Synthesis and Characterization of Poly(ether sulfone) and Poly(ether sulfone ketone) Copolymers

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ABSTRACT: Poly(ether sulfone) and poly(ether sulfone ketone) copolymers (I–V) were synthesized by the nucleophilic substitution reaction of 4,4′-dihydroxy diphenyl sulfone (DHDPS, A) with various mole proportions 4,4′-difluoro benzophenone (DFBP, B) and 4,4′-difluoro diphenyl sulfone (DFDPS, C) using sulfolane as solvent in the presence of anhydrous K_2CO_3. The polymers were characterized by physicochemical and spectroscopic techniques. All polymers were found to be amorphous, and the glass transition temperature (T_g) was found to increase with the sulfonyl content of the polymers. ^{13}C-nuclear magnetic resonance (NMR) spectral data was interpreted in terms of the compositional triads, BAB, BAC, CAC, ABA, and ABB, and indicate that transetherification occurs at high concentration of DFBP units in the polymer (IV). The good agreement between the observed and calculated feed ratios validates the triad analysis. Thermal decomposition studies reveal that the thermal stability of the polymers increases with increase in the carbonyl content in the polymer. Activation energies for thermal decomposition were found to be in the range of 160–203 kJ mol^{-1} with the cleavage of ϕ—SO_2 bond being the preponderant mode of decomposition and depended on the block length of the sulfonyl unit. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2113–2121, 1999

Key words: poly(ether sulfone); poly(ether sulfone ketone) copolymer; Fourier transform infrared spectroscopy; ^{13}C nuclear magnetic resonance spectroscopy; thermogravimetry; X-ray diffraction

INTRODUCTION

In recent years, engineering thermoplastics are gaining rapid acceptance for use as matrices in advanced thermoplastic composites for aerospace structural applications. Poly(ether sulfone) (PES) is one such useful engineering thermoplastic[1] because of its high thermal stability,[2] high T_g, and

high heat distortion temperature and easy processability in the melt or in solution.[3] However, the solvent resistance of PES is poor due to its amorphous nature. On the other hand, poly(ether ether ketone) and poly(ether ketone) (ICI, Victrex) exhibit superior solvent resistance due to their crystalline nature. However, PEEK and PEK has a relatively low T_g[4] compared to PES,[5] which results in a decrease of modulus at elevated temperatures. In addition, high price and insolubility in common organic solvents limit their widespread applications. Various attempts have been made by several researchers to increase the solubility of poly(ether ketones) in organic solvents by

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the incorporation of bulky substituents such as ter-butyl or phenyl-substituted hydroquinones[6] for widespread applications. Ogawa and Marvel[7] have reported polyaromatic ether ketone sulfones by incorporating ether sulfone groups along with the keto groups, and the resulting polymers showed solubility in a variety of solvents. Similar polymers have also been synthesized by nucleophilic substitution reaction of dihalogenodiphenylsulfone with dihydroxybenzophenones[3,8,9] or by reacting dihalogeno diphenyl sulfone and dihalogenobenzophenone with dihydroxybenzophenone by copolyetherification reaction.[10] Roovers and Toporowski[11] and our own studies[12] introduced various substituents into the poly(ether ketone) main chain, and structure–property relationships were studied.

Polymers containing ether, carbonyl, and sulfone groups, connected by aromatic rings within the polymeric backbone, are expected to have the advantages of both PEEK and PES in their properties, such as high T_g, high-temperature resistance, toughness, and solvent resistance. Therefore, we have undertaken systematic studies on the synthesis and evaluation of properties of copoly(ether ketone sulfones) derived from various monomers. In this article, we report the synthesis of poly(ether sulfone) and poly(ether sulfone ketone) copolymers derived from 4,4′-dihydroxy diphenyl sulfone (DHDPS) with 4,4′-difluorodiphenyl sulfone (DFDPS) and with various mole proportions of DFDPS and 4,4′-difluorobenzophenone (DFBP) in the presence of K_2CO_3 and the sulfolane medium. The copolymers were characterized by physical and spectral methods. Composition and sequence distribution of comonomers in the copolymers were studied by ^{13}C-NMR spectra. Thermal characterization of the polymers was carried out by thermogravimetry, and the activation energy for decomposition were evaluated.

EXPERIMENTAL

Materials

High-purity DFDPS (Aldrich) and 4,4′-dihydroxy diphenyl sulfone (Aldrich) were used as received.

Flurobenzene (Navin fluorine) and carbon tetrachloride (BDH) were distilled before use and kept over anhydrous $CaCl_2$ overnight. Anhydrous $AlCl_3$ (Nice) was used as received. Anhydrous K_2CO_3 (BDH) was dried in vacuum at 100°C before use. Sulfolane (Aldrich) was dried with molecular sieve (type 4A) and distilled over NaOH pellets under reduced pressure. The middle fractions were collected and stored over molecular sieve.

Monomer Synthesis

4,4′-difluorobenzophenone (DFBP) was synthesized from fluorobenzene and carbon tetrachloride in the presence of $AlCl_3$ as per the procedure described earlier[4] (yield, 55%; mp, 105–106°C).

Elemental analysis; calculated for $C_{13}H_8F_2O$: C, 71.56; H, 3.67; found: C, 71.46; H, 3.61.

POLYMER SYNTHESIS

Ether sulfone polymer and ether, sulfone ketone copolymers were synthesized by the nucleophilic substitution reaction of DHDPS with DFDPS and DFDPS–DFBP using anhydrous K_2CO_3 in sulfolane medium at 20% solid content, under a N_2 atmosphere as per the procedure described earlier.[13] The product was refluxed with water repeatedly and subjected to Soxhlet extraction with methanol, filtered, and dried under vacuum at 100°C for 12 h.

CHARACTERIZATION

Elemental analysis was performed with a Perkin–Elmer model 2400 CHN analyzer. Inherent viscosities were obtained for 0.4% polymer solution in NMP at 25°C using an Ubbelhode-suspended level viscometer. Glass transition temperatures (T_g) were measured using a Mettler thermal analyzer model 3000 coupled to a DSC 20, at a heating rate of 20 K min^{-1}.

Fourier transform infrared (FTIR) spectra of the polymers in KBr pellets (2%) were recorded using a Nicolet FTIR (510P) spectrophotometer.

Figure 1 Chemical shifts of polymer I.

Table I   Conditions and Some Properties of Polymers

Polymer	Feed Ratio			Elemental Analysis (%)		Inherent Viscosity (dL/g)	T_g (°C)
	DHDPS	DFDPS	DFBP	C	H		
I	0.5	0.5	0.0	66.9 (62.06)	2.9 (3.44)	0.32	228
II	0.5	0.25	0.25	66.90 (65.91)	3.5 (3.58)	0.27	209
III	0.5	0.125	0.375	69.60 (67.96)	2.7 (3.66)	0.31	207
IV	0.5	0.0	0.5	69.99 (70.09)	3.7 (3.73)	0.33	194
V	0.5	0.375	0.125	65.5 (63.95)	3.2 (3.51)	0.17	210

^{13}C-NMR spectra were recorded at 100 MHz using Brucker AMX-400 spectrometer. Methane sulfonic acid and a CDCl$_3$ mixture was used as solvent with tetramethyl silane (TMS) as an internal standard. Thermogravimetric analysis (TGA) of the polymers was carried out under N$_2$ atmosphere using a Dupont TA 2000 in connection with a 951 thermogravimetric analyzer at a heating rate of 20 K min^{-1}.

Wide-angle X-ray scattering (WAXS) data were obtained on pellets of the polymer using a Phillips X-ray unit PW 1710 diffraction counting unit and PW 1729 X-ray generator with Nickel-filtered CuK$_\alpha$ radiation at 30 kV and 20 mA. Samples were recorded at room temperature over the 2θ angular range of 10–50°.

RESULTS AND DISCUSSION

Ether sulfone ketone copolymers were synthesized by the aromatic nucleophilic displacement of fluorine from an activated substrate (DFDPS)/(DFBP) by DHDPS. Polymers I–V were obtained by varying the mole ratio of DFDPS to DFBP.

Polymer I, as shown in Figure 1, contains bisphenol S and 4,4′-difluorodiphenyl sulfone and corresponds to Victrex PES developed by ICI. Feed ratios and some properties of the polymers are given in Table I.

CHARACTERIZATION

The elemental analysis, that is, the C and H contents of polymers I–V, is listed in Table I. The values are in reasonable agreement with theoretical values confirming the proposed structures.

The IR spectra of all the polymers show no absorption bands in the 3500–3000-cm^{-1} region, indicating the absence of —OH group, but all the spectra show characteristic bands at 1300–1350 cm^{-1}, (SO$_2$, as), and 1140–1160 cm^{-1} (SO$_2$, s) due to sulfonyl group and a band at 1250 cm^{-1} due to phenylene ether stretching vibrations (s, $v_{\phi-o}$). In addition, all the polymers show characteristic bands at 1650 cm^{-1} (S, $v_{C=0}$) except for polymer I, where carbonyl groups are absent.

The ^{13}C-NMR spectra of polymers I–IV were recorded at 100 MHz in methane sulfonic acid and CDCl$_3$ with TMS as the internal standard. The mode of synthesis of polymers I and IV indicates that the polymers will have the following structures (Figs. 1 and 2).

This was confirmed by elemental analysis (Table I) and also by ^{13}C-NMR spectral data. The ^{13}C-NMR spectrum of polymer I (Fig. 3) shows four absorptions corresponding to the four distinguishable carbons indicated in its structure. Similarly, polymer IV (Fig. 4) is expected to show nine absorptions. The chemical shift assignment of various carbons in I and IV were based on additivity constants for substituted benzenes and are in agreement with the values reported in literature. The chemical shift assignments and relative peak intensities are given in Table II.

Figure 2   Chemical shifts of polymer IV.

Figure 3 ^{13}C-NMR spectra of polymer I.

However, the ^{13}C-NMR spectra of IV shows ten lines in addition to the expected nine lines. This can only be rationalized if transetherification is assumed to be taking place during the course of the reaction, as indicated below (Fig. 5).

Thus, transetherification results in the formation of additional triads like AAB and BBA. The chemical shifts of carbons of central A and B units of these triads should be different from the corresponding carbons in BAB and ABA triads, giving rise to additional absorptions in the ^{13}C-NMR spectrum. The chemical shift assignments of these lines were based on the expected close similarities of the triads and are shown in Table II. However, it is to be

noted that C and A units are indistinguishable in the polymers since both have sulfonyl groups connecting the aromatic rings. Hence, C-centered triads are identical to A-centered triads and are not considered separately in this discussion. These assignments were further confirmed by triad analysis of the copolymers II and III.

Copolymers II–III can be represented by the following structures (Fig. 6):

$$—(BA)_n—(CA)_y—(BACA)_z—$$

The sensitivity of ^{13}C chemical shifts to the environment, which enables one to distinguish

Figure 4 ^{13}C-NMR spectra of polymer IV.

Table II ^{13}C-NMR Data for Polymers I–IV

S1 No	Chemical Shift (ppm)	Relative Peak Intensities (%)			
		P-1	P-2	P-3	P-4
1*	135.51	8.89	3.66	1.90	0.0
2*	130.15	46.03	18.58	8.50	0.0
3*	120.06	32.38	19.44	10.70	0.0
4*	160.10	12.70	5.15	2.56	0.0
5**	135.30	0.0	1.74	1.84	1.23
6**	130.20	0.0	8.18	8.50	5.72
7**	(120.06)	0.0	—	—	—
8.**	160.22	0.0	2.03	2.38	1.40
9**	136.97	0.0	1.97	2.20	1.66
10**	130.38	0.0	7.38	7.84	6.78
11**	(121.36)	0.0	—	—	—
12**	158.70	0.0	1.60	2.97	—
13+	136.78	0.0	1.40	2.85	4.34
14+	130.52	0.0	3.97	8.20	13.58
15+	121.36	0.0	6.83	10.99	14.27
16+	158.60	0.0	2.49	2.32	4.30
17***	126.11	0.0	1.43	3.51	3.54
18***	138.23	0.0	4.03	7.43	11.57
19***	119.10	0.0	7.78	10.57	14.27
20***	165.63	0.0	1.26	2.67	3.61
21***	200.92	0.0	1.09	2.08	2.29
22++	126.16	0.0	0.0	0.0	1.27
23++	137.82	0.0	0.0	0.0	3.13
24++	120.28	0.0	0.0	0.0	4.45
25++	163.73	0.0	0.0	0.0	1.10
26++	201.22	0.0	0.0	0.0	1.43

the possible triad structures. The various distinguishable triad structures are given below (Fig. 7). The assignment of chemical shifts to various carbons in the copolymers was based on the assumption that only the nearest neighboring units will affect the ^{13}C-NMR shifts. Consequently, the chemical shift of carbons of B unit in ABA, of A units in BAB, and of BAC triads of the copolymers would be identical to the corresponding carbons of the respective triads of polymer IV. Similarly, the carbons of A units in CAC triads will have same values in the copolymers as well as in polymer I. These considerations lead to a complete assignment of chemical shifts, as given in Table II.

The presence of common lines corresponding to AAB ($\equiv$CAB) in the spectra of polymer IV & the

copolymers confirms the transetherification reaction occurring during the synthesis of polymer IV. Such transetherification reactions were also observed earlier under similar experimental conditions for the copolymer systems of 4,4′-bis(4-fluoro benzoyl) biphenyl with 4,4′-dihydroxy diphenyl and 4,4′-dihydroxydiphenyl sulfone.[14]

Further, the copolymer composition was calculated by considering the relative peak intensities of carbons ortho to O atom in the triads CAC, BAB, and ABA. Since A and C units are indistinguishable, the molar ratio of A+ C to B could only be obtained, as shown in Table III. A satisfactory agreement between the calculated and the feed ratio validates the triad analysis is discussed above.

Figure 5 Transetherification of polymer IV.

SOLUBILITY

All polymers are found to be soluble in dipolar aprotic solvents, such as DMF, DMSO, DMAc, NMP, and in chloroform, but insoluble in THF.

Figure 6 ^{13}C-NMR spectra of polymer II.

THERMAL TRANSITIONS

The T_g's of the copolymers were determined by differential scanning calorimetry (DSC), and the results are given in Table I. The T_g values of the copolymers increase with increase in concentration of sulfonyl content in the polymer. This gradual increase can be attributed to the greater polarity of the polymer chain due to the incorporation of sulfonyl groups. All polymers failed to show melting points, even with the incorporation of carbonyl groups. This may be due to the differ-

ence in bond angle[15] in the sulfone groups, which disturbs parallel alignment of the chains, leading amorphous polymers. This is further confirmed from X-ray diffractograms (Fig. 8). Polymer I shows low T_g compared to the commercial polymer ICI, victrex PES, and the same polymer reported by us earlier[5] and may be attributed to lower molecular weight.

THERMOGRAVIMETRIC STUDIES

Thermal degradation behavior of polymers I–V was studied by thermogravimetry (TG) in a N_2 atmosphere at a heating rate of 20 K min^{-1}. From TG trace, the initial decomposition temperature (IDT), the maximum decomposition temperature (D_{max}) and the char residue at 600, 700, and 900°C were determined, and the values are given in Table IV. All polymers were stable up to 430°C. A maximum decomposition temperature was observed between 530 to 590°C. All polymers gave a char residue of about 32% at 900°C. The relative thermal stabilities of polymers can be assessed by

Figure 7   Triad structures of polymers.

Table III   Monomer Ratios Calculated from ^{13}C-NMR Spectra

Polymer	Calculated	Feed
II	3.38	3.0
III	2.0	1.7
IV	1.06	1.0

Figure 8   X-ray diffractogram of polymer IV.

their integral procedural decomposition temperature (IPDT) proposed by Doyle.[17] IPDT values indicate that the thermal stability of the polymers is higher for the ketone containing polymers the sulfone-containing polymers alone. However, with the increase in ketone content in the polymers does not reflect much on the overall thermal stability of the polymers.

The overall activation energy (E_a) for decomposition was calculated using Coats and Redfern,[16] assuming the order of the reaction is 1.

$$\ln[-\ln(1 - \alpha)/T^2]$$
$$= \ln[AR/\Phi(1 - 2RT/Ea)]Ea/RT$$

Figure 9   Typical Coats–Redforns plot for polymer I.

where α is the fraction decomposed at temperature T, Φ is the heating rate, R is the gas constant, and A is the Arrhenius frequency factor. E_a was calculated from the plot of $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$. A typical Coats–Redfern plot is shown in Figure 9.

The results obtained are given in Table V.

The Coats–Redfern plot indicates a two-stage decomposition. The first and main stage of decomposition occurs in the temperature range 430–600°C and corresponds to a weight loss of $\sim$ 75% of the active material decomposed. The overall activation energy (ΔE_a) for polymer I, which contains only sulfonyl linkages is 159 kJ mol^{-1}, whereas the corresponding value is 203 kJ/mol^{-1} for polymer IV, which contain both carbonyl and sulfonyl linkages in equal proportion. Copolymers II, III, and V, which contain varying proportions of carbonyl and sulfonyl linkages show nearly equal ΔE_a values ($\Delta E_a = 188 + 3$ kJ mol^{-1}).

Table IV   Thermal Analysis of Polymers I–V

Polymer	IDT (°C)	D_{max} (°C)	Char Residue (%)			IPDT
			600°C	700°C	900°C	
I	447	579	47	38	35	649
II	450	529	56	47	43	661
III	489	589	67	48	32	665
IV	460	567	56	48	45	668
V	440	576	53	43	35	655

IDT is the initial decomposition temperature.
D_{max} is the maximum decomposition temperature.
IPDT is the integral procedural decomposition temperature.

Table V   Kinetic Parameters of Polymers I–V

Polymer	T (°C)	α Range	ΔE (kJ/mol)	Correlation Coefficient
I	430–590	0.0042–0.7529	159.4	0.9982
	600–680	0.8468–0.9819	58.0	0.9979
II	450–540	0.0140–0.4620	192.4	0.9983
	570–690	0.6885–0.9939	64.5	0.9987
III	450–600	0.0047–0.7566	184.5	0.9976
IV	460–600	0.0026–0.7039	202.7	0.9961
	610–690	0.7879–0.9934	83.5	0.9968
V	450–580	0.0054–0.5608	188	0.9976

In view of the magnitudes of the observed ΔE_a values and the fact that ϕ—SO_2 linkage has the lowest bond energy in the molecule, a probable decomposition mechanism for polymer I is outlined below (Fig. 10).

The near constancy of ΔE_a values for copolymers II, III, and V coupled with nearly equal CAB triad intensities for polymers II and III (Table II) suggest ΔE_a values depended on the block length of the sulfonyl units.

The ΔE_a values ($\Delta E_a = 70 \pm 12$ kJ mol^{-1}) for the second stage of decomposition suggest that it is a physical process, which involves the volatilization of the products formed during the first stage of decomposition.

CONCLUSIONS

1. ^{13}C-NMR spectral data was interpreted in terms of the compositional triads BAB, BAC, CAC, ABA, and ABB and indicates that transetherification occurs at high concentration of DFBP units in the polymer IV.
2. The good agreement between the observed and calculated feed ratios validates the triad analysis.
3. All polymers were found to be amorphous and the glass transition temperature (T_g) was found to increase with the sulfonyl content of the polymers but decrease in thermal stability of the polymers.
4. Activation energies for thermal decomposition were found to be in the range 160–203 kJ mol^{-1} with the cleavage of ϕ—SO2 bond being the preponderant mode of decomposition and depended on the block length of the sulfonyl unit. and
5. The E_a values ($\Delta E_a = 70 \pm 12$ kJ mol^{-1}) for the second stage of decomposition suggest that it is a physical process, which involves the volatilization of the products formed during the first stage of decomposition.

Figure 10   Mode of thermal decomposition of polymer I.

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