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Nucleophilic Synthesis and Characterization of Hyperbranched Poly(phenylene Sulfide)

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Abstract — The synthesis of hyperbranched poly(phenylene sulfide) by the reaction of tris-1,3,5(4-chlorophenylene-thio)benzene with lithium sulfide in polar solvents such as N-methyl pyrrolidone by one pot method at 180 °C has been reported. The resulting hyperbranched poly(phenylene sulfide) is soluble at 25 °C in typical organic solvents such as tetrahydrofuran, chloroform, dimethylformamide, etc. The molar mass of the polymer estimated by light scattering method is 80,000.

Keywords : Poly(phenylene sulfide), hyperbranched polymer, synthesis

INTRODUCTION

Poly(thio-1,4-phenylene) (PPS), the well known engineering polymer, is commercially produced by the reaction of 1,4-dichlorobenzene with sodium sulfide in polar solvent such as N-methyl pyrrolidone at high temperature and pressure [1]. The first successful, precise synthesis of PPS was a self-condensation of metal salts of 4-halothiophenols [2]. Since then, there have been reports of the synthesis of PPS by various methods [3]. However, the commercially synthesized PPS is restricted to be oligomeric in molar mass character, since the growing polymeric chain precipitates out from the reaction mixture [4]. PPS is insoluble in most of organic solvents at ambient conditions, which limits its use in many applications [3, 5].

Highly branched molecules such as hyperbranched polymers and dendrimers attract the attention of various research groups because of their unique physical and chemical characteristics [6]. Both divergent and convergent approaches produce well-defined nanostructures, which can be used as ideal model systems for the study of relationship between physical properties and molecular size [7]. Hyperbranched polymers could be

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useful as polymer rheology control agents as well as spherical multifunctional macromonomers. Hyperbranched polymer properties (viscosity, solubility, etc.) lie between linear and dendritic polymers are characterized by increased solubility in organic solvents than their linear analogues [8].

Hyperbranched PPS will be useful in processing and manufacturing solid thin films and solution blending with different polymers to obtain the desired properties^[3] which are difficult in linear PPS. By modifying film surface of PPS hyperbranched polymer, useful surface properties will be added such as surface functionalization, biocompatibility, hydrophilicity and adhesion, which are useful in surface science and technology.

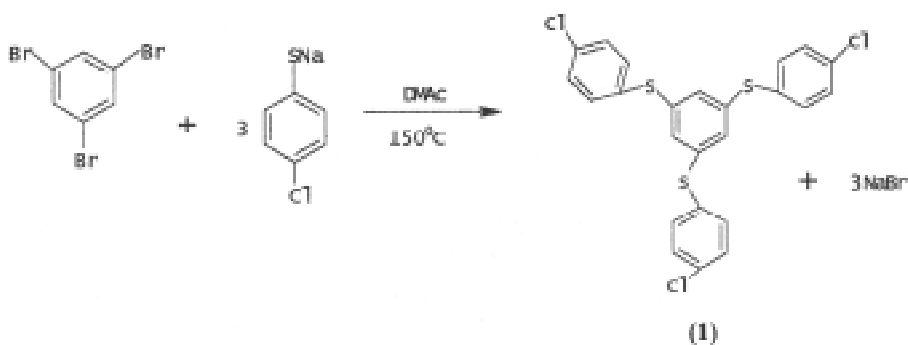
Attempts have been made to synthesize the hyperbranched PPS using electrophilic synthesis method [9] as well as *p*-phenylene sulfide molecular asterisks [10]. However, since it used costly reagents and multistep process with lower yields, there is a need to develop techno-economical alternative process.

In the present work we report one pot synthesis of hyperbranched poly(phenylene sulfide) with high molar mass which may be suitable for mass industrial production.

EXPERIMENTAL

Materials : 4-chloro-thiophenol, 1,3,5-tribromo benzene, *N,N*-dimethyl acetamide (DMAc), lithium sulfide, *N*-methyl pyrrolidone (NMP), methanol and other chemicals were procured from either Aldrich Chemical Co. or TCI Chemicals and were used without further purification.

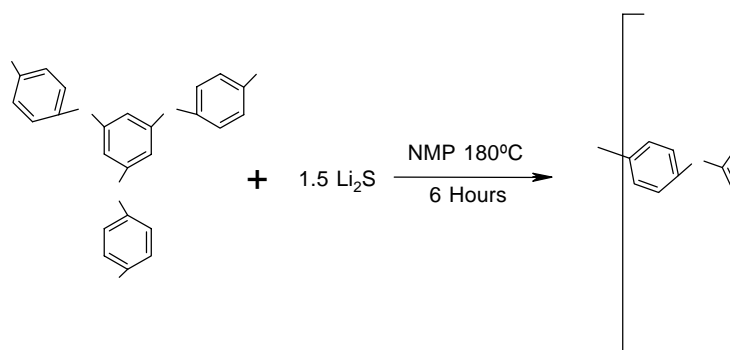
Methods : *Synthesis and characterization of tris-1,3,5(4-chlorophenyl-1-thio)benzene (1)* – Tris-1,3,5(4-chlorophenyl-1-thio)benzene (1) was synthesized from 1,3,5-tri bromo ben-



Scheme 1. Synthesis of tris-1,3,5(4-chlorophenyl-1-thio)benzene monomer (1) by nucleophilic condensation reaction

zene through nucleophilic substitution as follows (**Scheme 1**): A two-neck round bottom flask equipped with nitrogen gas inlet and reflux condenser was charged with 12.8 g (10 mmol) of 1,3,5-tribromo benzene, 23.8 g (30 mmol) of 4-chloro thiophenol sodium salt and 50 ml of dimethyl acetamide solvent. Nitrogen gas was bubbled through the solution to completely displace air. The reaction mixture was gradually heated up to 150°C for 6 hours under stirring and then cooled to room temperature. The product was extracted in chloroform. It was further recrystallized in ethylacetate/hexane (1:4) solvent mixture and dried at 25°C till constant weight. The yield was 90%. It was characterized as follows: mp 280°C; Elemental analysis $C_{24}H_{15}S_3Cl_3$ (FW 505) Calcd. C 56.97, H 2.98, S 19.01, Cl 21.02; Found C 56.10, H 2.51, S 18.42, Cl 20.23; IR (KBr): 3110, 3072, 2362, 2340, 1739, 1714, 1556, 1527, 1405, 1374, 1351, 1096, 846, 744, 656 cm^{-1} ; UV-Vis ($CHCl_3$) $\lambda_{max} = 248$ nm (4121 $mol^{-1}cm^2$), 275nm; fluorescence emission (CH_2Cl_2) $\lambda_{max} = 396$ nm; 1H -NMR (500 MHz, $CDCl_3$) $\delta = 7.5 \sim 7.7$ (m, 15H).

Polycondensation of tris-1,3,5(4-chlorophenyl-1-thio)benzene (1) to poly(tris-1,3,5(4-phenyl-1-thio)benzene) hyperbranched polymer (2) – Monomer (1) was polycondensed



Scheme 2. Polycondensation of monomer tris-1,3,5(4-chlorophenyl-1-thio)benzene (1) to poly(tris-1,3,5(4-phenyl-1-thio)benzene) (2)

with lithium sulfide reaction, as follows (**Scheme 2**): To a thick walled pressure tube, 0.50 g (10 mmol) of tris-1,3,5(4-chloro phenyl-1-thio)benzene (1), 0.070 g (15 mmol) of lithium sulfide and 5 ml of *N*-methyl pyrrolidone were taken. Nitrogen gas was bubbled through the mixture to remove all air inside and the tube was held airtight by proper sealing. The tube was heated at 180 °C in thermostatically controlled oil bath for 6 hours. Then it was cooled to room temperature and the reaction mixture was poured into hydrochloric acid in methanol (5 vol%) to quantitatively precipitate the solid. The solid was filtered, washed with warm distilled water and methanol to remove excess reactants and

side products, and dried until constant weight. The yield was 80%. The solid product was characterized by elemental analysis, spectroscopy, NMR and XRD. Elemental analysis ($C_{24}H_{15}S_4$)_n (FW 431)_n Calcd. C 66.78, H 3.50, S 29.71; Found C 65.10, H 3.00, S 25.14; IR (KBr) : 3110, 3072, 1690, 1560, 1543, 1396, 1292, 1099, 985, 846, 789, 756, 735, 671 cm^{-1} ; UV-Vis ($CHCl_3$) λ_{max} = 266 nm ($46249 \text{ mol}^{-1}cm^2$); fluorescence emission (CH_2Cl_2) λ_{max} = 373nm; 1H -NMR (500MHz, $CDCl_3$) δ = 7.2 ~ 7.3 (m, 10H), δ = 7.4 ~ 7.5 (m, 5H).

Elemental analysis was performed on a LECO CHN – 900 C CHN analyzer. Fourier transform infrared (FT-IR) absorption spectra of potassium bromide discs were recorded using a Bio-Rad FTS575C FT-IR spectrometer. UV-Visible absorption spectra were recorded on a Shimadzu UV 2200 spectrometer, while fluorescence spectra were measured on a Hitachi F-4010 fluorescence spectrophotometer. The solution ($1mg/cm^3$) was prepared by dissolving solids in chloroform for UV measurement, while in dichloromethane for fluorescence spectra. NMR spectra were recorded in deuterated chloroform on JEOL JNM-L500. X-ray diffraction (XRD) measurement was carried out by scanning rate of $0.5^\circ/min$ on a Rigaku RINT 2100 V X-ray diffractometer with radiation source CuK_α ($\lambda = 1.5405 \text{ \AA}$). Samples were prepared by casting polymer on silicon film. Light scattering measurement was performed by using a cylindrical cell (10 mm ϕ) on an Otsuka Electronics DLS-700 light scattering photometer equipped with 15 mW argon ion laser operating at a wavelength $\lambda_0 = 488 \text{ nm}$. Differential scanning calorimetric (DSC) measurements performed on Seiko instrument under nitrogen atmosphere at $10^\circ C/min$ heating rate. All the measurements were carried out at $25^\circ C$.

RESULTS AND DISCUSSION

Tris-1,3,5(4-chlorophenyl-1-thio)benzene (1) was synthesized from 1,3,5-tribromo benzene through nucleophilic substitution (**Scheme 1**). The UV-Vis spectrum of monomer (1) displayed a maximum absorption band at 248 nm assigned to phenylene sulfide and a weak band at 275 nm assigned to sulfurated benzene core (Fig. 1). The excitation at 240 nm produced a maximum fluorescence emission band at 396 nm. The FTIR bands of tris-1,3,5(4-chlorophenyl-1-thio)benzene (1) in the range 900 to 700 cm^{-1} correspond to the type of aromatic substitution of benzene ring. The IR spectrum shows bands at 1556, 1405, and 1374 cm^{-1} which are assigned to phenyl ring stretching [11]. The band at 1096 cm^{-1} can be assigned to phenyl chloride stretching, since such characteristic band is observed in the spectra of 4-chloro-thiophenol [12]. There is no peak around 2600 to 2550 cm^{-1} range, which corresponds to thiol group. Bands at 1323, 1163, 1032 and 641 cm^{-1} attributed to sulfone and bands at 1030 to 1000 cm^{-1} attributed to sulfoxide are also absent, indicating no oxidized product in the compound (1). Thianthrene peaks at 1428, 1258 and 880 cm^{-1} are also absent, hence the product is free from cross-linking. Finally, the structure was confirmed by NMR spectrum of the monomer (1) which shows phenyl protons at δ 7.7 to 7.5 ppm and elemental analysis also agrees well with theoretical values as expected for the structure.

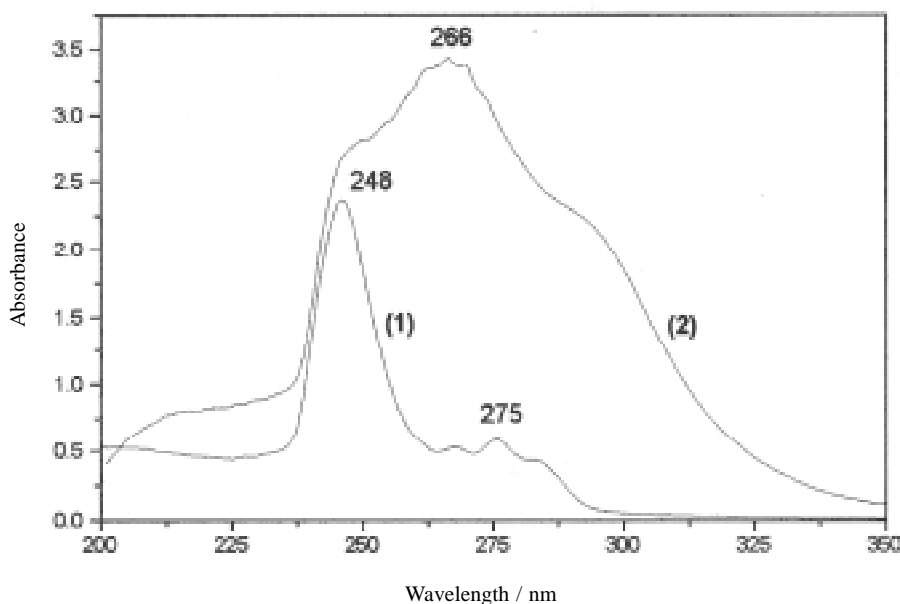


Fig. 1. Comparative UV-Visible spectrum of tris-1,3,5(4-chlorophenyl-1-thio)benzene (1) with poly(tris-1,3,5(4-phenyl-1-thio)benzene) (2)

Monomer (1) was polycondensed by a reaction with lithium sulfide (**Scheme 2**). The hyperbranched polymer (2) is highly soluble in typical organic solvents such as tetrahydrofuran, chloroform, dimethylformamide, etc. at 25°C. The UV-Visible spectrum of the polymer solution displayed a maximum absorption band at 266 nm, which corresponds to phenylene sulfide. The polymer displays the maximum fluorescence emission at 373 nm, when excited at 280 nm. The comparative UV-Visible spectra of monomer (1) and hyperbranched polymer (2) is presented in (Fig. 1). The FT-IR spectrum of the polymer displays bands at 1690, 1543 and 1396 cm^{-1} which are assigned to phenyl ring stretching [11]. It also shows a band at 1099 cm^{-1} which is assigned to phenyl chloride group. However, the intensity of this band in the polymer is weak compared to the same in the monomer, indicating the lesser fraction of terminal unreacted chloro group, which may be the reason for lower sulphur estimation in elemental analysis. There are no peaks in the region 2600 ~ 2550 cm^{-1} , indicating no thiol group in the polymer. On the contrary, the previously reported hyperbranched PPS shows thiomethyl end groups in the product [9]. The proton NMR spectrum of polymer shows the peaks for phenylene protons at δ 7.3 to 7.2 ppm and at δ 7.6 to 7.5 ppm, which is assigned to the polymer structure. The XRD scan of hyperbranched PPS (2) is presented in (Fig. 2). While the linear PPS is highly crystallized with 70% crystallinity [3], the hyperbranched PPS is in 35% crystalline and 65% amorphous determined from XRD. The molecular weight estimated

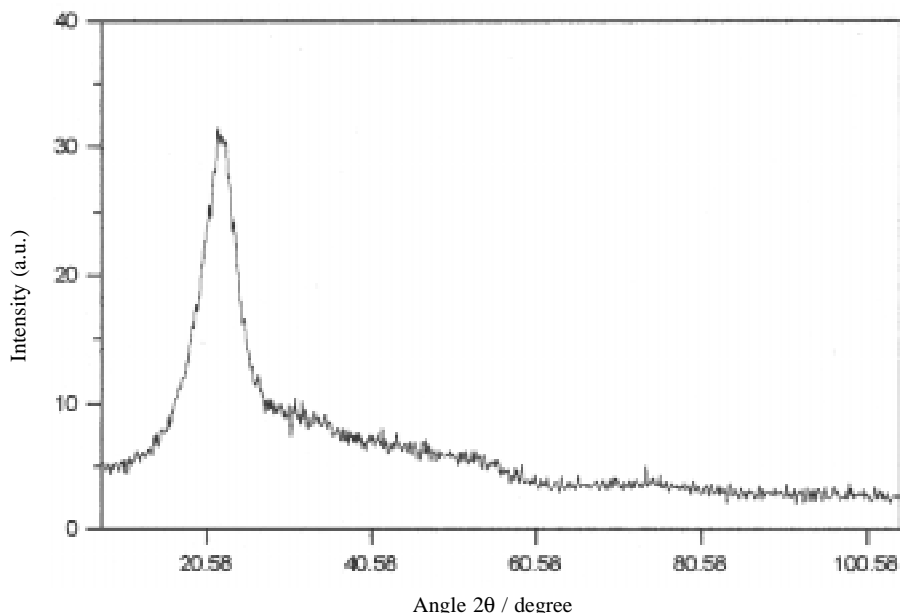


Fig. 2. Wide angle X-ray diffraction scan of poly(tris-1,3,5(4-phenyl-1-thio)benzene) (2)

from light scattering with a specific refractive index increment value of 0.429 g/cm^3 was 80,000. The molar mass value of hyperbranched PPS in the present work is higher in comparison with the previously reported value [9], since the former method employed is nucleophilic route while the latter is electrophilic method. It has been proved that in case of linear PPS synthesis, nucleophilic method yielded higher molar mass material than electrophilic method [13].

An additional structural proof for the formation of hyperbranched PPS is the glass transition temperature (T_g), determined by DSC. T_g measured for hyperbranched PPS synthesized by the present method shows 82°C , which is comparable with linear PPS (85°C). The DSC scan of hyperbranched PPS (2) is presented in (Fig. 3). It is reported that T_g values of hyperbranched polymers are almost the same as those of linear polymers [14]. However, T_g of previously reported hyperbranched PPS is higher (124°C).^[9]

In conclusions, we reported the nucleophilic synthesis of high molar mass hyperbranched poly(phenylene sulfide) which is highly soluble in most organic solvents at room temperature. On the other hand, linear poly(phenylene sulfide) is oligomeric in nature and insoluble in almost all organic solvents at room temperature. The present method comprises two steps and the high yielding procedure with low cost starting materials can be scaled up to pilot plant for industrial production which eliminates the drawbacks of previously reported methods in literature [3, 9].

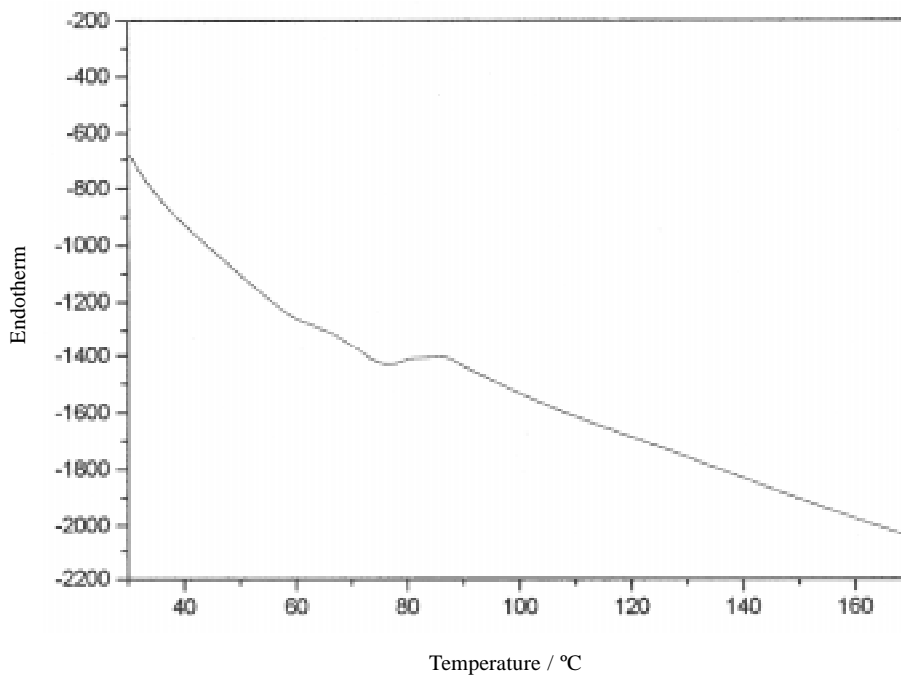


Fig. 3. DSC scan of poly (tris-1, 3, 5 (4-phenyl-1-thio) benzene) (2) under nitrogen atmosphere at heating rate of 10C / min.

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