Synthesis and Properties of Poly(ether nitrile sulfone) Copolymers with Pendant Methyl Groups

Akanksha Saxena,[1] R. Sadhana,[2] V. Lakshmana Rao,[1] P. V. Ravindran,[2] K. N. Ninan[3]

[1]*Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala 695022, India*
[2]*Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala 695022, India*
[3]*Propellants and Special Chemicals Group, Propellants, Chemicals & Materials Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala 695022, India*

ABSTRACT: Poly(ether nitrile) and poly(ether nitrile sulfone) copolymers with pendant methyl groups were prepared by the nucleophilic substitution reaction of 2,6′-dichlorobenzonitrile with methyl hydroquinone and with varying mole proportions of methyl hydroquinone and 4,4′-dihydroxydiphenylsulfone using N-methyl pyrrolidone as a solvent in the presence of anhydrous K_2CO_3. The polymers were characterized by different physicochemical techniques. Copolymer composition was determined using the FTIR technique. Thermogravimetric data revealed that all polymers were stable up to 420°C with a char yield above 40% at 900°C in a nitrogen atmosphere. The glass-transition temperature increased and the activation energy and inherent viscosities decreased with an increase in the concentration of the 4,4′-dihydroxydiphenylsulfone units in the polymer. Trimerization reactions were favorable with an increase in the concentration of methyl hydroquinone units in the polymer. The crystallinity of the polymer was also studied using wide-angle X-ray diffraction. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1987–1994, 2005

Key words: poly(ether nitrile); differential scanning calorimetry; thermogravimetric analysis; FTIR; trimerization; ^{13}C-NMR

INTRODUCTION

Recently, engineering thermoplastics are gaining rapid acceptance for use as matrices in advanced composites for structural applications in aerospace. Poly(ether sulfone) (PES) is one such useful engineering thermoplastic[1] because of its high thermal stability,[2] high glass-transition temperature (T_g), high heat distortion temperature, and easy processability in the melt or in solution.[3] However, the solvent resistance of PES is poor because of its amorphous nature. In contrast, poly(arylene ether nitrile)[4] (PEN) exhibits superior solvent resistance because of its crystalline nature. Owing to their crystalline/semicrystalline nature, PENs exhibit high tensile strength and melting points that qualify their composites for use at elevated temperatures and in aggressive chemical environments encountered in aerospace, industrial, and automotive applications. In addition, the pendant nitrile group on the aromatic ring in PEN appears to promote adhesion of the polymer to many substrates,[5,6] possibly through polar interaction with other functional groups. It also serves as a potential site for polymer crosslinking.[7,8] However, PEN[9] has a relatively low T_g compared to PES,[10] which results in a decrease of modulus at elevated temperatures. Moreover, high price and insolubility in common organic solvents limit their widespread applications.

Various attempts have been made by several researchers and in our laboratory to improve the solubility of PEN-type polymers by the incorporation of bisphenol monomers containing imido or dicyanoarylene groups,[11] sulfide groups,[12] sulfone groups,[13,14] pendant alkyl groups,[15] isomeric monomers,[9] and amide or amide–imide groups.[16] The resultant polymers were found to be soluble in dipolar aprotic solvents at room temperature or on heating.

However, it appears that poly(ether nitrile)s containing sulfone groups and pendant alkyl groups within the polymeric chain have not been studied in detail in the open literature. They are expected to have the property advantages of both poly(ether nitrile)s and PES such as high T_g, high temperature resistance, toughness, and solvent resistance. In addition, the pendant methyl groups are expected to promote trimerization of nitrile groups, leading to thermally stable polymers with high activation energies.[15] Therefore, we have undertaken systematic studies on the synthesis and characterization of poly(ether nitrile sulfone) with pendant methyl groups derived from various
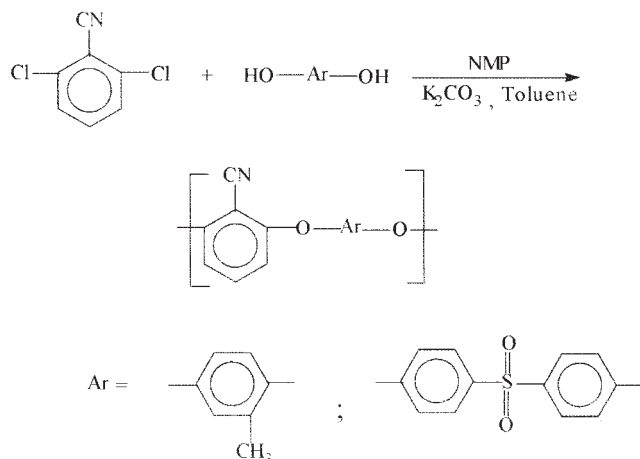
Scheme 1 The preparation of poly(ether nitrile) and poly-(ether nitrile sulfone) copolymers with pendant methyl groups.

monomers. In this article we report the synthesis of poly(ether nitrile) and poly(ether nitrile sulfone) copolymers with pendant methyl groups. The copolymers were characterized by physical and spectral methods. Copolymer composition was determined by the FTIR technique. Thermal characterization of the polymers was carried out by thermogravimetry (TG), and the activation energy for decomposition was evaluated.

EXPERIMENTAL

Materials

High purity 2,6′-dichlorobenzonitrile (DCBN, Fluka), methyl hydroquinone (MeHQ, Lancaster), and 4,4′-dihydroxydiphenylsulfone (DHDPS, Aldrich) were used as received. Anhydrous K_2CO_3 (BDH) was dried in a vacuum at 100°C before use. N-Methyl pyrrolidone (NMP, SRL) was distilled under a vacuum over phosphorous pentoxide and stored over 4-Å molecular sieves.

Polymer synthesis

Poly(ether nitrile) and poly(ether nitrile sulfone) copolymers with pendant methyl groups were prepared

as shown in Scheme 1. The reaction was carried out by a nucleophilic substitution reaction of DCBN with MeHQ and varying mole proportions of MeHQ and DHDPS using anhydrous K_2CO_3 in NMP medium with 28% solid content at 200°C under a nitrogen atmosphere according to the procedure described earlier.[17]

The viscous reaction mixture was cooled to room temperature and precipitated in water. The product was refluxed repeatedly with water and subjected to Soxhlet extraction with methanol, filtered, and dried under a vacuum at 100°C for 15 h.

Instruments

Elemental analysis was performed with a Perkin–Elmer model 2400 CHN analyzer. The inherent viscosities were obtained for 0.2% polymer in p-chlorophenol at 60°C using an Ubbelhode suspended level viscometer. The T_g and melting points were measured using a TA instrument DSC-2920 modulated differential scanning calorimeter operated in standard DSC mode at a heating rate of 10°C min^{-1} under nitrogen.

The FTIR spectra of the polymers in KBr pellets were recorded using a Perkin–Elmer spectrum GX A FTIR spectrometer. The ^{13}C-NMR spectra were recorded at 75.4 MHz using a Bruker Avance-300 spectrometer with deuteriated DMSO as a solvent and tetramethyl silane (TMS) as an internal standard. Wide-angle X-ray scattering data were obtained on pellets of the polymer using a Seimens D5005 X-ray

TABLE II
Solubility Behavior of Polymers I–V

Polymer	Solvents				
	DMSO	DMF	NMP	CHCl₃	THF
I	++	++	++	−	−
II	++	++	++	−	−
III	++	++	++	−	−
IV	+−	+−	++	−	−
V	−	−	−	−	−

++, soluble; +−, partially soluble; −, insoluble.

TABLE I
Conditions and Properties of Polymers

Polymer	Feed ratio			Elemental analysis (%)			Inherent viscosity[a] (dL/g)	T_m (°C)	T_g (°C)
	DHDPS	DCBN	MeHQ	C	H	N			
I	0.5	0.5	—	64.7 (65.3)	3.5 (3.1)	3.9 (4.0)	0.21	—	199
II	0.375	0.5	0.125	66.9 (67.08)	3.1 (3.3)	4.2 (4.4)	0.20	—	186
III	0.25	0.5	0.25	67.8 (69.2)	3.6 (3.5)	5.0 (4.9)	0.19	—	184
IV	0.125	0.5	0.375	70.5 (71.9)	4.0 (3.7)	5.4 (5.5)	0.32	—	181
V	—	0.5	0.5	74.4 (75.3)	3.9 (4.03)	6.2 (6.21)	1.22	325	180

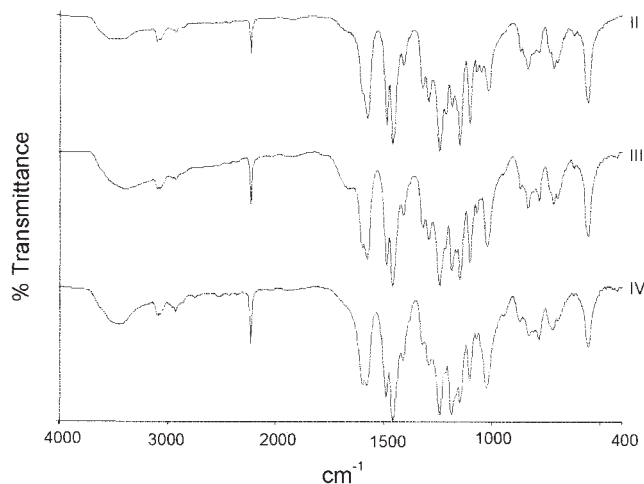[a] Inherent viscosity in p-chlorophenol for a 0.2% polymer solution at 60°C.

Figure 1 The FTIR spectra of polymers II, III, and IV.

Figure 2 The chemical shifts of polymer I.

diffractometer with Cu-K$_\alpha$ radiation at 40 kV and 30 mA. The diffractograms were recorded at room temperature over the 2θ range of 10–40 θ. Thermogravimetric analysis of the polymers was carried out using a TA instrument model SDT-2960 thermal analyzer at a heating rate of 20 K min^{-1} under N$_2$. Solubilites were determined at a 1% (w/w) concentration.

RESULTS AND DISCUSSION

Poly(ether nitrile sulfone) copolymers with pendant methyl groups were prepared by aromatic nucleophilic displacement of chlorine from an activated substrate DCBN by MeHQ/DHDPS. Polymers I–V were obtained by varying the mole proportion of MeHQ to DHDPS. Feed ratios and some of the properties of the polymers are given in Table I. Inherent viscosity values reveal that the incorporation of DHDPS units into the polymeric chain lowers the viscosity of the polymers, indicating the lower reactivity of DHDPS toward the nucleophilic substrate. This may be due to the presence of electron withdrawing sulfone groups, which reduces the nucleophilicity of DHDPS. Conversely, the electron releasing methyl groups (+I effect) in MeHQ enhance the nucleophilicity of MeHQ. However, the copolymers do not show much change
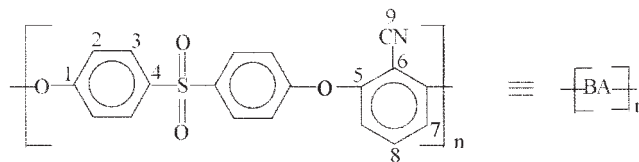
in their viscosities. All polymers are insoluble in common organic solvents such as CHCl$_3$ and THF but soluble or partially soluble in dipolar aprotic solvents such as DMF, NMP, and DMSO for the polymers up to 75% MeHQ content, as shown in Table II.

Characterization

The elemental analysis (C, H, and N content) results for polymers I–V are listed in Table I. The values are in reasonable agreement with the theoretical values, confirming the proposed structures.

FTIR study

The FTIR technique was used for polymer characterization and for semiquantitative information on the copolymer composition. The FTIR spectra of all polymers show characteristic bands at 2230 cm^{-1} that are due to symmetrical stretching of nitrile groups. The FTIR spectra of polymers II, III, and IV with different mole ratios of MeHQ and DHDPS are shown in Figure 1. The reaction between DCBN and MeHQ/DHDPS is indicated by the disappearance of —OH and ϕ—Cl stretching vibrations at 3444 and 783 cm^{-1}, respectively. The peak at 1150 cm^{-1} is attributable to the stretching vibrations of the S═O group and the peaks in the region between 1100 and 1250 cm^{-1} are due to ϕ—O skeletal vibrations. The formation of the product can be confirmed by the shift in the ring vibrations from 1490 to 1450 cm^{-1} in the polymer, indicating a change in the substitution pattern. The peak at 1600 cm^{-1} is assigned to C═C stretching of the benzene ring where oxygen is ortho to CN. In polymer V, a weak band at 2924 cm^{-1} is due to the stretching vibrations of the CH$_3$ group. The peak at 1450 cm^{-1}, which is attributable to the —CH$_3$ bending vibration, overlaps with the C═C stretching vibration of the benzene ring and the peak at 1187 cm^{-1} is attributed to the ether linkages ortho to MeHQ. The presence of bands at 2924 and 1187 cm^{-1} and the increase in intensity of the 1459 cm^{-1} peaks with respect to the methyl content confirms the presence of MeHQ in the polymer.

The formation of the copolymers is confirmed by the characteristic peaks at 1150 and 1187 cm^{-1}, corresponding to $\nu\phi$—S═O (DHDPS) and $\nu\phi$—O— (MeHQ), respectively. An attempt was made to obtain

TABLE III
Feed Ratio and Intensity Ratio of Comonomers in Copolymers

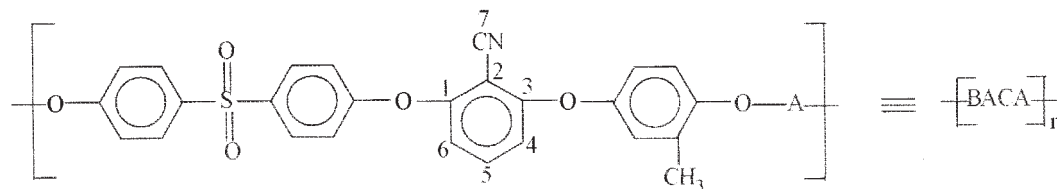| Polymer	Feed ratio		Intensity in copolymers	
	DHDPS	MeHQ	DHDPS	MeHQ
III	0.5	0.5	0.48	0.48
II	0.75	0.25	0.74	0.22
IV	0.25	0.75	0.18	0.74

Figure 3 The chemical shifts of polymer III.

semiquantitative information on the relative amounts of DHDPS and MeHQ in the copolymers using the integral intensities of the νCN, $\nu\phi$—S=O (DHDPS), and $\nu\phi$—O (MeHQ) peaks. The intensities of $\nu\phi$—O (MeHQ) and $\nu\phi$—S=O (DHDPS) are ratioed with respect to νCN (DCBN) and then normalized to 1 in order to attain the approximate information of the components present in the copolymers with different feed ratios. The percentage compositions computed from these intensities are given in Table III. The values are in close agreement with the feed ratio.

^{13}C-NMR study

The ^{13}C-NMR spectra of polymers I, II, and III were recorded at 75.4 MHz in DMSO-d_6 with TMS as an internal standard on a Bruker Avance-300 spectrometer.

The mode of synthesis of polymers I, III, and V indicates that the polymers have the structures shown in Figures 2–4. This was confirmed by elemental analysis (Table I) and by the ^{13}C-NMR spectra of polymer I. However, the ^{13}C-NMR spectra of polymer V could not be recorded because of the insolubility of the polymer. The chemical shift assignments of various carbons in polymers I and III were based on the additivity constants for substituted benzenes and are in close agreement with the values reported in the literature.

Copolymers II–IV can be represented by the structure —(BA)$_x$—(CA)$_y$—(BACA)$_z$—, where A is the nitrile moiety, B is the sulfone moiety, and C is the methyl moiety. In the copolymers, the B unit exists only as ABA compositional triads. Hence, the carbons in the B units in the copolymers have the same chemical shifts as those of the corresponding carbons of the
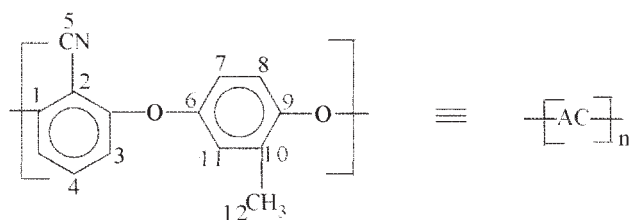
B units in polymer I. This is based on the reasonable assumption that only the nearest neighboring units affect the ^{13}C chemical shifts. Similarly, the carbon C units in the copolymers have the same chemical shifts as those of the corresponding carbons in polymer V.

However, the A units in the copolymers can exist in three different compositional triads: BAB, BAC, or CAB and CAC. The chemical shifts of the carbons of the A unit in BAB and CAC are the same as those of the corresponding carbons of the A unit in polymers I and V, respectively. Thus, the ^{13}C-NMR spectra of the copolymers show all resonance absorptions present in polymers I and V. This was indeed found to be the case as shown by the chemical shift data of polymer III given in Table IV.

The carbons of the A moiety in BAC or CAB as is shown in Figure 3 have chemical shifts distinctly different but close to the chemical shifts of the corresponding carbons of polymers I and V. Thus, carbon 1 in Figure 3 shows resonance at $\delta = 159.9$ ppm compared to the corresponding carbon 5 in Figure 2 (δ

TABLE IV
Assignment of ^{13}C-NMR Chemical Shifts for Polymer III

Peak no.	Chemical shifts[a] (δppm)	Assigned carbon[b]
1	161.2 (159.9)	I$_1$
2	160.4	III$_3$
3	159.9	III$_1$
4	158.4 (158.4)	I$_5$
5	137.1 (137.1)	I$_8$
6	136.7	III$_5$
7	135.6 (137.0)	I$_4$
8	130.6 (130.7)	I$_3$
9	120.4 (120.4)	I$_2$
10	119.9	III$_4$
11	119.4	III$_6$
12	119.2 (119.1)	I$_7$
13	113.0 (112.7)	I$_9$
14	112.8	III$_7$
15	96.3 (98.1)	I$_6$
16	95.4	III$_2$
17	16.1	V$_{12}$

[a] The values in parentheses represents chemical shifts for polymer I.
[b] I, V, and III refer to the structures of polymers I, V, and III in Figures 2–4 and the number represents the carbon designated therein.
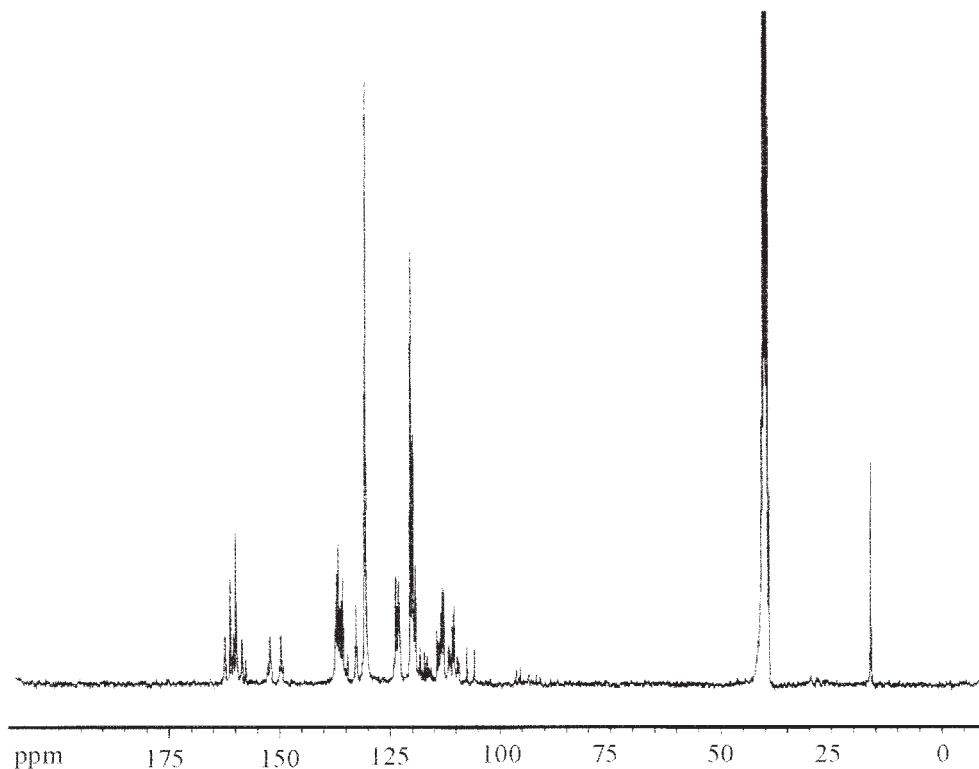

Figure 4 The chemical shifts of polymer V.

Figure 5 The ^{13}C-NMR spectra of polymer III.

= 158.4 ppm). Similar carbons 2, 4, and 5 show chemical shifts close to the shifts of the corresponding carbons of polymer I (Fig. 2). A complete list of chemical shift assignments is given in Table IV and the ^{13}C-NMR spectrum of polymer III is given in Figure 5. Because of the insolubility of polymer V, the chemical shifts for polymer V could not be assigned in the ^{13}C-NMR chemical shifts of polymer III (Table IV). However, the presence of a characteristic peak at 16.1 ppm confirms the incorporation of methyl units in the copolymer.

Thermal transition

The T_g values of the copolymers were determined by DSC and the results are given in Table I. Samples were heated to 300°C (polymers I, II, III, and IV) and 350°C (polymer V) at a rate of 10 K min^{-1} in an N$_2$ atmosphere, quenched to −50°C, and rerun to obtain the T_g. The T_g values of the copolymers increase with an increase in concentration of DHDPS in the polymers. This gradual increase can be attributed to the greater polarity of the polymer chain because of the incorporation of sulfonyl groups.

X-ray diffractograms (Fig. 6) reveal that the tendency toward an amorphous nature increases with increases in the concentration of DHDPS in the polymer. This is further confirmed from the DSC studies in which all polymers failed to show melt crystallization

temperatures, except for polymer V (Table I). Similar observations were made in our earlier works.[18,19]

Thermogravimetric analysis

The thermal degradation behavior of polymers I–V was studied by TG in an N$_2$ atmosphere at a heating rate of 20 K min^{-1}. From the TG trace, the initial decomposition temperature and the char yield at 500, 700, and 900°C were determined and the values are given in Table V. All polymers were stable up to 420°C and gave a char yield of 40–55% at 900°C. The relative thermal stability of the copolymers can be assessed by their integral procedural decomposition temperature (IPDT) as proposed by Doyle.[20] The IPDT values indicate that the thermal stability of the polymers increases gradually with the increase in MeHQ content in the polymers.

The overall activation energy (E) for decomposition was calculated using the Coats and Redfern[21] equation, assuming the order of reaction is 1.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\Phi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

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. The value of E was calcu-
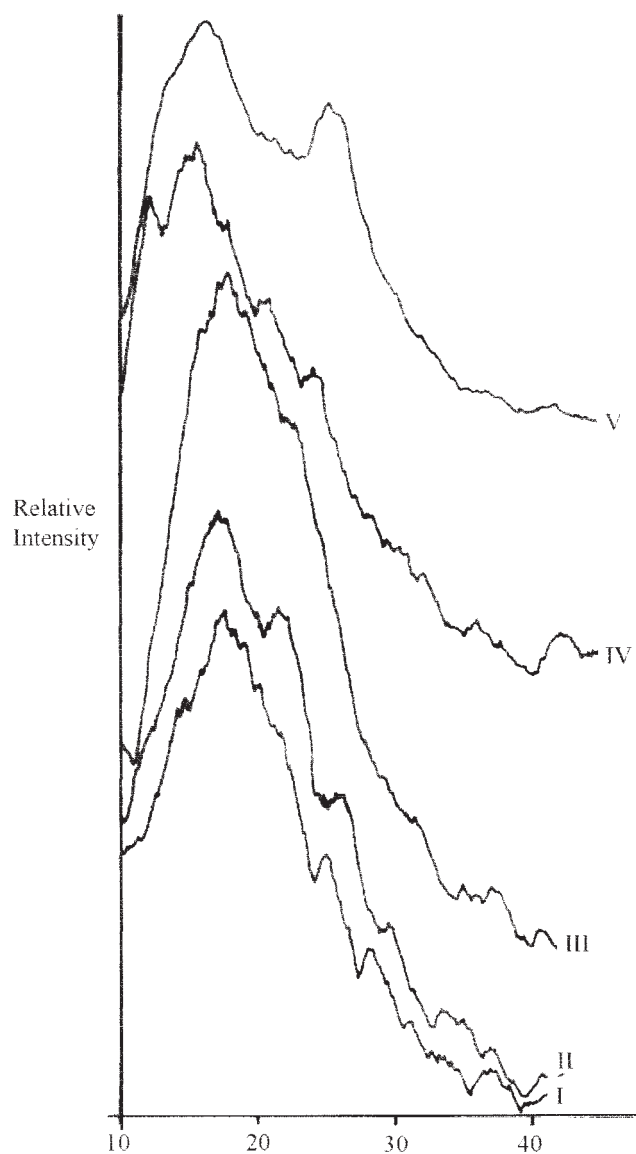
Figure 6 The X-ray analysis of polymers I–V.

TABLE V
Thermal Properties of Polymers I–V

Polymer	IDT	Char residue (%) 500°C	700°C	900°C	IPDT
I	420	70	53	40	1328
II	430	71	55	43	1483
III	430	73	59	47	1593
IV	430	77	63	54	1950
V	450	79	65	55	1982

IDT, initial degradation temperature; IPDT, integral procedural decomposition temperature.

In order to confirm the trimerization reaction, polymer V was heated at 350°C in an inert atmosphere at various time intervals and the IR spectra were recorded. The IR spectra (Fig. 7) showed that there is a gradual decrease in the intensity of the characteristic nitrile peak at 2230 cm^{-1} and the time confirms that the trimerization reaction has taken place. This was further confirmed by nitrogen analysis for the heated polymer V (350°C, N$_2$, 660 min) where the nitrogen value was found to be 5.9%, which is in close agreement with the theoretical value (6.2%), indicating that no degradation of the nitrile group has taken place (Table VI). However, the low values of C and H may be explained on the basis of degradation of pendant alkyl groups or from the degradation of alkyl phenoxy groups after the cyclization of nitrile groups. For polymer I no appreciable change was observed in the intensity of the nitrile group at 2230 cm^{-1} for the heated sample with respect to time (Fig. 8). The trimerization reaction of nitrile groups are not favorable in the case of polymer I because of the presence of electron withdrawing sulfone groups.
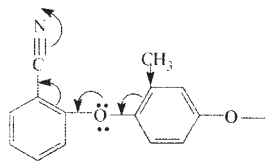
The E values for the second stage of decomposition suggests that it is a physical process, which involves volatilization of the products formed during the first stage of decomposition.

CONCLUSIONS

The important conclusions that can be drawn from the present study are as follows:

TABLE VI
Kinetic Parameters of Polymers I–V

Polymer	T (°C)	αRange	E (kJ/mol)	Correlation coefficient
I	410–560	0.0133–0.6797	103	0.9912
	570–780	0.7073–0.9762	16	0.9877
II	410–500	0.0160–0.5592	186	0.9936
	520–780	0.6251–.09857	15	0.9905
III	410–480	0.0121–0.4865	230	0.9946
	490–730	0.5186–0.9035	14	0.9867
IV	410–480	0.0160–0.5371	.244	0.9944
	490–730	0.5723–0.9338	14	0.9918
V	410–500	0.0014–0.4906	335	0.9974
	510–720	0.5353–0.8907	19	0.9966

lated from the plot of $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$. The results obtained are given in Table VI.

The Coats–Redfern plot indicates a two-stage decomposition. The first and main stage of decomposition occurs in the 410–560°C temperature range and corresponds to a weight loss of ~20–35% of the active material decomposed. The overall E for polymer V, which contains only MeHQ units, is 335 kJ mol^{-1} whereas the corresponding value is 103 kJ mol^{-1} for polymer I, which contains only DHDPS units. Copolymers II, III, and IV, which contain varying mole proportions of MeHQ and DHDPS units, show synergic effects (i.e., with an increase in MeHQ units the activation energy increases). This may be due to the electron releasing (+I effect) of the methyl group that activates the nitrile group in the cyclization reaction for trimerization according to Scheme 2.

Scheme 2 The scheme for trimerization.

Polymer	Annealing time (min)	Elemental analysis (%)		
		C	H	N
V	405	59.5 (75.3)	2.7 (4.03)	5.8 (6.2)
V	660	50.8 (75.3)	2.3 (4.03)	5.9 (6.2)

1. As the sulfone content increases in the feed the viscosity of the polymer decreases, confirming the low reactivity of DHDPS toward DCBN compared to that of MeHQ.
2. The glass-transition temperature increases with an increase in sulfone content in the copolymer.
3. As the sulfone content increases the crystallinity decreases in the copolymer and thus fails to obtain the melt crystallization temperature because of its amorphous nature.
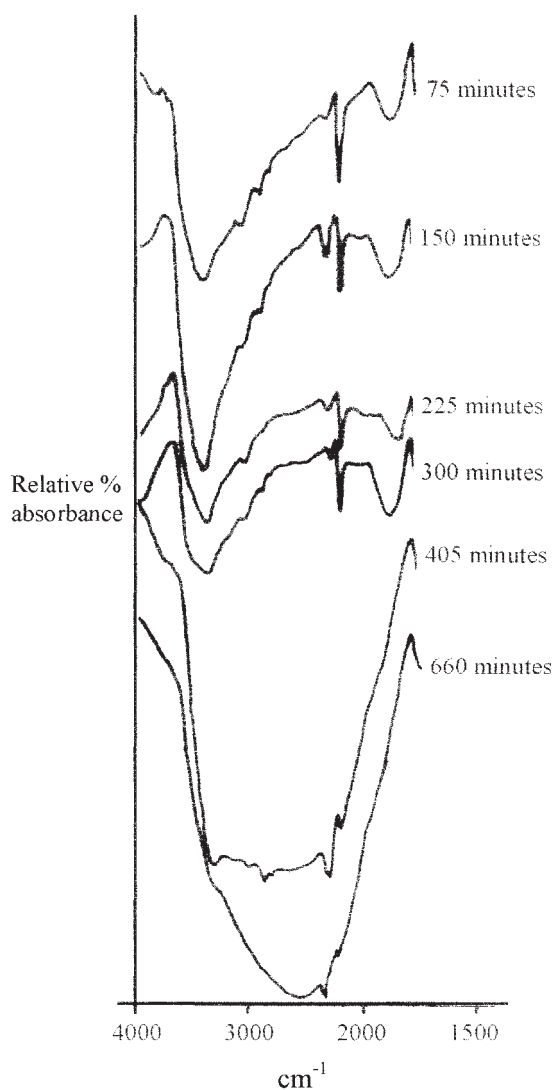
4. The overall thermal stability and activation energy for thermal decomposition increases with increasing MeHQ content, which may be attributable to the presence of the electron releasing (+I effect) methyl group that activates the nitrile group in the cyclization reaction for trimerization.
5. The IR spectrum of the MeHQ-DCBN-DHDPS system shows the presence of two characteristic peaks at 1187 [$\nu\phi$—O— (MeHQ)] and 1150 cm^{-1} [$\nu\phi$—S=O (DHDPS)]. This indicates that both MeHQ and DHDPS are incorporated in the copolymer chain.
6. A kinetic analysis shows a two-stage thermal decomposition process with the second stage having very low activation energy, which is indicative of a physical process.

Figure 7 The trimerization behavior of polymer V at 350°C.
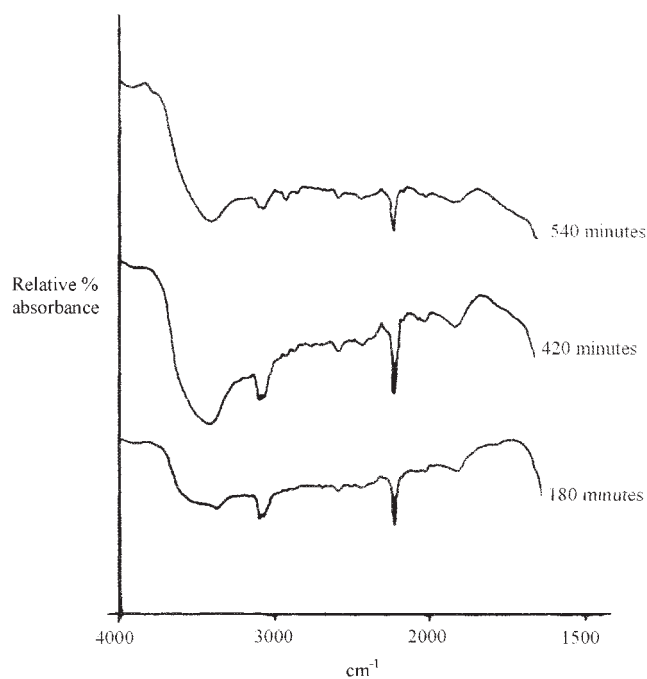
Figure 8 The trimerization behavior of polymer I at 320°C.

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