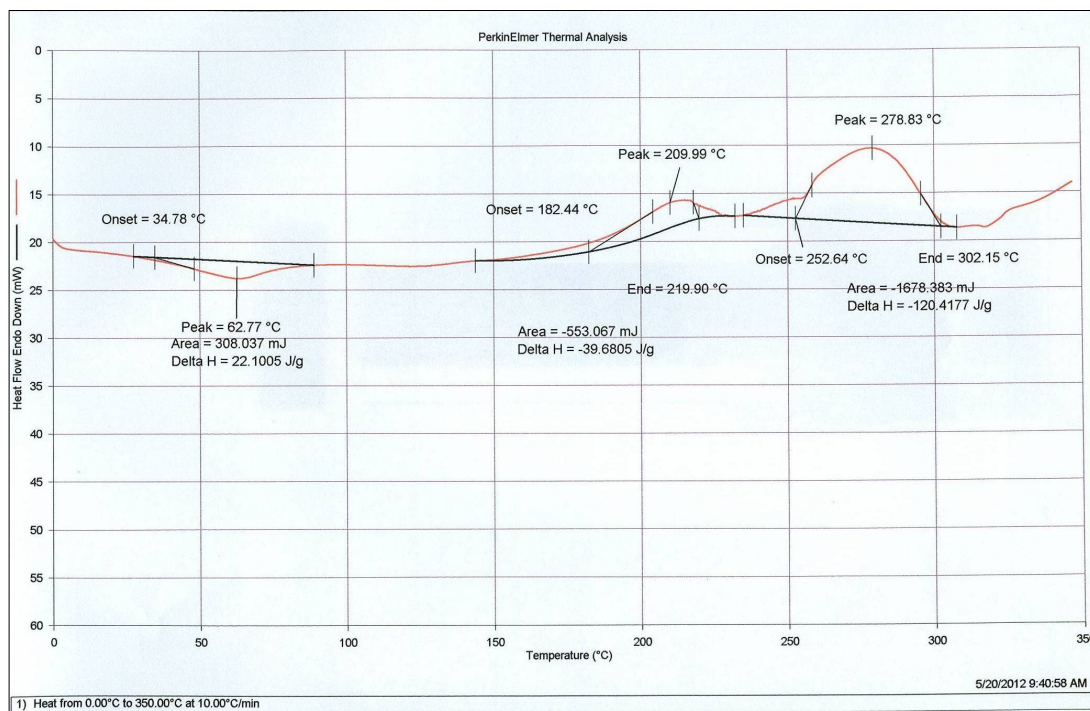


Figure C.13. DSC thermogram of Poly(N-MDPA-cANBP)

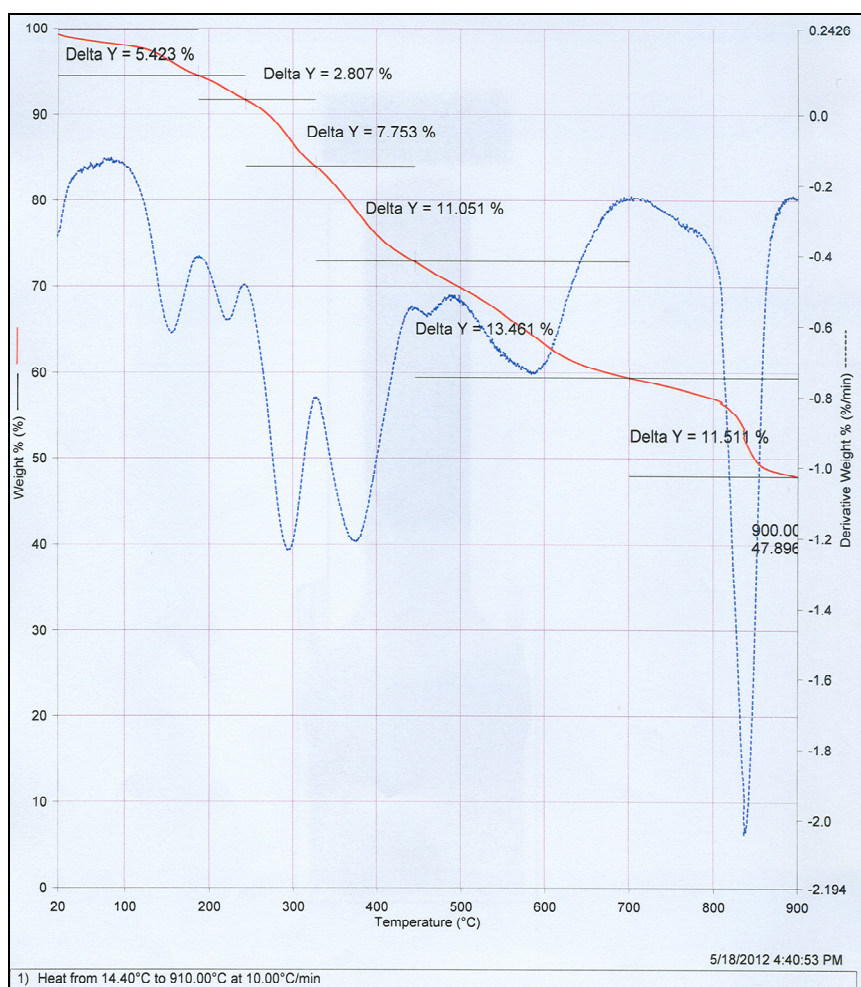


Figure C.14. TGA thermogram of Poly(N-MDPA-cANBP)

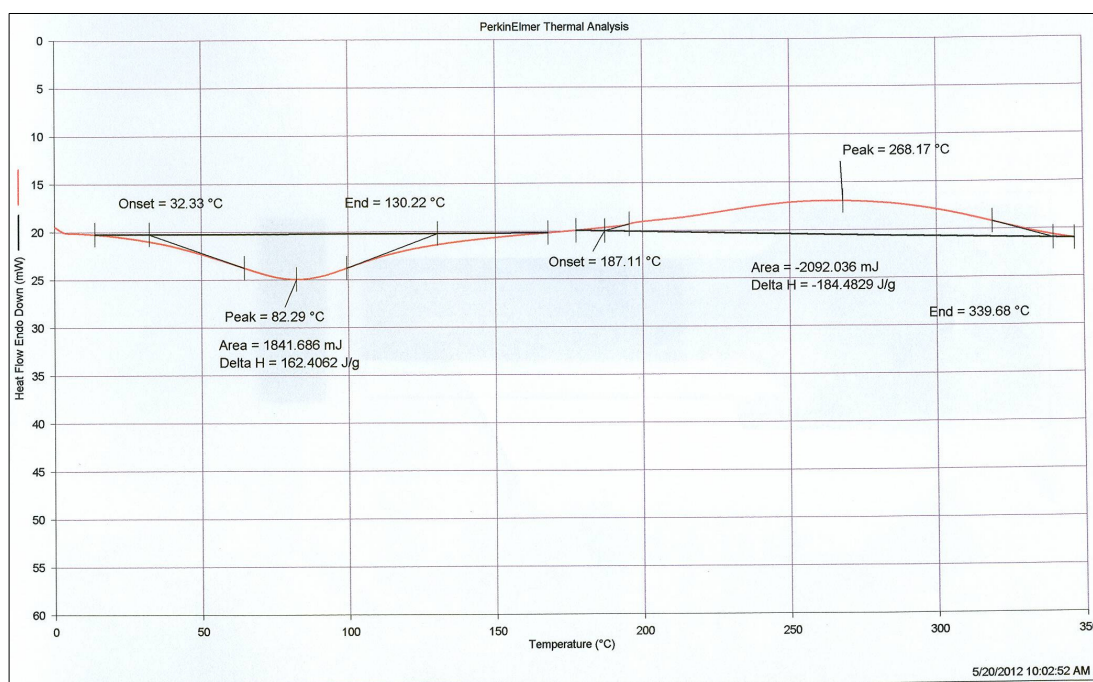


Figure C.15. DSC thermogram of Poly(N-MDPA-cANNP)

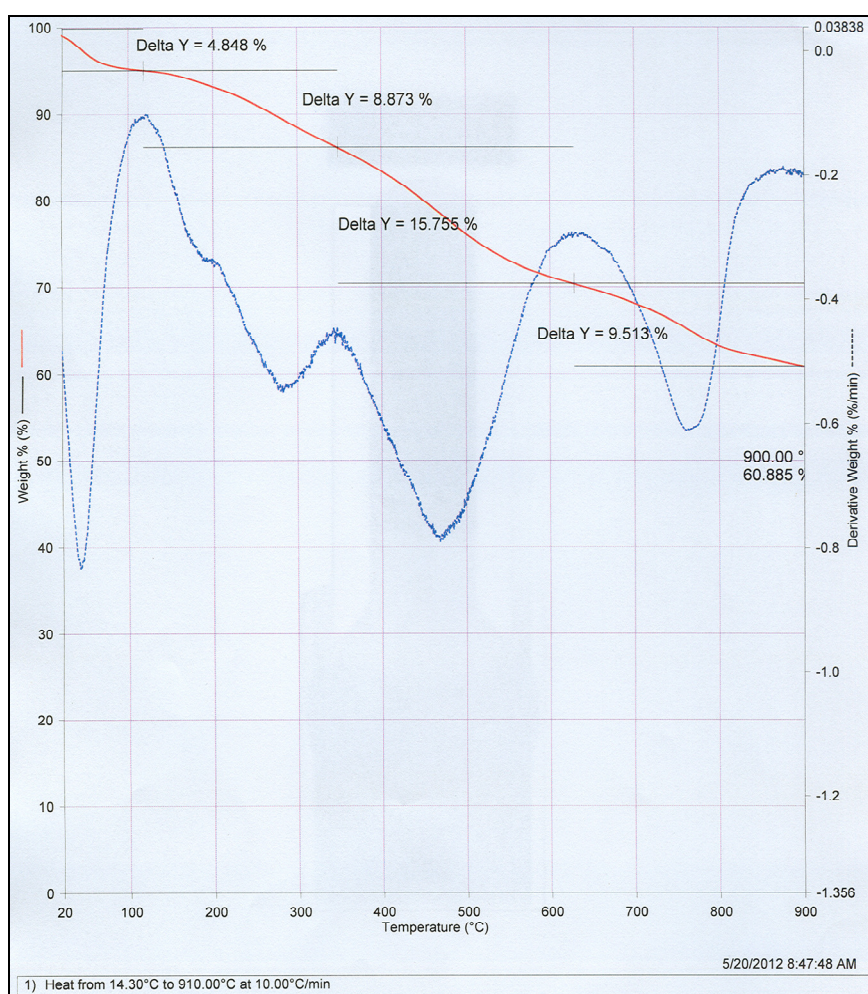


Figure C.16. TGA thermogram of Poly(N-MDPA-cANNP)

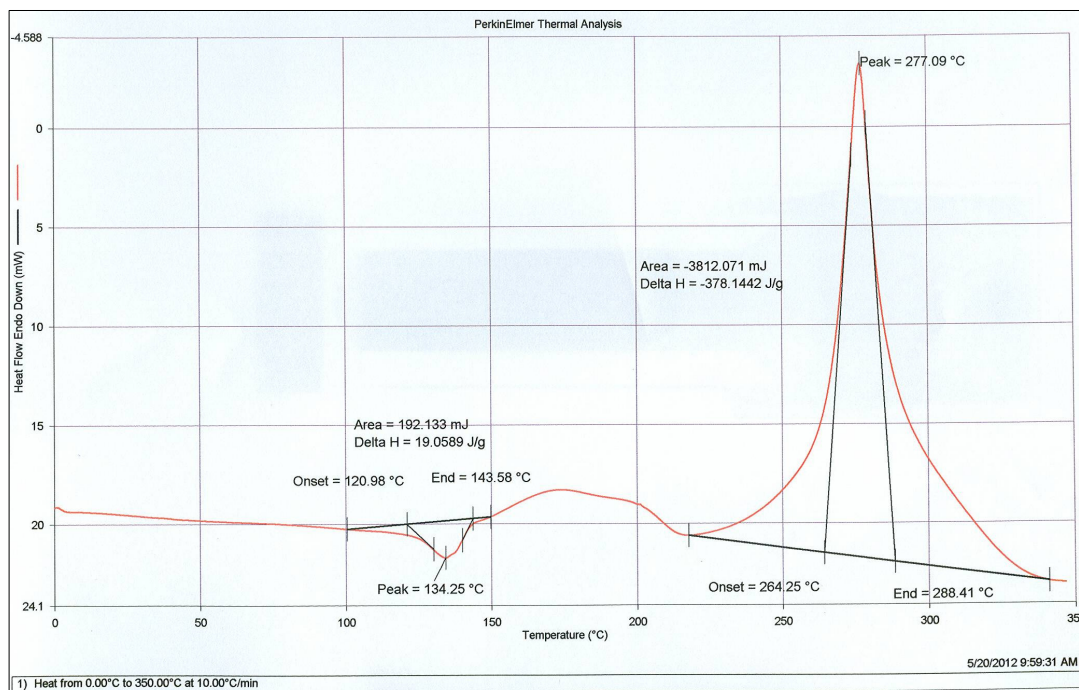


Figure C.17: DSC thermogram of Poly(N-MDPA-cANBE)

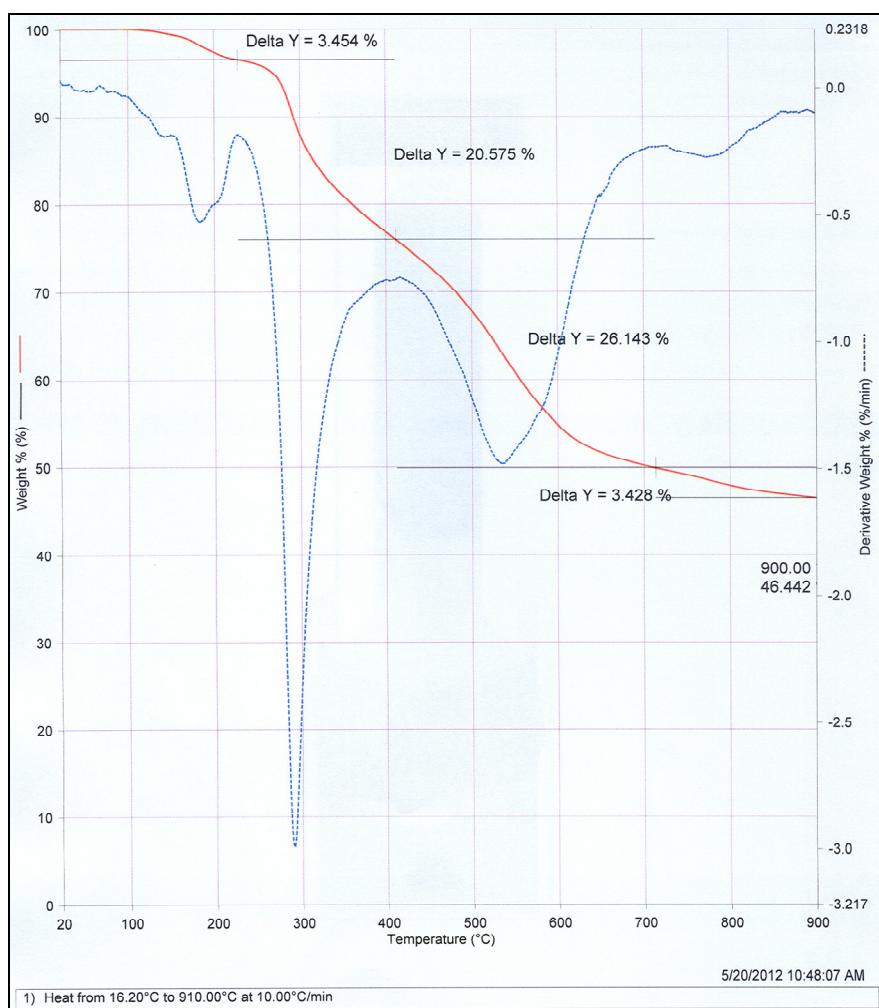


Figure C.18: TGA thermogram of Poly(N-MDPA-cANBE)

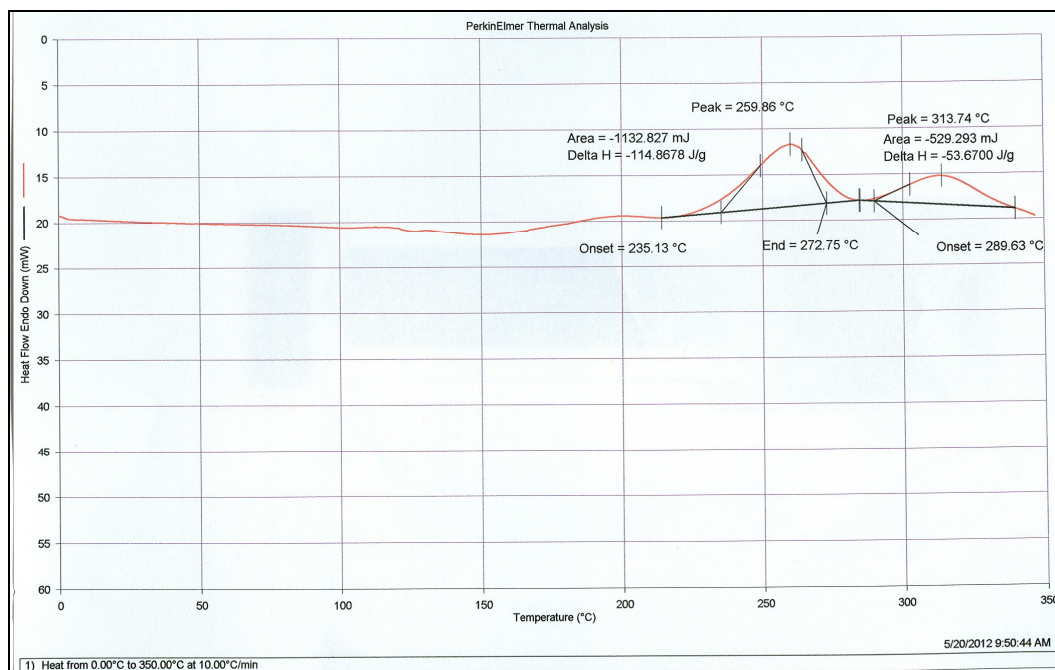


Figure C.19. DSC thermogram of Poly(N-MDPA-cANBS)

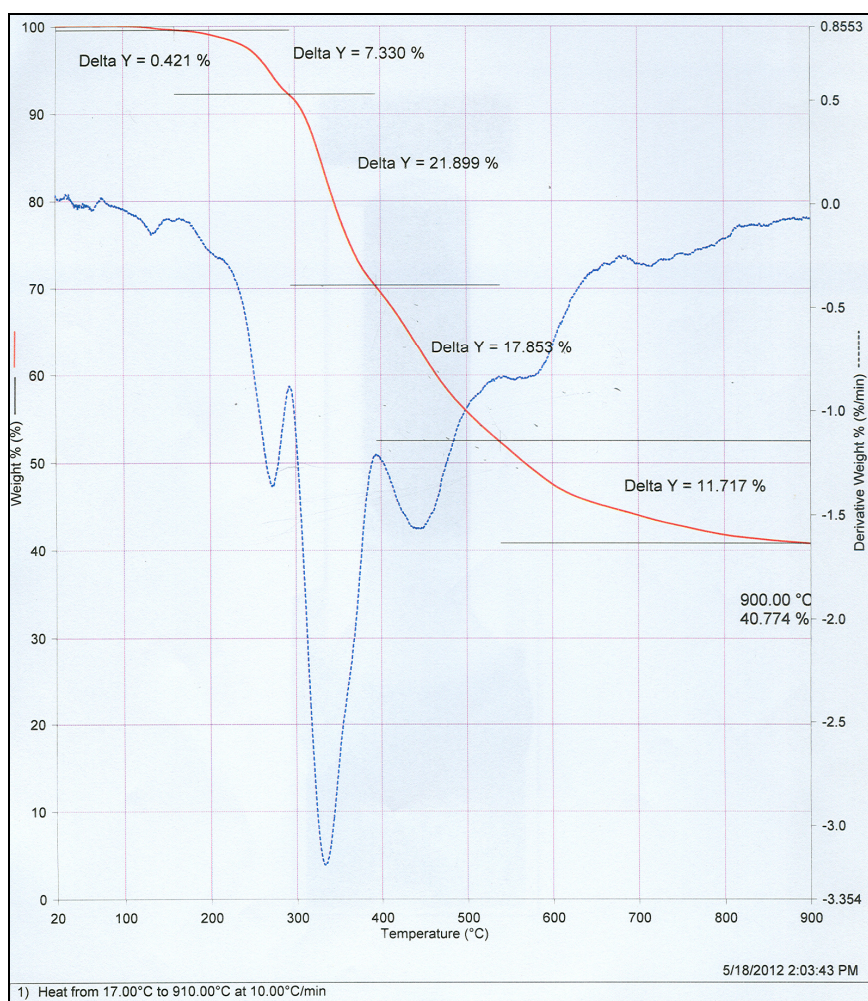


Figure C.20. TGA thermogram of Poly(N-MDPA-cANBS)

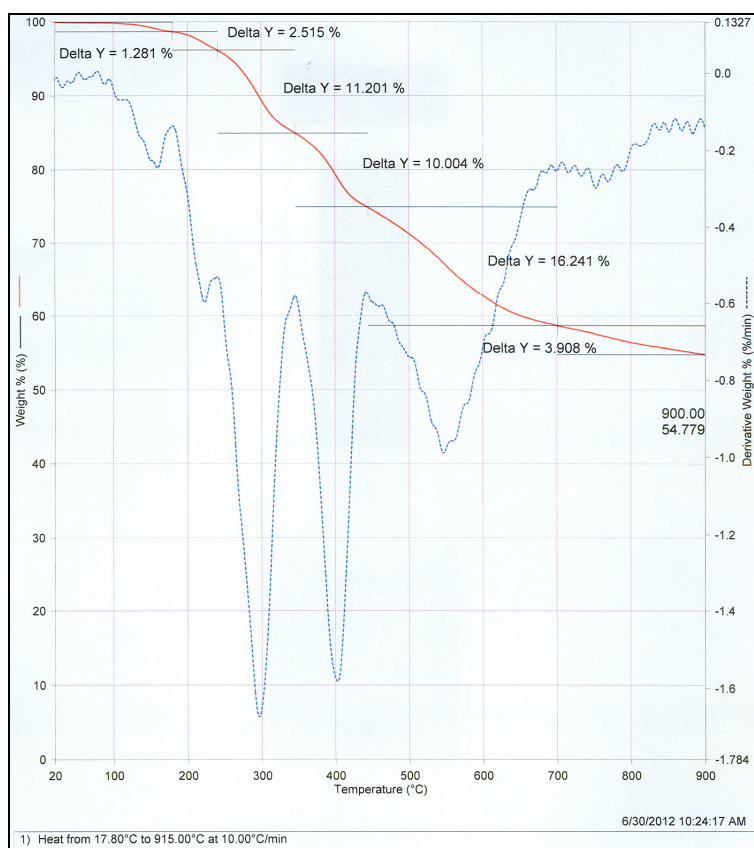


Figure C. 21. TGA thermogram of Poly(TPP-cANBP)

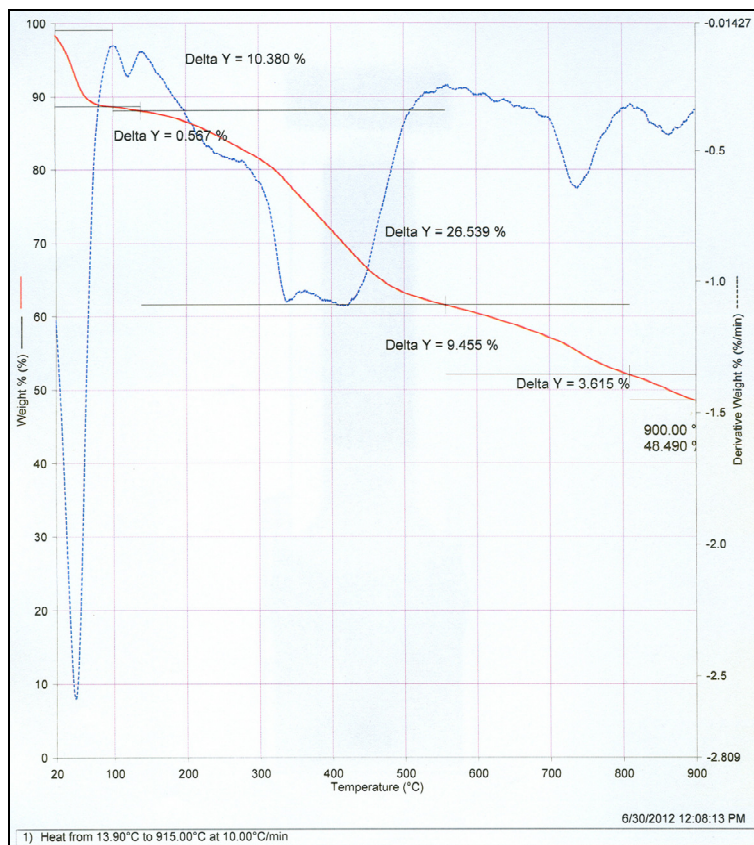


Figure C. 22. TGA thermogram of Poly(TPP-cANNP)

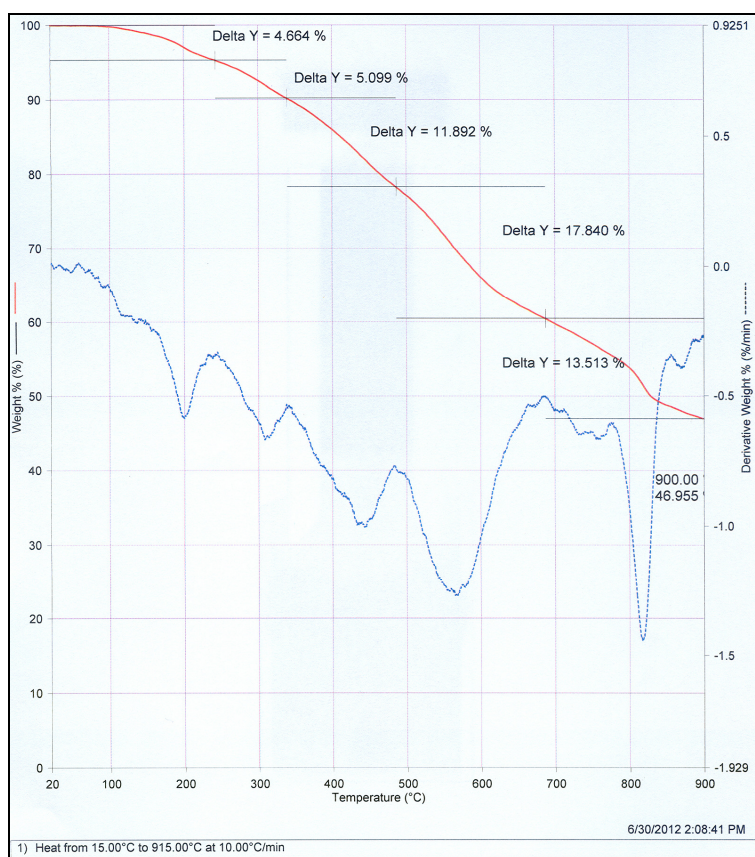


Figure C.23. TGA thermogram of Poly(TPP-cANBE)

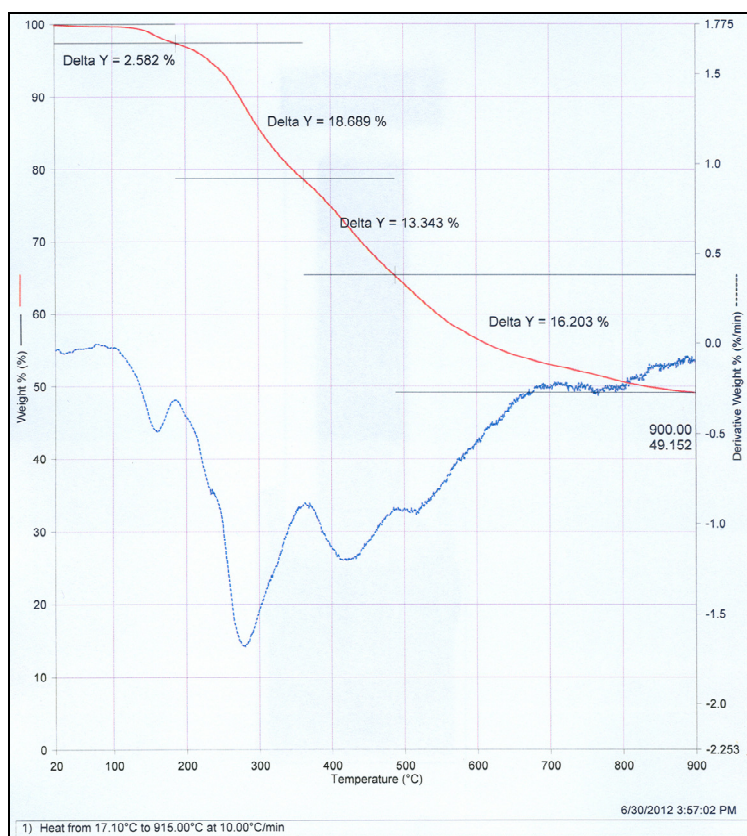


Figure C.24. TGA thermogram of Poly(TPP-cANBS)

APPENDIX D: UV/VIS

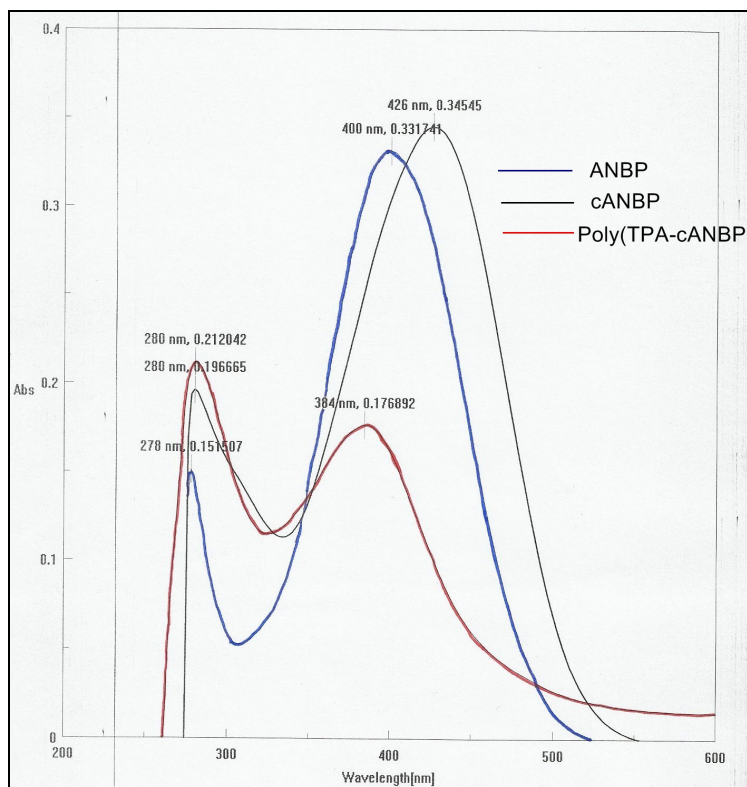


Figure D.1. UV-Vis spectra of ANBP, cANBP and Poly(TPA-cANBP)

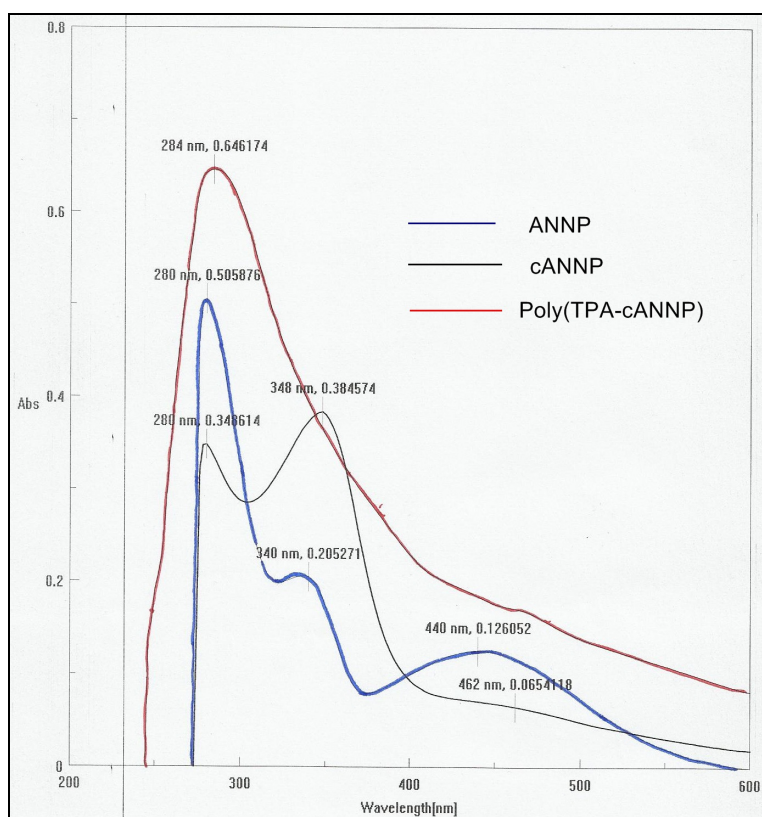


Figure D.2. UV-Vis spectra of ANNP, cANNP and Poly(TPA-cANNP)

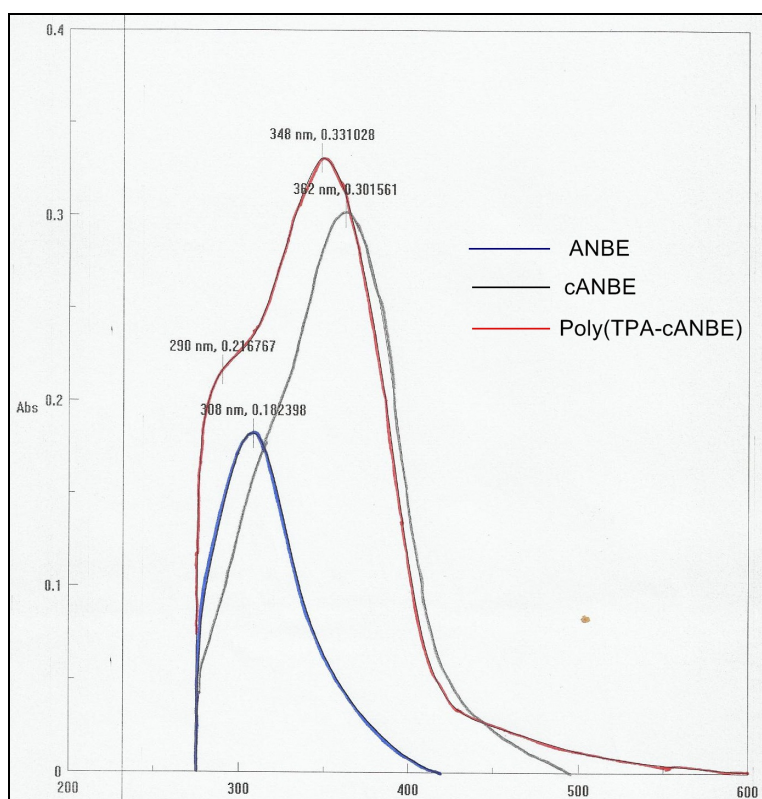


Figure D.3. UV-Vis spectra of ANBE, cANBE and Poly(TPA-cANBE)

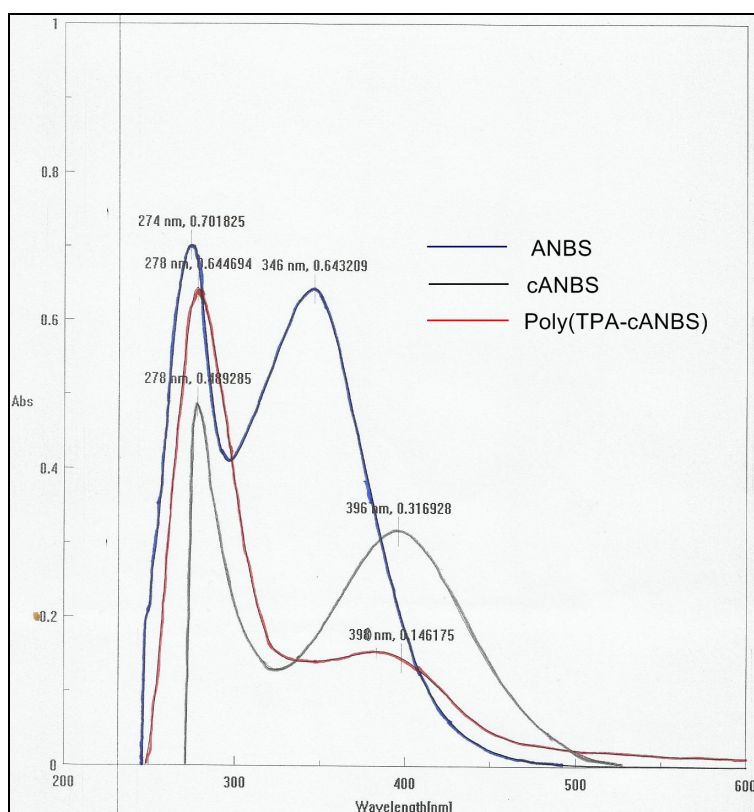


Figure D.4: UV-Vis spectra of ANBS, cANBS and Poly(TPA-cANBS)

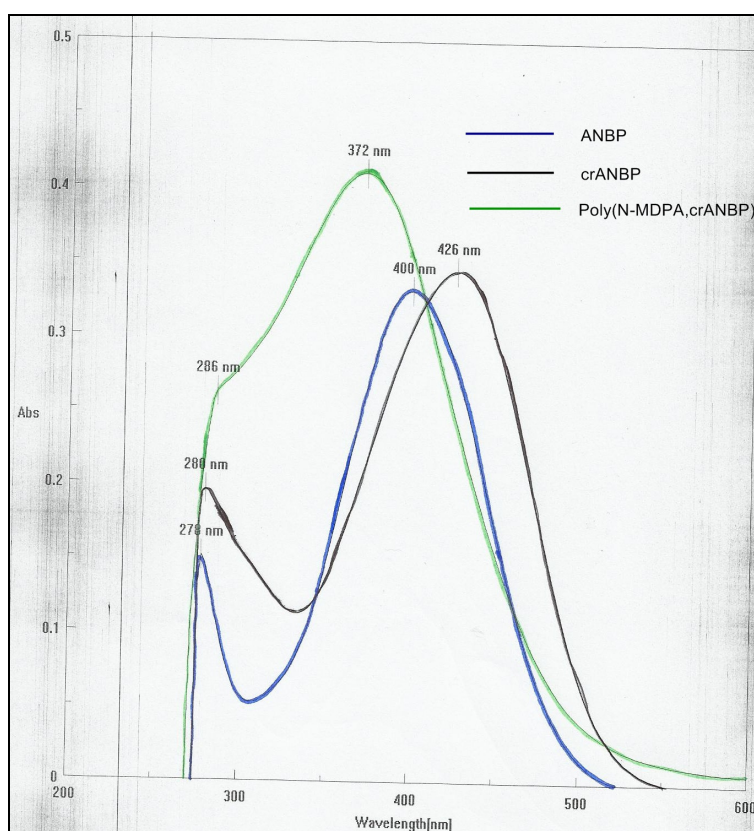


Figure D.5. UV-Vis spectra of ANBP, crANBP and Poly(N-MDPA-crANBP)

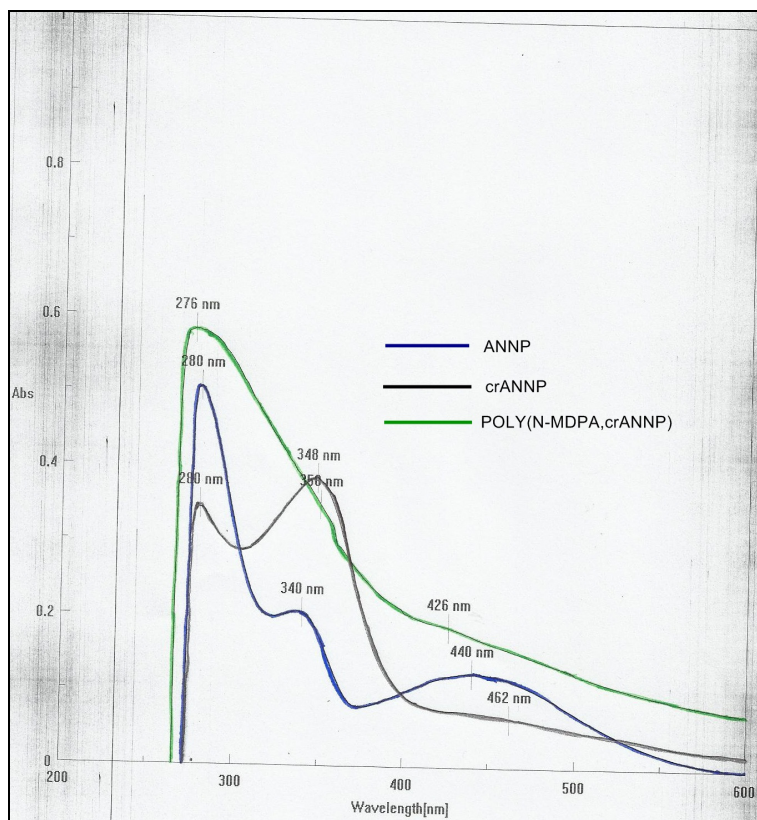


Figure D.6. UV-Vis spectra of ANNP, cANNP and Poly(N-MDPA-cANNP)

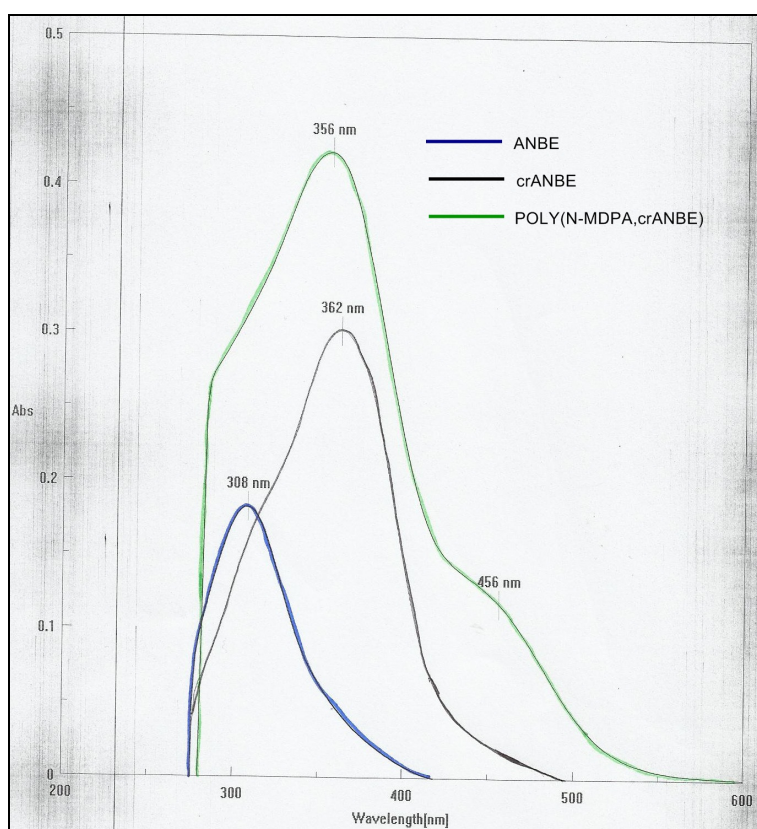


Figure D.7. UV-Vis spectra of ANBE, cANBE and Poly(N-MDPA-cANBE)

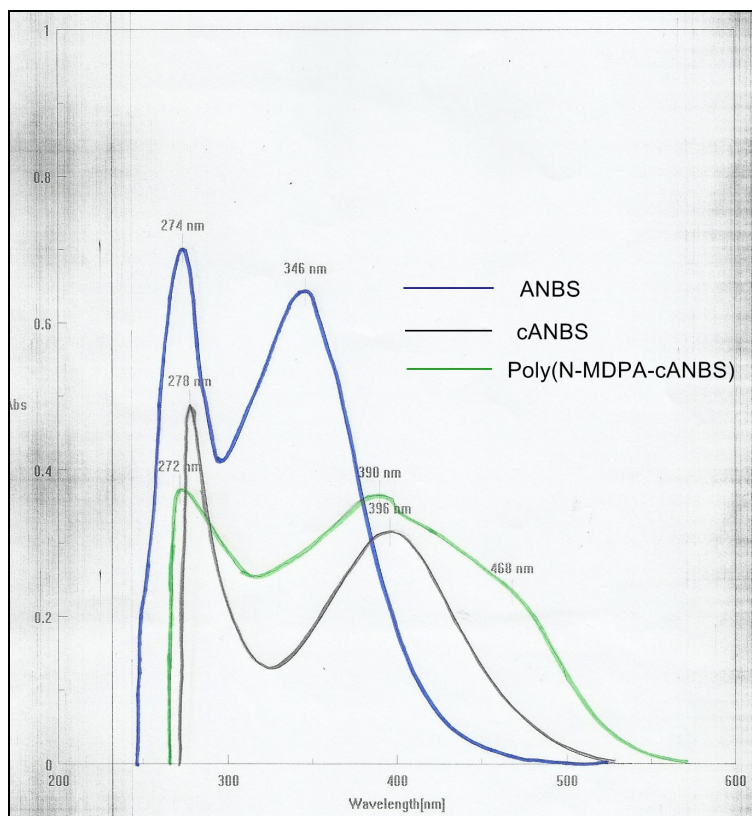


Figure D.8. UV-Vis spectra of ANBS, cANBS and Poly(N-MDPA-cANBS)

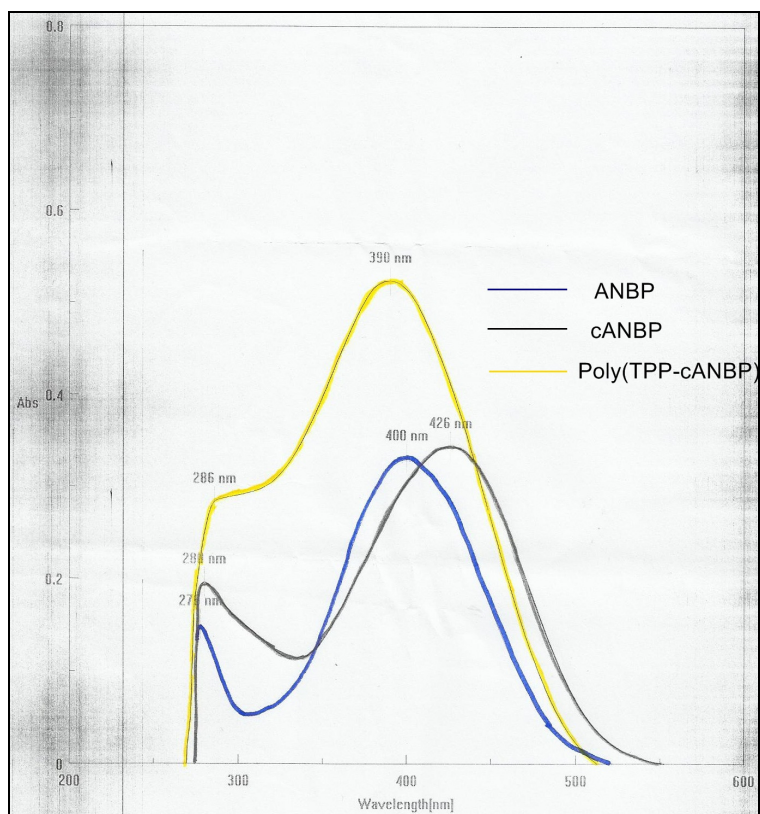


Figure D.9. UV-Vis spectra of ANBP, cANBP and Poly(TPP-cANBP)

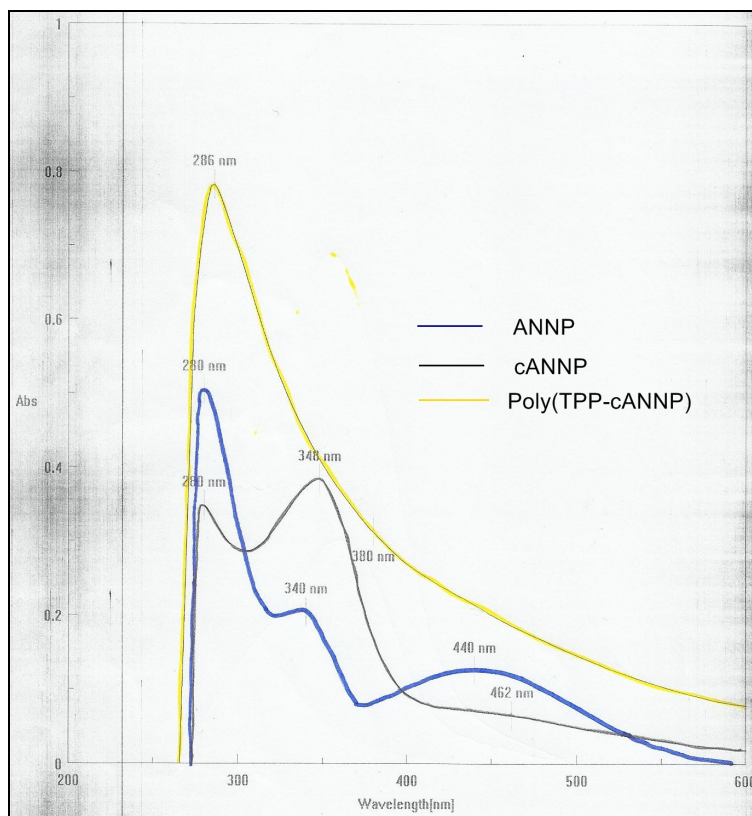


Figure D.10. UV-Vis spectra of ANNP, cANNP and Poly(TPP-cANNP)

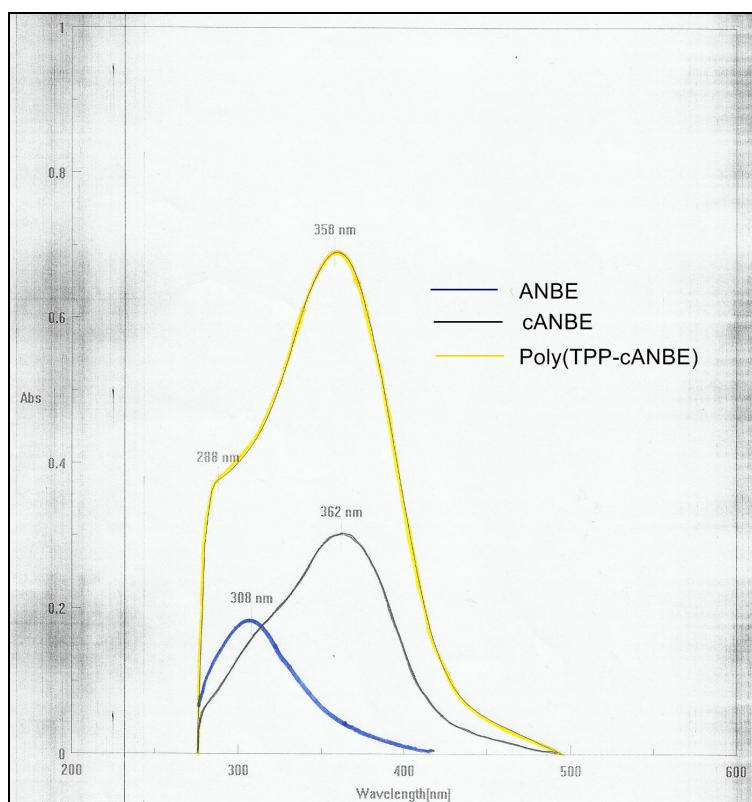


Figure D.11. UV-Vis spectra of ANBE, cANBE and Poly(TPP-cANBE)

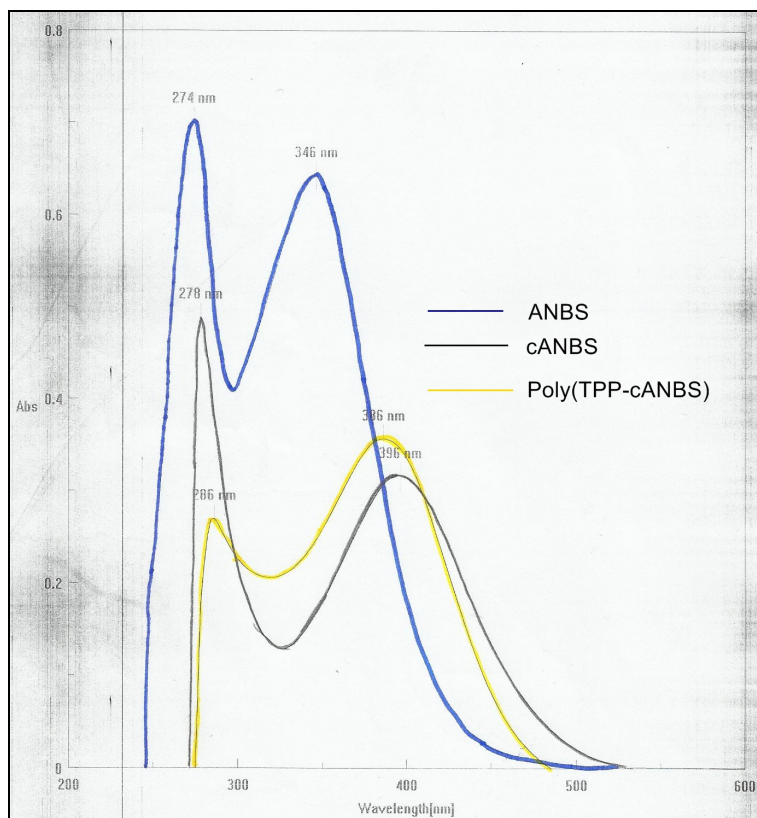


Figure D.12. UV-Vis spectra of ANBS, cANBS and Poly (TPP-cANBS)
