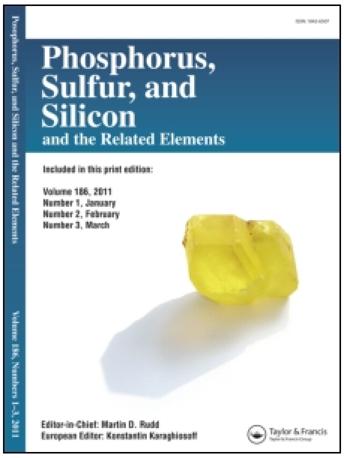

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Synthesis and Characterization of Poly(1,1'-Bi-2-naphthylidene-toluene-2,4-disulfonate)

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SYNTHESIS AND CHARACTERIZATION OF POLY(1,1′-BI-2-NAPHTHYLIDENE-TOLUENE-2,4-DISULFONATE)

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Poly(1,1′-bi-2-naphthylidene toluene-2,4-disulfonate) (PBNTDS) was synthesized by the interfacial polycondensation of 1,1′-bi-2-naphthol and toluene-2,4-disulfonyl chloride using water:1,2-dichloroethane as an interphase, alkali as an acid acceptor, and cetyl trimethyl ammonium bromide as an emulsifier. PBNTDS is highly soluble in common solvents. The structure of PBNTDS is supported by elemental and spectral (FTIR and FTNMR) data. Weight average molecular weight $\bar{M}_w$ (17877), number average molecular weight $\bar{M}_n$ (6918), and polydispersity $\bar{M}_w/\bar{M}_n$ (2.58) confirms formation of moderate molecular weight of PBNTDS. The intrinsic viscosity of PBNTDS was determined in chloroform at 30°C, and the observed value is 0.24 dlg^{-1} further supports formation of moderate molecular weight of PBNTDS. The density was determined by specific volume method. The observed values (1.1507–1.7182 gcm^{-3}) differ considerably from calculated value (1.4084 gcm^{-3}). DSC thermogram (10°C/min in nitrogen atmosphere) showed Tg to be 171.6°C. The observed endothermic transition at 335.2°C is due to decomposition reaction. PBNTDS is thermally stable up to about 285°C in an inert atmosphere and then undergoes a single step decomposition reaction (285–400°C). The temperature of maximum weight loss is 319.8°C with 30.4% weight loss and producing about 36% residue at 500°C. The least squares kinetic parameters of thermal degradation: E, A, n, and ΔS^* are found to be, respectively, 399.8 kJ mol^{-1}, 3.33 10^{33} s^{-1}, 4.26, and 391.1 J K^{-1}.

Keywords Aromatic polysulfonate; density; glass transition; interfacial polycondensation; IR; kinetic parameters; NMR; thermal stability

INTRODUCTION

Novel materials with controlled stereochemistry have found numerous applications. 2,2′-Substituted 1,1′-binaphthyl systems have been found to be extensively useful in controlling many asymmetric processes because of their stable conformation.[1] 1,1′-Bi-2-naphthol (BINOL) often serves as the starting material for obtaining chiral binaphthyl compounds. The 2,2′-hydroxyl groups can easily be converted into other functional groups and the 3,3′-4,4′- and 6,6′-positions can be selectively functionalized, leading to a variety of binaphthyl derivatives. BINOL is a well known chiral auxiliary used in host–guest chemistry for its high chiral recognition properties[2–4] and in asymmetric synthesis.[5–11]

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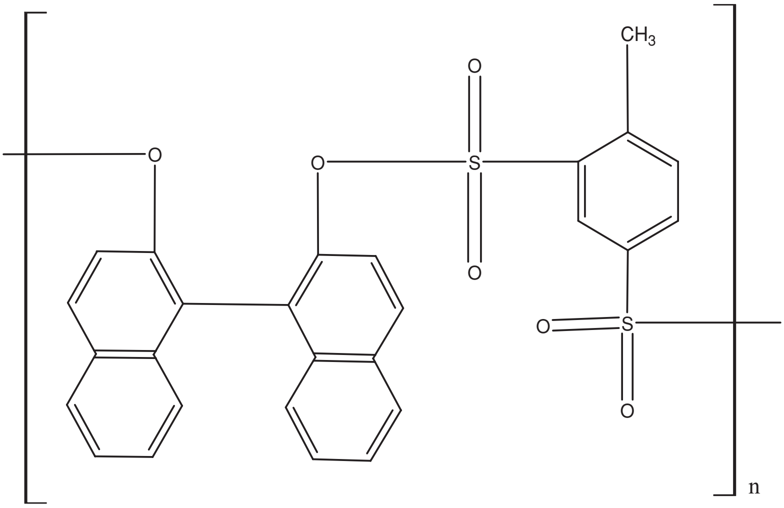
Polymers containing inorganic atoms have attracted attention as high performance polymers in so-called engineering plastics.[12] Aromatic polysulfonates are a unique class of polymers and possess good to excellent thermomechanical and electrical properties and unique hydrolytic stability.[12–14] They are useful as molded materials, films, fibers, adhesives, and coatings. Thermally stable polymers containing a rigid backbone exhibit high softening temperature and poor solubility.[15–19] The solution casting of such polymers is often difficult. Such problems can be overcome by the introduction of thermally stable linkages such as ether, sulfide, sulfone, sulfonate, or ketone in the polymer backbone, which decrease the softening temperature and increase the solubility. The thermal analysis enables information about their end use temperature, molecular architecture, bond strength, and degradation mechanism to be obtained. Polysulfonates of varying structure and having low viscosities with improved solubility, high Tg, and high thermal stability are well documented in the literature.[12,14,20–28]

To our knowledge, no work has been reported on aromatic polysulfonates containing 1,1′-bi-2-naphthylidene moiety. The aim of the present work was to synthesize thermally stable polysulfonate (Scheme 1) containing a naphthylidene rigid moiety with improved solubility.



I

Scheme 1 Poly(1,1′-bi-2-naphthylidene-toluene-2,4-disulfonate) (PBNTDS).

EXPERIMENTAL

Materials

The laboratory grade solvents and chemicals were purified by appropriate treatment[29] prior to their use in this work. BINOL was synthesized by oxidative coupling of 2-naphthol using Fe(III) as a catalyst.[30] Toluene-2,4-disulfonyl chloride (TDSC) was synthesized as described in the literature.[31] BINOL was purified four times by successive crystallization from toluene and methanol–water system. TDSC was recrystallized four times from a chloroform-*n*-hexane system. The obtained yield of BINOL was 80% and that of TDSC 47%. Their melting points were respectively 218°C and 52°C. The analytical grade emulsifier cetyl trimethyl ammonium bromide (CTAB) was used as received.

Polymer Synthesis

Into a 250 mL three-necked flask equipped with a high speed mechanical stirrer and thermometer, BINOL (0.005 mol), sodium hydroxide (0.015 mol), and distilled water (50 mL) were placed. The solution was first cooled to 0°C, and then 50 mg of CTAB was added to it. The solution was stirred vigorously for about 15 min, after which a solution of TDSC (0.005 mol) in 1,2-dichloroethane (12.5 mL) was added dropwise into it over a period of 10 min. The emulsion thus formed was stirred vigorously for 3 h while maintaining its temperature at 0°C. The organic layer was separated and thoroughly washed with water to remove excess CTAB and subsequently added dropwise into an excess of methanol (30 mL) under constant stirring. The separated polymer was filtered, washed (first with water and finally with methanol), and dried in an oven at 50°C. The obtained yield of poly(1,1′-bi-2-naphthylidene toluene-2,4-disulfonate), hereafter abbreviated as PBNTDS, was 91%. PBNTDS was found to be soluble in common solvents such as chloroform, 1,2-dichloroethane, DMSO, DMF, 1,4-dioxane, and tetrahydrofuran.

Characterization

The IR (KBr pellet) absorption spectrum of PBNTDS was recorded on a Shimadzu FTIR-8400 spectrometer. Its ^{1}H NMR spectrum was obtained on a Bruker Avance II 400 MHz FTNMR spectrometer using DMSO-d_6 as a solvent and TMS as an internal standard. The solution viscosity was measured in chloroform at 30 ± 0.1°C by a Ubbelohde suspended level viscometer. The viscosity measurements were accurate to ± 0.001dl g^{-1}. The density was determined by specific volume method and was accurate to ± 0.0001g cm^{-3}. Differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses of PBNTDS were carried out at 10°C min^{-1} heating rate in nitrogen atmosphere employing a Perkin Elmer DSC-TGA (Model Pyris-I). The elemental composition of polymer was estimated by Thermo Finnigan 1396 CHNS [O] Analyzer (Model Flash 1112 Series). Molecular weights and polydispersity measurements were made on a Perkin Elmer GPC (Series 200) using THF as a solvent and standard polystyrene mixed bed at 30°C.

RESULTS AND DISCUSSION

The TDSC end group in PBNTDS resulted in marginally lower values of weight percent elemental composition of C (62.74%), H (3.55%), and S (13.28%) as compared to those calculated from the empirical formula (C 64.54%, H 3.58%, and S 12.75%).

Spectral Analysis

Figure 1 shows the IR absorption spectrum of PBNTDS. In addition to the normal vibration frequencies of alkyl and aromatic groups, this spectrum shows two characteristic absorption bands at 1323.21 and 1145.7 cm^{-1} of S=O functionality in PBNTDS assigned to asymmetric and symmetric vibrations respectively. Figure 2 shows the ^{1}H NMR spectrum of PBNTDS. The observed chemical shift (ppm) and types of protons are 1.72 (s, 3H, $-CH_3$),

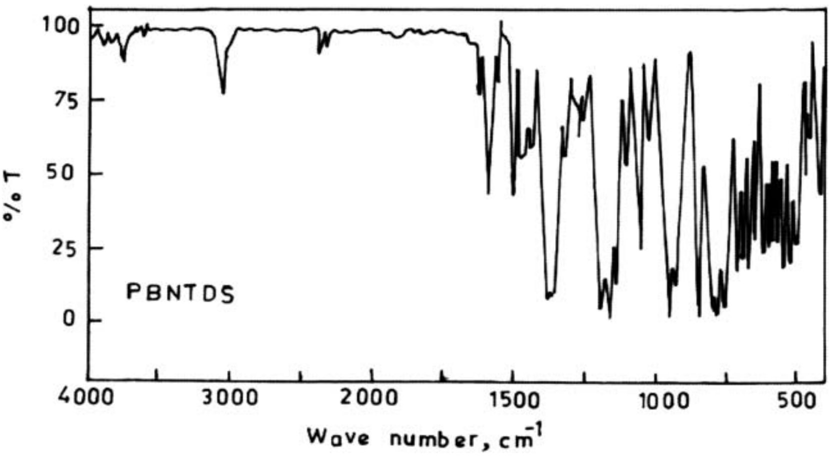


Figure 1 IR (KBr Pellet) absorption spectrum of PBNTDS.

5.80–5.68 (m, 1H, —OH), 6.39–6.08 [m, 3ArH (a+h)], 7.22–6.81 [m, 5ArH (d+e+i)], and 7.71–7.37 [m, 7ArH (b+c+f+g)]. The integrated peak areas are found in agreement with the theoretical number of protons. Thus, the elemental and spectral analyses support the structure of PBNTDS.

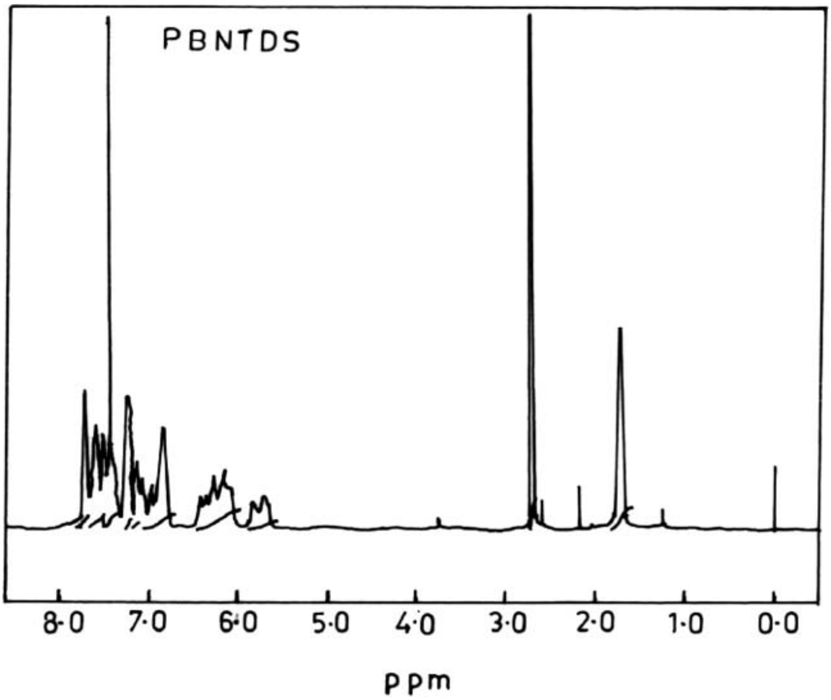


Figure 2 NMR (DMSO-d_6) spectrum of PBNTDS.

Molecular Weights, Polydispersity, and Solution Viscosity

Weight average molecular weight $\bar{M}_w$ (17877), number average molecular weight $\bar{M}_n$ (6918), and polydispersity $\bar{M}_w/\bar{M}_n$ (2.58) confirms the formation of a moderate molecular weight of PBNTDS. The formation of a moderate molecular weight is due to the rigidity and steric hindrance of BINOL moiety. The intrinsic viscosity $[\eta]$ of PBNTDS in chloroform, determined according to the Huggins relation, is found to be 0.24dl g^{-1}, which indicates PBNTDS to have moderate molecular weight. PBNTDS possesses a brittle film forming property, further supporting this result.

Density Measurements

The densities of solutions of PBNTDS at different concentrations (0.25–2.0 w/v %) in four different solvents viz., chloroform (CF), 1,2-dichloroethane (DCE), 1,4-dioxane (DO), and tetrahydrofuran (THF), were determined at 35 ± 0.2°C by the usual method. The experimental data were placed into the following well-known equation:

$$\frac{1}{\rho_{i12}} = \frac{W_{i1}}{\rho_1} + \frac{W_{i2}}{\rho_{i2}} \tag{1}$$

where W_i and ρ_i denote, respectively, the weight fraction and density of solvent (1), polymer (2), and solution (12). The least square densities of polymer thus estimated are given in Table I along with regression coefficients (R^2). The density of PBNTDS was also derived from the following well-known relation[32]:

$$\rho = \frac{KM}{N_A \Sigma \Delta V_i} \tag{2}$$

where K (= 0.681) is the packing coefficient, M(= 502 Da) is the molecular weight of repeat unit of PBNTDS, N_A is Avogadro's number, and $\Sigma\Delta V_i$ (= 403.02×10^{-24} cm^3) is the intrinsic volume of the PBNTDS repeat unit. The experimental and theoretically derived densities of this polymer differ considerably presumably because of the solvation phenomena (polymer–solvent interactions) occurring in solution, which alter both apparent molar volume and apparent molecular mass and hence the measured density. It is evident from Table I that the apparent molecular mass predominates over the apparent molar volume of polymer solution in chloroform and dioxane, while it is reversed in solution in 1,2-dichloroethane and THF systems. Dipole–dipole interactions of the opposite types lead to solvolysis of the molecules and hence change in apparent molar volume and apparent molecular mass.

Table I Theoretical and Experimental Densities of PBNTDS

Solvent	ρ, gcm^{-3}	% Error	Regression Coefficient, R^2
Chloroform	1.7182	22.00	0.998
1,2-Dichloroethane	1.3369	−5.08	0.999
1,4-Dixane	1.5267	11.83	0.991
THF	1.1507	−25.77	0.997

M = 502, $\Sigma\Delta V_i = 403.02 \times 10^{-24}$ cm^3, K = 0.681, and $\rho_{cal} = 1.4084$ g cm^{-3}.

Thermal Analysis

The DSC thermogram in Figure 3 showed one exothermic and two endothermic transitions. The exothermic peak at 101.3°C is due to moisture release and further supported a slight weight loss around this temperature in TG thermogram. The endothermic peaks observed at 171.6°C and 335.2°C are ascribed probably due to glass transition temperature and decomposition of PBNTDS chains. The later transition has been confirmed by drastic weight loss of PBNTDS observed between 300°C and 350°C in TG thermogram (Figure 4). PBNTDS is thermally stable up to about 285°C. After that, it undergoes apparently a single step decomposition reaction between 285°C and 400°C showing 30.4% weight loss. The residual weight of the sample at 500°C is about 36%. The maximum weight loss is observed at 319.8°C. The above results (high Tg and high thermal stability) confirm to similar observations on moderate to high molecular weight polysulfonates of varying structures.[12,14,20–28] However, PBNTDS is comparatively less thermally stable than polysulfonates based on bisphenols.[12,14,20–28]

The associated kinetic parameters, namely energy of activation (E), frequency factor (A), order of the reaction (n), and entropy change (ΔS^*) were derived using the Freeman–Anderson method[33]:

$$\Delta \ln dW/dt = n\Delta \ln W - (E/R)\Delta(1/T) \tag{3}$$

$$A = (E\beta/RT^2)e^{E/RT} \tag{4}$$

$$\Delta S^* = R\ln(Ah/kT) \tag{5}$$

where β is rate of heating, h is Planck's constant, k is the Boltzmann constant, R is the gas constant, and T is temperature. Thus derived least squares values of E, A, n, and ΔS^* are found to be, respectively, 399.8 kJ mol^{-1}, 3.33×10^{33} s^{-1}, 4.26 and 391.1 JK^{-1}, and $R^2 = 0.991$. These high values of the kinetic parameters indicate the rigid nature of the PBNTDS molecule. The large and positive magnitude of ΔS^* suggests that the transition state could be less ordered than that of individual molecules.[33] Polymer degradation is

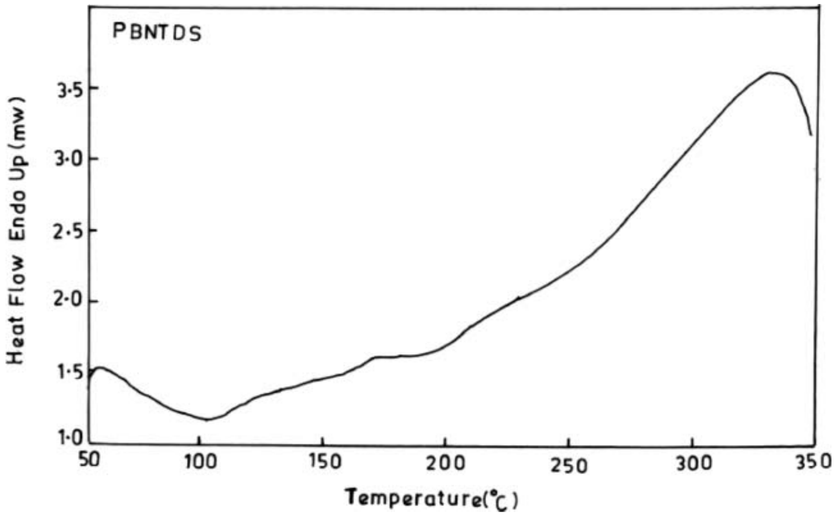


Figure 3 DSC thermogram of PBNTDS at 10°C/min heating rate in nitrogen atmosphere.

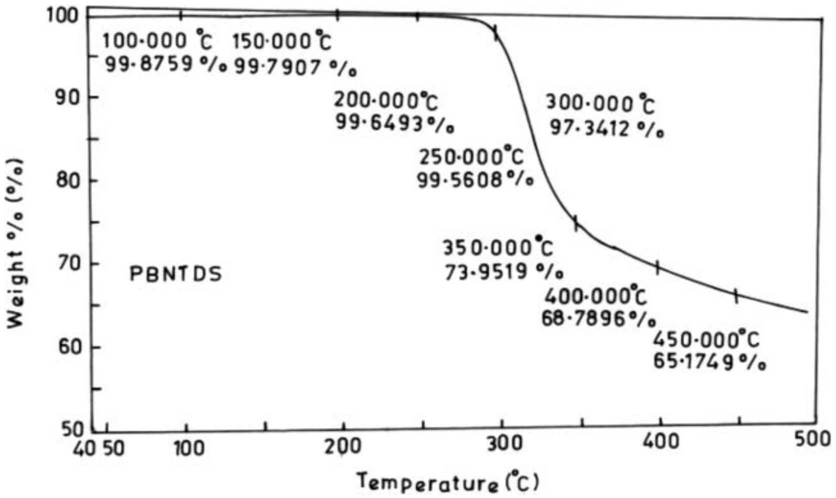


Figure 4 TG thermogram of PBNTDS at 10°C/min heating rate in nitrogen atmosphere.

a complex process and involves a variety of reactions such as cross-linking, branching, rearrangement, and decomposition of segments. It is supposed that the sulfonate linkage in the main chain and methyl side substituents in PBNTDS are weak points that would degrade selectively, forming radicals. The radicals thus produced would recombine and form new compound(s), which would subsequently degrade at elevated temperatures. The decomposition of the sulfonate linkage would lead to evolution of sulfur dioxide. A large amount of residue (~36%) above 500°C indicates that it could be a highly thermally stable, cross-linked product of the degradation of PBNTDS.

CONCLUSIONS

PBNTDS appears to be a moderate molecular weight polymer having excellent solubility in common solvents, high Tg, high thermal stability, and high values of kinetic parameters.

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