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Synthesis and characterization of new poly(azomethine ester)s having phenylthiourea units

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Abstract

New polyesters having azomethine and phenylthiourea groups in the polymer backbone were synthesized by interfacial polycondensation method. The dihydroxy monomer *N*-(4-hydroxy-3-methoxybenzal) *N*′-(4′-hydroxyphenyl)thiourea was condensed with six diacid chlorides: terephthaloyl, isophthaloyl, azeloyl, suberoyl, pimeloyl and adipolyl chlorides. The resulting polyesters were characterized by viscosity, IR, NMR and TGA analysis. The wholly aromatic poly(azomethine ester) derived from terephthaloyl chloride when blended with polyaniline/NH_4OH, polyaniline/HCl and pure polyaniline shows conductance in the range 3.2×10^{-3}–0.91×10^{-1} S cm^{-1}.

Keywords: Poly(azomethine ester)s; Phenylthiourea; Polyaniline blends; Electrical conductivity

1. Introduction

Polyesters have always been an attraction from the early days of Carothers [1]. Purely aromatic polyesters are well known for their fibre and film forming nature and some of them are biodegradable, hence their use in both medical and non medical areas are widely accepted [2–4]. Consequently, it was of interest to investigate the thermal stability of aromatic polyesters with various linking groups in their backbone. The azomethine linkage is of special interest due to its interesting properties such as *syn–anti* isomerism [5], good thermal stability [6], non-linear optical activity [7], ability to form metal chelates [8], fibre-forming ability [9,10], liquid crystalline property [11–13] and semiconductivity [14,15]. The introduction of azomethine moiety in the polymer backbone will incorporate the above mentioned properties in the newly synthesized polymer.

Further the introduction of thiourea group into the poly(azomethine ester) backbone is relatively an unexplored area. The thiourea group introduces additional features like biomedical activity [16], corrosion inhibition [17–21], as organic thermal stabilisers [22] and semiconductivity [23,24]. The major drawback of poly(phenylthiourea azomethine ester)s is their insolubility in common organic solvents due to their chain stiffness introduced by the imine group and the intermolecular hydrogen

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bonding introduced by the phenylthiourea group [25,26]. Some of the general methods to improve the solubility are insertion of flexible bonds between mainchain aromatic rings, introduction of structural irregularities as kinks, bends, crankshaft-shaped, etc. [27]. The need to solubilize these compounds is to enable their utilization in the preparation of optical devices, films, fibers, dielectric and semiconductor materials, for biomedical purposes and in corrosion inhibition.

In poly(Schiff base)s, in addition to the p_z orbitals of carbon the p_z orbitals of nitrogen also contribute to the conjugation. This extended spatial conjugation offered by the π electrons will help in conductivity and the use of conducting polymers in various fields are note worthy [28–30]. Recent reports from our laboratory involved the synthesis, characterization and electrical conducting properties of certain poly(azomethine ester)s/polyaniline blends [31] and synthesis of new polyesters containing azo and phenylthiourea groups [32].

In this paper, we report the synthesis and characterization of six new poly(phenylthiourea azomethine ester)s by interfacial polycondensation method and conducting properties of one of the wholly aromatic poly(phenylthiourea azomethine ester) with different polyaniline blends.

2. Experimental

2.1. Materials

Vanillin and *p*-aminophenol were twice recrystallised from absolute alcohol. Thionyl chloride was refluxed with quinoline (15% v/v) for 30 min and distilled. Terephthaloyl, isophthaloyl, azeloyl, suberoyl, pimeloyl and adipolyl chlorides (Aldrich) were used as received. Solvents and other reagents were purified according to the standard procedures.

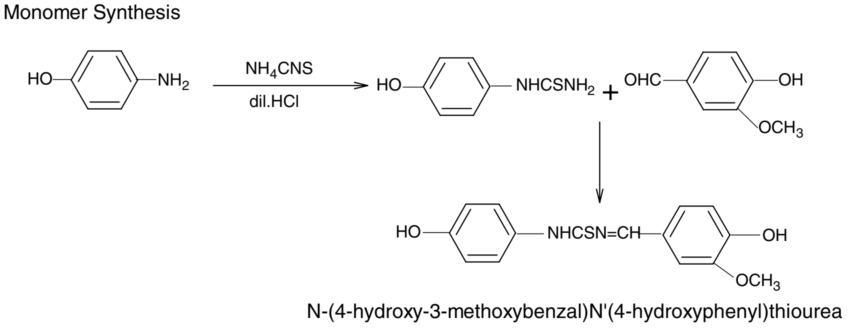
2.2. Preparation of N-(4-hydroxy 3-methoxybenzal) N′-(4′-hydroxyphenyl)thiourea

This monomer was prepared in two stages (Scheme 1), which involves the preparation of *N*-(4-hydroxyphenyl)thiourea from *p*-aminophenol and condensing it with vanillin. In a porcelain dish *p*-aminophenol (0.09 mol), 8.3 ml of conc.HCl, ammonium thiocyanate (0.099 mol) and 75 ml of deaerated water were thoroughly mixed and heated on a steam bath for 1 h and allowed to cool to room temperature. It was again evaporated slowly to dryness over a period of 4–6 h. The solid obtained was boiled with small quantities of charcoal in ethanol, filtered and cooled. The solid *N*-(4-hydroxyphenyl)thiourea obtained was twice recrystallized and dried.

N-(4-hydroxyphenyl)thiourea (0.05 mol), Vanillin (0.05 mol) and 100 ml of absolute alcohol were stirred in a Dean-Stark apparatus for 15 min at room temperature. After the removal of calculated quantities of azeotropic mixture at 90 °C, it was further refluxed for 1 h. About 30 ml of ethanol was distilled off and the contents were cooled to collect the solid. It was washed with dil.HCl, hot water, dried and recrystallized from ethanol.

Yield: 62%, m.p.: 198–201 °C, form of the crystal: needle, colour of the crystal: indigo. FT-IR (KBr) Fig. 1: 1610 (–CH=N–), 3195 and 3306 (–NH symmetric and asymmetric), 3406 (–OH) and 1074 cm^{-1} (C=S).

Analysis Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.7; H, 4.63; N, 9.3; S, 10.59; O, 15.87. Found: C, 59.5; H, 4.28; N, 9.16; S, 10.2; O, 16.68.



Scheme 1.

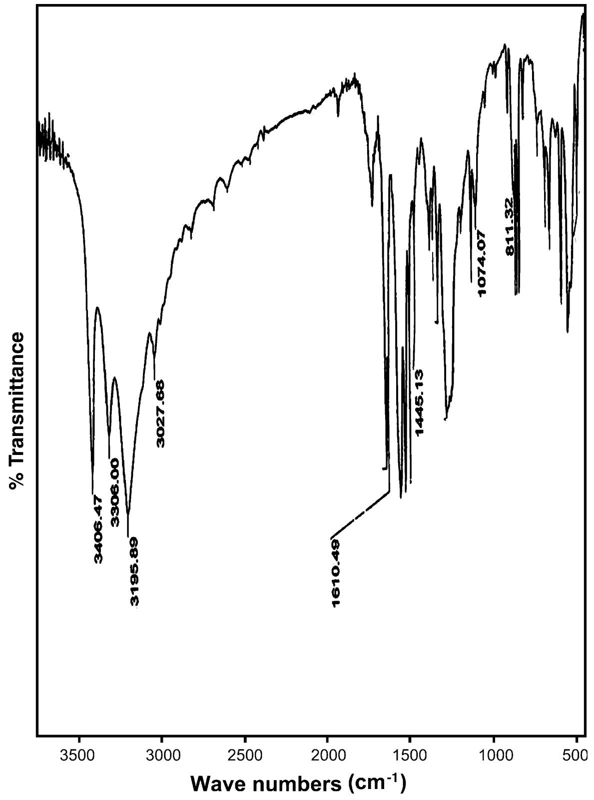


Fig. 1. IR spectrum of monomer.

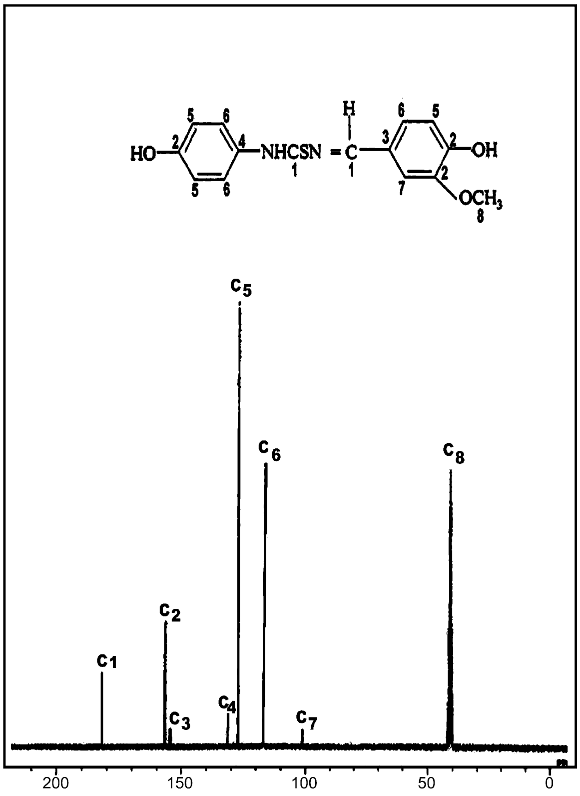


Fig. 2. ^{13}C NMR Spectrum of monomer.

Fig. 2 shows the ^{13}C NMR spectrum of the prepared monomer in DMSO-d_6. ^{13}C NMR of the monomer shows the peaks at: 182.4 ppm and 182.2 ppm (C_1), 156.3 ppm and 154.6 ppm (C_2), 151.14 ppm (C_3), 131.1 ppm (C_4), 127.7 ppm and 127.3 ppm (C_5), 117.2 ppm and 116.7 ppm (C_6), 104.4 ppm (C_7) and 40.03 ppm (C_8); the peak at 41.98 ppm is due to OCH_3 and solvent, respectively.

2.3. Preparation of polymers

All the poly(phenylthiourea azomethine ester)s were synthesized through interfacial polycondensation method. Monomer *N*-(4-hydroxy-3-methoxybenzal) *N*′-(4′-hydroxyphenyl)thiourea was stirred with aqueous NaOH in a 1:2 mol ratio in the presence of sodiumlaurylsulphate under dry nitrogen atmosphere at room temperature, and one equivalent of the diacid chlorides in a minimum volume of freshly distilled carbon tetrachloride/chloroform was then quickly added. The emulsified reaction mixture was vigorously stirred for 20–30 min and allowed to stand overnight. The precipitated polymer was filtered, washed several times with water, 5% Na_2CO_3 solution, 5% HCl solution, again with water and dried at 60 °C under vacuum until a constant weight was obtained.

2.4. Preparation of poly(phenylthiourea azomethine ester)/polyaniline blends

Polyaniline (PANI) was synthesized by oxidative polymerization of distilled aniline with $(NH_4)_2S_2O_8$ according to the literature report [33]. Polyaniline was treated with 0.1 M HCl and 0.1 M NH_4OH solutions, filtered and dried in vacuum at 40 °C for 6 h to get PANI/HCl, PANI/NH_4OH powder. The dried powders stored in polyethylene containers for more than 6 months were used for the preparation of various blends. Poly(phenylthiourea azomethine ester)/polyaniline in the required weight ratio percentage were weighed and the powder was grounded in crucible for homogenous mixing. The powder was put in a hydraulic press of load 5 tons, for making the pellets. The pellet sizes are 10.06 mm in diameter and thickness of 1.21 mm. To exclude moisture, the pellets were dried in an oven at 40 °C under vacuum for 6 h.

3. Characterization

Inherent viscosities were determined by using an Ubbelohde viscometer in a concentration of 0.5 g dL^{-1} in DMSO or DMF at 25 °C. Infrared spectroscopy measurements were performed on a Perkin–Elmer system 1760 Fourier transform (FT-IR) spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 solvent using a Bruker instrument. Thermogravimetric analysis (TGA) were recorded on a Perkin–Elmer analyzer in N_2 atmosphere, at a heating rate of 20 °C min^{-1}. Conductivity measurements were carried out on a four-point probe connected to a Keithley voltmeter constant-current source system. Measurements are made by making a gentle contact at different positions of the pellet. The values obtained were completely reproducible.

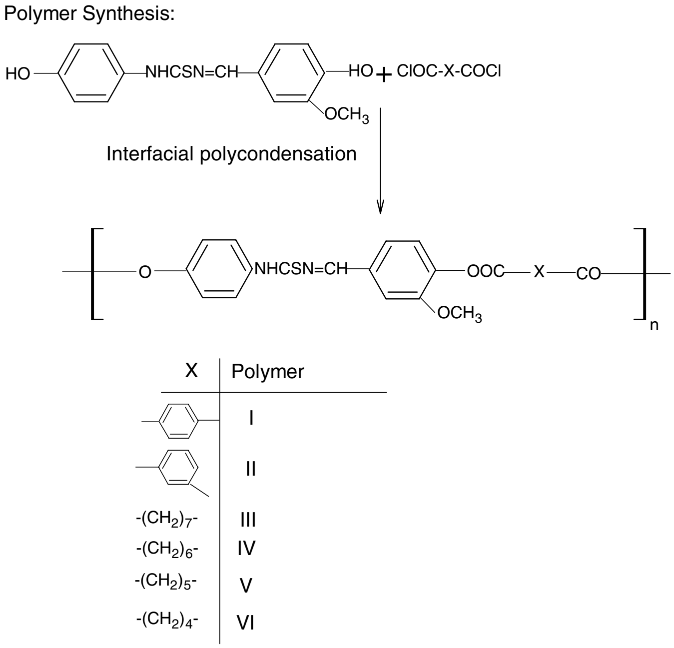
4. Results and discussion

4.1. Polymer synthesis

N-(4-hydroxy3-methoxybenzal) *N*′-(4′-hydroxyphenyl)thiourea (Scheme 1) was condensed with six diacid chlorides through interfacial polycondensation method (Scheme 2).

Colour, yield and η_{inh} values of the polymers are given in Table 1. Generally, poly(azomethine ester)s are yellow in colour owing to the presence of azomethine groups. In the present case the change in the characteristic yellow colour may be due to the presence of phenylthiourea groups in the polymer backbone. The yield and η_{inh} values are comparable to those of simple poly(azomethine ester)s reported earlier [34]. IR-spectra of the polymers are shown in Fig. 3. The disappearance of the –OH stretching frequency of the monomer (3406 cm^{-1}) and the appearance of characteristic carbonyl stretching frequency (1735 ± 5 cm^{-1}) of the ester group in all the polymers confirms the presence of ester linkages. The –CH=N– stretching frequency and –CH imine absorption of the polymers appears in the region 1618 ± 2 cm^{-1} and 2850 ± 2 cm^{-1} respectively. The C–S stretching frequency (810 ± 5 cm^{-1}) of the monomer has been retained in all the polymers. ^{1}H NMR spectral analysis of the polymers I and III taken in DMSO-d_6 are as follows: (Polymer-I) δ 10 ppm (NH); δ 8.5 ppm (–N=CH–); δ 7.7–7.5 ppm (Ar H); δ 3.5 ppm (–OCH_3) [35]. (Polymer-III): δ 9.7 ppm (NH); δ 9.5 ppm (–N=CH–); δ 7.8–6.9 ppm (Ar H); δ 1.7–1.4 ppm –$(CH_2)_7$-protons [36].

A major drawback of the linear poly(azomethine ester)s is their limited solubility in most organic solvents due to their rigid chain structure. In the present case, even though polymer-I and -II are wholly aromatic, all the polymers are soluble in aprotic



Scheme 2.

Table 1
Physical characteristics of polymers

Polymer	Colour	Yield (%)	η_{inh}
I	Yellow	63	0.32[a]
II	Grayish white	68	0.15
III	Pale yellow	71	0.18
IV	Brown	65	0.17
V	Pale brown	55	0.28
VI	Brown	52	0.24

0.5 g dL^{-1} in DMF at 25 °C.

[a] 0.5 g dL^{-1} in DMSO at 25 °C.

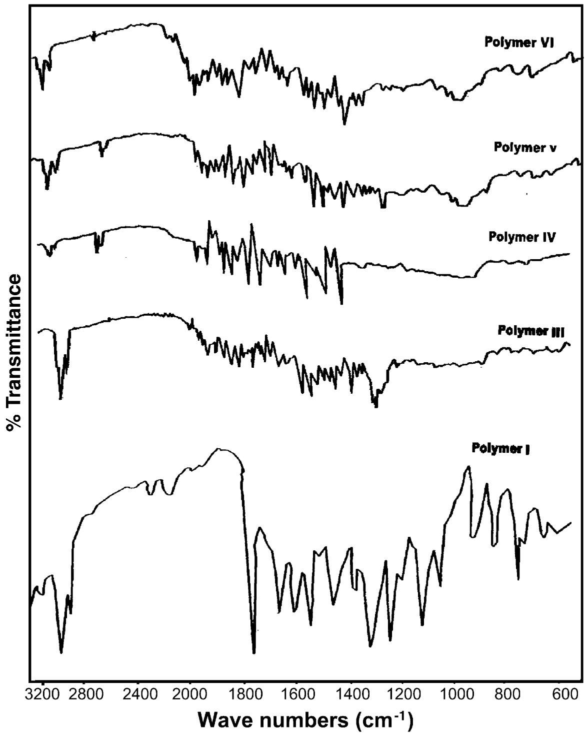


Fig. 3. IR spectra of polymers.

polar solvents like DMSO, DMF, DMAc and NMP (Polymer-I is partially soluble in DMF). The introduction of bent structure in the aromatic ring and the aliphatic flexible spacers in the backbone has a positive effect on the solubility of the polymers.

4.2. Liquid crystalline property

All the poly(phenylthiourea azomethine ester)s were examined between cross polarizer with controlled heating to examine their liquid crystalline behaviour. New soluble and thermally stable poly(phenylthiourea azomethine ester)s I and II decompose before melting due to their aromatic nature. Other aromatic/aliphatic polymers also decompose before melting, except polymer III (having the highest methylene spacer – $(\text{CH}_2)_7$) which shows faint nascent focal conic texture. The reason for the other polymers for not showing any liquid-crystalline nature is probably due to the intermolecular hydrogen bonding induced by the phenylthiourea and ester groups, which increase the interchain interactions; thus preventing the formation of a mesophase [27].

4.3. Thermal stability of polymers

The thermal properties of the polymers were investigated by TGA at a heating rate of 20 °C/min under nitrogen atmosphere. The results are summarized in Table 2 and the thermograms are presented in Fig. 4. The degradation process presents two stages. Taking the 10% weight loss temperature (180–240 °C) as initial degradation, it was almost coincident with the weight fraction of the ester link in the polymer repeat unit. This suggests that the cleavage of ester link has resulted in the initial degradation. The second degradation is around 320–560 °C. Owing to the high temperature and taking into consideration of similar structure, one may assume that the –N=CH– linkage is the second to break in all the cases. In general these polymers exhibit poor thermal stability than poly(azomethine ester)s [37–39]. Among the poly(phenylthiourea azomethine ester)s, polymer derived from terephthaloyl chloride (polymer-I) shows the highest thermal stability. This may be attributed to the para oriented aromatic nature of the polymer backbone. Among the polymers derived from aliphatic diacid chlorides (polymers III–VI), it showed typical odd even effects (methylene linkages) like polyamides in thermal stability based on both 10% and 20%

Table 2
Thermal stability of polymers

Polymer	Thermal stability		
	10% Weight loss temperature (°C)	20% Weight loss temperature (°C)	Char residue (wt% at 600 °C)
I	246	295	34
II	194	220	10
III	212	246	11
IV	236	260	18
V	206	246	14
VI	216	258	16

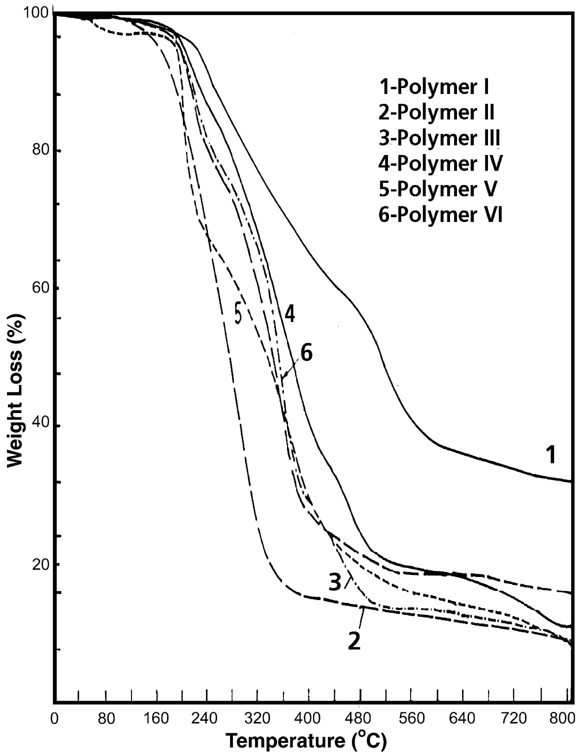


Fig. 4. TGA traces of polymers I–VI.

weight loss temperatures. The thermal stability seems to be governed by the number of carbon atoms in the aliphatic moiety. Those with an even number of aliphatic carbon atoms were more stable than their next higher odd numbered homologs. This effect is due to the formation of hydrogen bond in poly(phenylthiourea azomethine ester)s between the ester and thiourea groups in the polymer backbone. The interchain hydrogen bonding demand close proximity of the carbonyl ester and NH group (thiourea) of the adjacent chains and in polymers containing an even number of carbon atoms, this effect is more when compared to the odd numbered one.

4.4. Conductivity studies

Table 3
Electrical conductivity of poly(phenylthiourea azomethine ester)/polyaniline blends

Polymer I	PANI blend composition	Conductance (S cm^{-1})
	20% PANI	0.91×10^{-1}
	20% PANI/HCl	0.25×10^{-1}
	20% PANI/ NH_4OH	3.2×10^{-3}

Conductivity of the polymer I with various polyaniline(PANI) blends is given in Table 3. It is seen from the table that when the polymer I was blended with pure PANI, it showed the highest conductivity of the order of 0.91×10^{-1} S cm^{-1}. The conductivity of the polymer I when blended with protonated PANI(PANI/HCl) is 0.25×10^{-1} S cm^{-1}. Conductivites of the blends Polymer I/pure PANI and Polymer I/PANI-HCl are better when compared to that of poly(azomethine ester)s/PANI blends and poly(azomethine ester)s doped with silver reported earlier [31,40]. PANI/NH_4OH is the deprotonated (blue emeraldine base PANI) which is an non-conductor, when the polymer I was blended with it, showed conductivity as 3.2×10^{-3} S cm^{-1}. The conductivity of PANI bases is many orders of magnitude lower compared to that of PANI hydrochloride. Hence, the Polymer I/PANI-NH_4OH blend have resulted in lower conductivity. However, the average conductivity of PANI ammonium hydroxide was reported to be 2.4×10^{-8} S cm^{-1} [33]. In this report the higher conductivities of the polymer blends suggests the possibilities of interaction between PANI, PANI HCl and PANI NH_4OH with poly(phenylthiourea azomethine ester). Further work on the conductivity and spectral analysis of various poly(phenylthiourea azomethine ester)s/PANI blends are under progress.

5. Conclusions

New soluble and thermally stable poly(phenylthiourea azomethine ester)s have been prepared. The electrical conductivity of one of the aromatic polymer when doped with polyaniline is of the order of 0.91×10^{-1}–3.2×10^{-3} S cm^{-1}. This enhanced solubility, thermal stability and increased electrical conductivity offers the class of high performance polymers.

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