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Synthesis of Aromatic Conjugated Main Chain Azobenzene Polymers and Their Properties

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Abstract

Azobenzene polymers have great potential and impact on fundamental and applied research. However little is known about their thermal stability and degradation behavior. Herein, nine conjugated main chain azobenzene polymers were synthesized using the nitroamine derivatives of some diphenylene compounds such as 4-amino-4′-nitrobiphenyl 1, 4-amino-4′-nitrobiphenyl ether 2 and 4-amino-4′-nitrobiphenyl sulfide 3, and comonomers triphenylamine A, *N*-methyldiphenyl amine B and triphenylphosphine C via a diazo coupling reaction. These heteroatom-containing polymers were characterized by 1H- and 31P-NMR, FTIR, UV–Vis and Raman spectroscopy. The thermal stability and degradation behavior of these polymers were studied by means of TGA technique. Electronic spectra of the polymers recorded in DMF showed two strong maxima at ca. 280 and 380 nm. They were resistant to heat up to 270 °C and, produced 41-61% char under a nitrogen atmosphere at 800 °C. UL 94 burning tests performed for TPU Ravathane® (TPE-U) with added azobenzene polymer revealed that these polymers could be used as an intumescent reactive flame retardant additive, particularly for polyurethanes and elastomers, due to their high char yield at relatively high temperatures (e.g 800 °C). The carbonized materials were further characterized by XRD and SEM/EDX.

Keywords: Main chain azobenzene polymers; intumescent flame retardant additive; thermal stability; thermal degradation and carbonization.

1. Introduction

Polymer systems containing azobenzene moieties are known to have improved physical and chemical properties such as viscosity, photoresponsivitiy, refractive index, conductivity, nonlinear optical susceptibility, mechanical properties and polymer morphology [1]. Such changes enable azobenzene polymers to be used for various photonic applications including LEDs, edge-emitting lasers, optical fibre communications and optical storage [1]. Thus, considerable effort has been devoted to synthesizing both aromatic side-chain and main-chain azobenzene polymers [1]. A previous study revealed that the mobility of main-chain azobenzene polymers decreased due to the azobenzene groups in the polymer main-chain, however, the polymer backbone had enough flexibility for the alignment of the main chain [2]. The main-chain azo polymers have usually been investigated for the stability of photoinduced properties, liquid crystalline properties [3, 4] and third-order nonlinear optic properties [5, 6]. The azobenzene containing conjugated polymers have also been used for manufacturing functional materials with unexpected optical, electrical and magnetic properties [1]. For example, conjugated main chain azo polymers synthesized by Timpu and co-workers showed real photoconductor properties between 350 and 600 nm [7]. Poly(*p*-phenylene), poly(phenylene-ethylene) and poly(*p*-phenylene-vinylene) have been synthesized by Masuda and co-workers using the azobenzene as a conjugative unit in the backbone [1, 8-10]. Polyamides containing azobenzene moieties in the main chain have also been synthesized [11] and they showed high T_g (>220 °C) and thermal stability under nitrogen (~ 400 °C), with 50% char above 800 °C which were attributed to the participation of ether-group oxygen atoms in forming hydrogen bonds. Chen and co-workers have prepared flame-retardant-free and thermo-cross linkable epoxy resins containing azobenzene groups [12]. They observed that the enhanced flame retardance of the epoxy resins was due to the crosslinking reactions between the azobenzene groups which yield highly graphitized and flame-retardant material.

In this study, nine aromatic conjugated main-chain azobenzene polymers were synthesized and characterized by spectroscopy. Their thermal stability and degradation behavior were investigated and their likely use as flame-retardant additives was tested.

2. Materials and Methods

2.1 Materials

Starting compounds biphenyl, 4,4′-dinitrobiphenyl ether, 4-amino-4′nitro-biphenyl sulfide **3**, triphenylamine **A**, N-methyl-diphenylamine **B** and triphenylphosphine **C** were purchased from Sigma-Aldrich. Solvents used and acids, hydrochloric acid 35 %, sulfuric acid 98%, nitric acid 70% and formic acid 90% were all analytical grade reagents and purchased from Sigma-Aldrich. Iron (III) chloride ($FeCl_3$), activated charcoal, hydrazine monohydrate (N_2H_4), potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), Zinc dust (Zn) were purchased from Sigma-Aldrich and used in their commercial forms.

2.2 Experimental

Syntheses were carried out in three steps, Figure 1. The first step is the selective reduction of dinitro compounds to nitro-amine derivatives. 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. This step can be accepted as the preparation of diazo monomers. The last step is polymerization of diamino azobenzene monomers with comonomers, triphenylamine **A**, N-methyl-diphenylamine **B** and triphenylphosphine **C**. The method used is a traditional method based on the treatment of aromatic amines with nitrous acid and then with an activated aromatic ring. The resultant nine polymers and three azobenzene monomers were characterized via ^{1}H-NMR, FTIR, Raman, and TGA techniques.

2.2.1 Synthesis of Nitro Amine Derivatives by Selective Reduction

Syntheses were performed according to the literature [13]. Nitroamine products 4-amino-4′-nitro biphenyl **1**, 4-amino-4′-nitro-biphenyl ether **2** were obtained. 4-amino-4′-nitro-biphenyl sulfide **3** was purchased.

2.2.2 Synthesis of Azo Monomers

Syntheses of 4,4′-bis(p-aminophenyl)azobenzene **1m**, 4,4′-bis(*p*-aminophenoxy)- azobenzene **2m** and 4,4′-bis(*p*-aminophenylthio)azobenzene **3m** were performed by the metal-catalyzed reduction of nitro groups using Zn powder in aqueous hydroxide base, according to the literature [14]. Final purification was carried out in trace water-free ethyl acetate to remove unreacted starting nitro amine compound.

1m: Orange solid. Yield 86%, T_d: 267-269 °C. FTIR (KBr), ν (cm^{-1}): 3427-3338(NH$_2$), 3213(NH$_2$), 1593, 1489, 1273, 821. UV-VIS, λ_{max} (nm): 280, 426. ^{1}H-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.

2m: Dark green colored solid. Yield 65.6%, T_d: 267-269 °C. FTIR (KBr), ν (cm^{-1}): 3398-3308(NH$_2$), 3209(NH$_2$), 1581, 1508, 1492, 1232, 1151, 840. UV-VIS, λ_{max} (nm): 362. ^{1}H-NMR (400 MHz, 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), RAMAN ν (cm^{-1}): 1288, 1441(-N=N-), 1543.

3m: Orange solid. Yield 83.3%, T_d: 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}H-NMR (400 MHz, 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), RAMAN ν (cm^{-1}): 1165, 1376, 1440(-N=N-), 1543.

2.2.3 Polymerization by Diazo Coupling Reaction

Synthesis of nine polymers was carried out by diazocoupling reaction. 0.005 moles of azobenzene monomer **1m**, **2m**, **3m** was dissolved in a homogenous mixture of 20 mL glacial acetic acid, 5 mL DMF and 1.4 mL sulfuric acid. Sodium nitrite (0.015 mol/0.9 mL water) was added dropwise into an acid solution at 0 °C to obtain diazonium salt. The mixture was stirred an additional one hour at 0 °C. Diazonium salt was added dropwise into comonomer solution (**A**, **B**, **C**) (0.0025 moles in 40 mL DMF). After stirring 48 hours, the solution was poured into an excess of water and precipitate was filtered, washed and dried. The crude product was treated in hot DMF to remove low molecular weight and soluble materials. Dark brown-black powders were obtained. In order to purify the prepared materials, prepared dark brown-black powders were stirred in concentrated sulfuric acid for 2 hours at 40 °C, and then the dark violet acid solution was reprecipitated in 1:5 DMF/water (v/v) and washed with plenty of ethyl alcohol. Shiny black solids were obtained as azo macromolecular products (**1mA-C**, **2mA-C** and **3mA-C**).

Polymer 1mA: FTIR (KBr), ν (cm^{-1}): 3421, 3032, 1658, 1597, 1518, 1483, 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}H-NMR study failed due to very low solubility.

Polymer 2mA: FTIR (KBr), ν (cm^{-1}): 3448, 3064, 1585, 1487, 1384, 1332, 1238, 1080, 837. UV-VIS, λ_{max} (nm): 290, 348. ^{1}H-NMR (400 MHz, DMSO d-$_6$), δ_H (ppm): 7-8.2 (Ar-H).

Polymer 3mA: FTIR (KBr), ν (cm^{-1}): 3452, 3057, 1664, 1577, 1477, 1450, 1388, 1078, 827. UV-VIS, λ_{max} (nm): 286, 386. ^{1}H-NMR study failed due to very low solubility.

Polymer 1mB: FTIR (KBr), ν (cm^{-1}): 3460, 3030, 2875, 1664, 1591, 1124, 1111, 823. UV-VIS, λ_{max} (nm): 286, 372. ^{1}H-NMR (400 MHz, DMSO d-$_6$), δ_H (ppm): 2.5-3 (C-H); 7.5-8.5 (Ar-H).

Polymer 2mB: FTIR (KBr), ν (cm^{-1}): 3059, 2874, 2816, 1587, 1492, 1348, 1236, 1145, 837. UV-VIS, λ_{max} (nm): 280, 356, 456. ^{1}H-NMR (400 MHz, DMSO d$_{-6}$), δ_H (ppm): 2.5-3 (C-H); 6.9-8.2 (Ar-H).

Polymer 3mB: FTIR (KBr), ν (cm^{-1}): 3056, 2927, 2810, 1585, 1080, 837. UV-VIS, λ_{max} (nm): 286, 386, 468. ^{1}H-NMR (400 MHz, DMSO d-$_6$), δ_H (ppm): 2.5-3 (C-H); 6.9-8.2 (Ar-H).

Polymer 1mC: FTIR (KBr), ν (cm^{-1}): 3439, 3028, 1593, 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.

Polymer 2mC: FTIR (KBr), ν (cm^{-1}): 3470, 3059, 1587, 1533, 1491, 1238, 1143, 837. UV-VIS, λ_{max} (nm): 288, 358. ^{31}P-NMR (400 MHz, DMSO d-$_6$), δ_H (ppm): 25.

Polymer 3mC: FTIR (KBr), ν (cm^{-1}): 3057, 1674, 1583, 1492, 1078, 821. UV-VIS, λ_{max} (nm): 286, 386. ^{31}P-NMR (400 MHz, DMSO d-$_6$), δ_H (ppm): 25.

2.2.4 Carbonization of the Azobenzene Polymers

Carbonization was carried out in two stages using **1mA**, at 400 °C for an hour and then 800 °C for 2 hrs in an oven under a nitrogen atmosphere, in order to evaluate the gradual thermal decomposition of the polymers.

2.2.5 Characterization

FT-IR spectra of the polymers and monomers were obtained in KBr disc using a Shimadzu FTIR Spectrometer in the range of 400-4000 cm^{-1} frequency. Raman spectra were recorded on Homemade Confocal RAMAN Setup installed at material instrumentation, with a He-Ne laser source of 633 nm line width and a power of 20 mV. ^{1}H-NMR were recorded on Bruker 400MHz spectrometer in DMSO-d$_6$. ^{31}P-NMR spectroscopy of polymers consisting of TPP was recorded with using Varian 600 MHz in DMSO-d$_6$ solution. UV spectra were recorded by JASCO V-530 UV-vis spectrophotometer using DMF as a solvent. The thermal stability of polymers was studied by thermogravimetric analysis (TGA) over a temperature range from 25 at 900 °C under a nitrogen atmosphere at heating rates 20 ^{o}C/min using Perkin Elmer Pyris 1 model. X-ray diffraction (XRD) analysis of the carbonized polymers was obtained by a Rigaku Multiflex + XRD diffractometer with a monochromatic beam (wavelength of 1.54 Å) derived from a CuK$_\alpha$ target. A scanning electron microscope (SEM, JEOL 6390-LV) with the accelerating voltage of 20 kV was used to investigate the surface morphology and elemental composition of the carbonized polymers.

3. Results and Discussion

3.1 Characterization of the Polymers

Prepared monomers and polymers (**Figure 1**) were characterized by ^{1}H- and ^{31}P-NMR, FTIR, UV–Vis and Raman spectroscopy. The most informative signals in the FTIR spectra of nitroamine derivatives (**1m**, **2m**, **3m**) are observed at 1585-1600 cm^{-1} and 1400-1500 cm^{-1} (aromatic C=C stretching), 1500-1550 cm^{-1} and 1360-1290 cm^{-1} (asymmetric and symmetric NO$_2$ stretching), and near to 3500 cm^{-1} and 3400 cm^{-1} (asymmetric and symmetric N-H stretching). Furthermore, a strong band in the region of 1000-1260 cm^{-1} (asymmetric C-O-C stretching) in **2m** and its derivatives and a weak band in the region of 600-700 cm^{-1} (C-S-C stretching) in **3m** and its derivatives were also observed. To compare, the representative FTIR spectra of **1m** and its corresponding molecules, are given in **Figure 2**. The bands at 3385 cm^{-1} and 3489 cm^{-1} (symmetric and asymmetric 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$_{sp}$^{2}-N stretching), 1112 cm^{-1} (in-plane C-H bending), 825 cm^{-1} (out of plane C-H bending) suggest the presence of compound **1**. In the FTIR spectrum of **1m**, the formation of the azo group can be confirmed by the disappearance of the N-O stretching. The azobenzene polymers showed the characteristic peaks of its corresponding monomers, at 1587 cm^{-1}-1496 cm^{-1} (aromatic C=C, C-C ring stretching), 1278-1207 cm^{-1} (C$_{sp}$^{2}-N stretching), 1112 cm^{-1} (in-plane C-H bending), 825 cm^{-1} (out of plane C-H bending) as well as 1000-1260 cm^{-1} (asymmetric C-O-C stretching) for **2mA**, **2mB**, **2mC** and 600-700 cm^{-1} (C-S-C stretching) for **3mA**, **3mB**, **3mC** except the amino bands whose intensities decreased with the increase of azo group content in polymerization and so the spectra of polymers resemble each other since the only difference is the spacer atoms, N, S and P (see ***ESI Figure S1 and S2***). The -N=N- group peaks were not observed in the infrared spectra probably due to relatively symmetric nature of azo monomers.

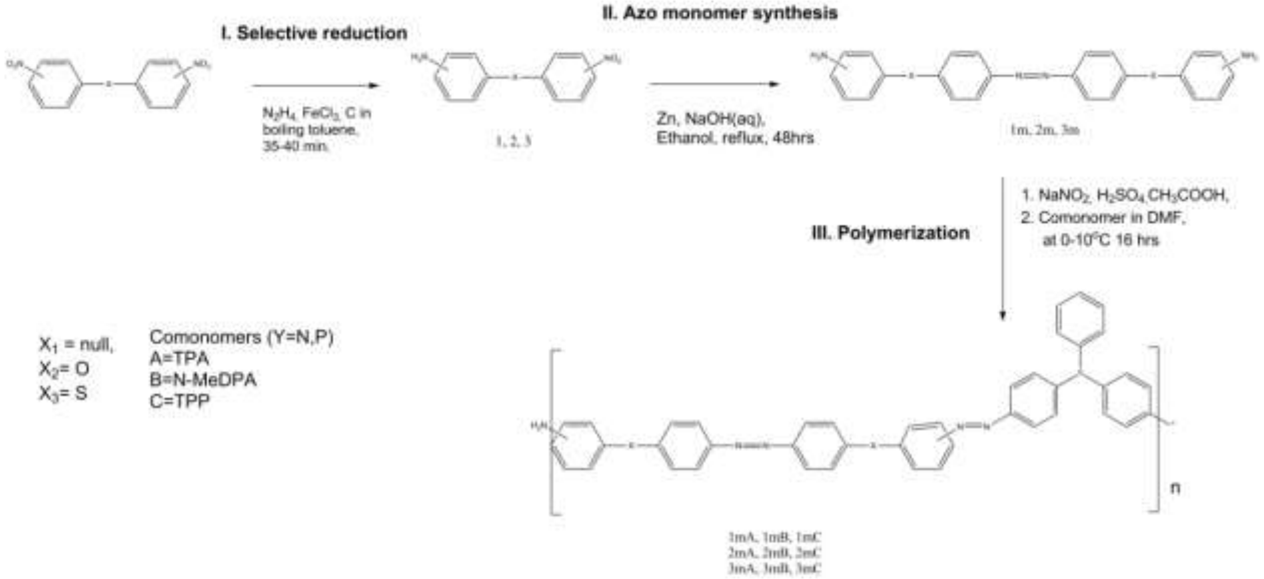

Figure 1. Synthesis procedure for the conjugated main chain azo polymers

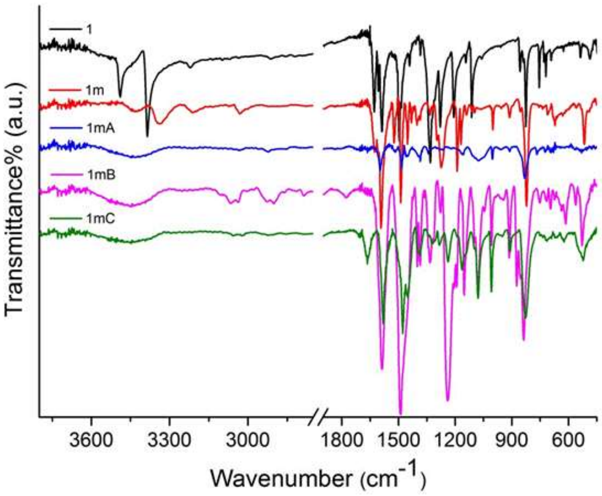

Figure 2. FTIR spectra of **1**, **1m**, **1mA**, **1mB** and **1mC**.

Azo group formation was further probed by using Raman spectroscopy. Raman stretching of -N=N- was observed at around 1441 cm^{-1} for monomers **1m**, **2m**, **3m** (Please see typical Raman spectra of **1m** and **1mA** in ***ESI Figure S3***). Polymers give aromatic -N=N- stretching at 1441 cm^{-1} and at 1444 cm^{-1}. Most azo N=N stretching bands occur between 1580 cm^{-1} and 1400 cm^{-1} in the Raman spectrum [15]. These peaks may be due to the two azo groups with different chemical environments.

^{1}H-NMR analysis of the polymers synthesized by the co-monomers **B** and **C** was challenging due to their low solubility in common NMR solvents, although the polymers with **B** showed better solubility in hot acetone, hot xylene and hot 1,2-dichlorobenzene, likely because of their linearity in the chain. Thus, we were only able to make a detailed ^{1}H-NMR analysis of **2mA**. A typical ^{1}H-NMR spectrum of the monomer (**2mA)** is given in **Figure 3**. (see ***ESI Figure S4-10*** for additional ^{1}H-NMR spectra of the monomers and their corresponding polymers) The peaks around 6.5-8.5 ppm are related to the aromatic hydrogens and the peak with very low intensity appearing at 5-5.5 ppm is attributed to the amine hydrogens. An increase in the intensity of H_a, H_b, H_c and H_d was attributed to polymerization of 2**m** with **A** because of the increase in the chain length. Furthermore, the peak at 5.1 ppm corresponds to the protons of the amino groups (H_e) was disappeared in the ^{1}H-NMR spectrum of **3m** after the polymerization reaction evidencing the polymerization. Chemical shift ranges of PPH_3 compounds were referenced to 0-10 ppm. ^{31}P-NMR spectroscopy of TPP polymers **1mC**, **2mC** and **3mC** showed a chemical shift of phosphorus at 25 ppm (see ***ESI Figure S11-13***). Furthermore, all monomers were soluble in common solvents and their polymers were slightly soluble in DMF, DMAc, DMSO and pyridine at room temperature. However, prepared polymers were soluble in DMF and DMSO at 100 °C and concentrated H_2SO_4 at 50 °C.

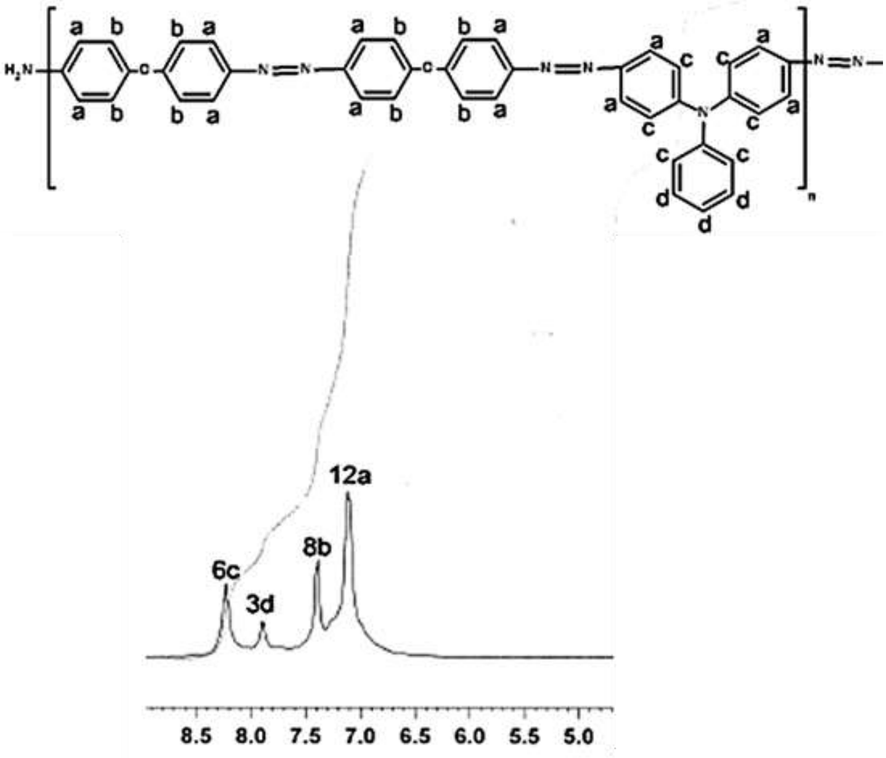

Figure 3. ^{1}H-NMR Spectrum of **2mA**.

3.2 Optical Properties of the Polymers

Representative UV–Vis spectra of azo molecules **2**, **2m** and **2mA** are shown in *ESI Figure S14* and the observed absorption peaks are given in **Table 1**. The peak observed at around 280-300 nm due to the benzenoid band, that is the characteristic of aromatic molecules π—>π* transition. The maximum wavelength of **1** is observed at 400 nm which is the longest wavelength among aromatic nitro amine derivatives that the molecule have no spacer to destroy conjugation. Molecules with spacer like **2** and **3**, were showed maximum absorption at shorter wavelengths, 308 nm and 346 nm, respectively. The characteristic absorption peak of azo-aromatic chromophores of **1m**, **2m** and **3m** were observed at approximately 382, 362 and 348 nm. All azo monomers were shifted either longer or shorter wavelength compared to those of the starting amino nitro derivatives. The UV–Vis spectra of polymers qualitatively independent of the length of the flexible segment along the chain and only depend on the active azo containing units. Their absorption maxima shift slightly to shorter wavelength, compared with monomers **1m**, **2m** and **3m** likely due to increasing conjugation. Overall UV–Vis results suggest that any change in spacer atom may alter the absorption maximum of the macromolecule.

Table 1. Wavelength maxima and the expected electronic transitions of the monomers (**1m**, **2m** and **3m**) and their corresponding polymers in DMF.

Product	**Max. Absorption**		
	π—>π* (Benzenoid Band)	π—>π* (Conjugation)	n—>π*
1m	280	426	-
2m	-	362	-
3m	278	396	-
1mA	284	392	-
2mA	290	348	-
3mA	286	386	-
1mB	286	372	-
2mB	280	356	456
3mB	286	386	468
1mC	286	390	-
2mC	288	358	-
3mC	286	386	-

3.3 Thermal and Degradation Properties of the Polymers

It is known that azobenzene groups commonly start to decompose at around 300 °C through nitrogen elimination [10, 16, 17]. This depends on the varying strength of N=N bond in the conjugation. Typical thermogram of **1mA** is given in **Figure 4**.

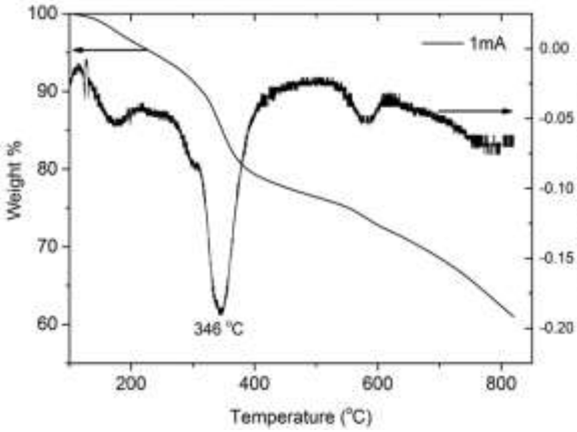

Figure 4. TGA thermogram of **1mA** under an Ar atmosphere and its first derivative.

The onset of 20% and 40% weight loss and char yields at 900 °C for all prepared polymer samples are also given **Table 2**. As expected polymers do not have so high thermal stability due to the low decomposition temperature of the azo bonds. Extrusion of molecular nitrogen facilitates the easy decomposition of polymers. Two different exothermic peaks in smaller intensity were observed at lower temperatures around 320 and 540-550 °C in a combination of all of the azobenzene polymers. The first weight-loss between 270 °C and 370 °C is attributed to the thermal degradation of azobenzene moieties, and the second weight-loss above 370 °C represents the thermal decomposition of the main chains. The thermal decomposition of the azobenzene polymers is matched closely with the literature [12, 15, 16, 18]. The glass transition temperature (T_g) was not detected likely because of the low molecular weight of the synthesized polymers. The melting point could not be determined for monomers **1m**, **2m**, **3m**, and their corresponding polymers due to the decomposition of azo moieties before melting temperature.

To further understand the carbonization process we subjected **1mA** to heat at 400 °C and 800 °C under a nitrogen atmosphere. In aggrement with FTIR analysis of as-prepared **1mA**, FTIR spectrum of **1mA** heated at 400 °C displayed stretching frequencies at around 1610, 1518, 1175 and 827 cm^{-1} which were attributed to partial decomposition of the polyaromatic polymer structure. (see ***ESI Figure S15***)

Table 2. Thermal & thermooxidative stabilities of the monomers (**1m**, **2m** and **3m**) and their corresponding polymers. *Decomposition start, confirmed by TGA under an Ar atmosphere.

Product	T_d (°C)			20% Weight loss (°C)	40% Weight loss (°C)	Residue(%) at 900°C
	Onset*	Peak max	Endset			
1m	267	355	395	-	-	44.4
2m	269	365	418	-	-	30.8
3m	266	348	415	-	-	34.5
1mA	265			410	>800	61.1
2mA	263			455	704	50.3
3mA	254			435	710	49.1
1mB	285			455	686	47.9
2mB	277			464	670	46.4
3mB	248			437	690	40.8
1mC	274			442	694	54.8
2mC	258			450	680	47.0
3mC	252			445	680	48.0

In contrast, no IR signals were detected in the spectrum of **1mA** carbonized at 800 °C, suggesting complete carbonization of the polymer structure. This was not surprising since these aromatic systems bearing potentially reactive heteroatoms (e.g. nitrogen) could ease the graphitization of aromatic main chain azo polymers like in the case of the graphene quantum dots (GQDs) produced via assembly of large aromatic molecules by connecting or fusing them to nanometerscale carbon structures in some appropriate way such as “bottom up” approach [12, 19]. Furthermore **1mA** yielded ~61% char at 800 °C probably following a crosslinking via aromatization processes of azobenzene, suggested by Chen and co-workers [12]. Formed carbon material was characterized by SEM/EDX and XRD, SEM image together with EDX data revealed the formation of highly stacked layered material consisting of 87.2% carbon (**Figure 5**).

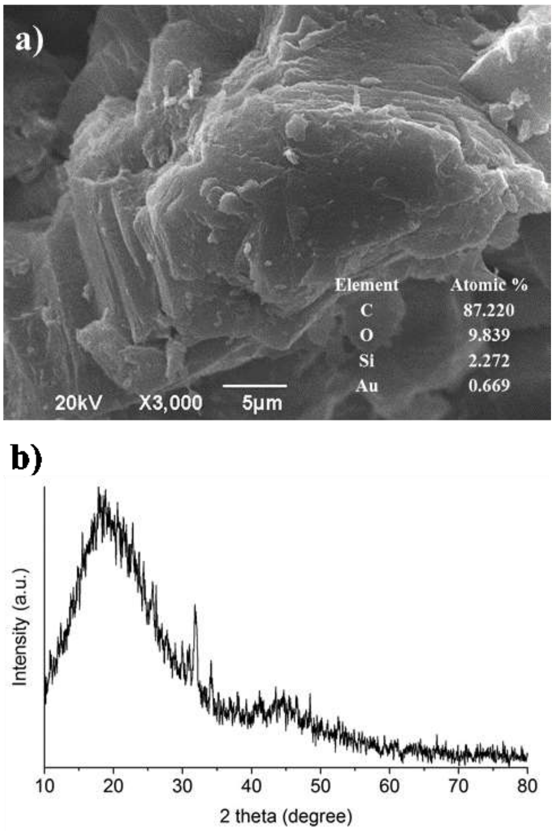

Figure 5. a) SEM image of the carbon material formed by heating **1mA** at 800 °C under a nitrogen atmosphere. Inset shows the elemental composition of the material identified by EDX. b) XRD diffractogram of the formed carbon material.

Surprisingly, no nitrogen was detected by EDX, suggesting complete removal of nitrogen moieties at 800 °C (**Figure 5a**). Complementary XRD further confirmed the formation of carbon nanosheet formation, showing two broad peaks at ca. 21 and 45°, characteristic of amorphous carbon nanostructures (**Figure 5b**). Besides, two sharp XRD peaks at ca. 32 and 34° were observed, however, they could not been identified.

3.4 Flame Retardancy of the conjugated main-chain azobenzene polymers

Polymers yielding high chars after subjecting to elevated temperatures can be utilized as flame retardant additives [20]. Thus we have investigated the flame retardancy property of the azobenzene polymer **1mA**. The effect of azo polymers on burning behavior of TPU Ravathane® (TPE-U) was examined following UL 94 flammability test. In a typical procedure TPU sample was mixed with varying amounts of **1mA**. Slight gas evolution followed by self-extinguishing was characteristic for all tested composite structures. Test results, which showed improved flame retardancy of the TPU samples, are given in Table 3.

Table 3. Flaming characteristics of 1mA added TPU samples (Yes=Y, No=N).

1mA (weight% in sample)	**0.0**	**0.01**	**0.1**	**1.0**	**1.5**
After flame or afterglow of any specimen up to the 125mm mark	N	N	N	N	N
Cotton indicator ignited by flaming particles or drops	Y	Y	Y	N	N
UL94 rating	V-2	V-2	V-2	V-1	V-0

4. Conclusion

In this study nine different main chain azobenzene polymers were synthesized from three monomers and three co-monomers. Our reaction conditions usually yielded low molecular weight polymers which are probably due to the low nucleophilic reactivity of aromatic co-monomers and the low solubility of the in-situ formed pre-polymers. Raman spectroscopy analysis and thermal analyses (TGA) were confirmed the existence of two nonequivalent azo groups on polymer chains. The processibility of polymers in organic solvents was limited due to their low solubility. However, the azobenzene polymers can readily be carbonized into highly flame-resistant carbon nanosheet-like materials. This makes conjugated main chain azobenzene polymers interesting candidate as an intumescent fire retardant-reinforcing material in industrial applications, exploited here, to improve the flame retardancy of TPU Ravathane®.

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Ethics

There are no ethical issues after the publication of this manuscript.

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