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, Propellants, Chemicals & Materials Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala-695022, India*
[2]*Analytical and Spectroscopy Division, Propellants, Chemicals & Materials Entity, 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 solvent in the presence of anhydrous K_2CO_3. The polymers were characterized by different physicochemical techniques. Copolymer composition was determined using FTIR technique. Thermogravimetric data reveals that all the polymers were stable up to 420°C with a char yield above 40% at 900°C in N_2 atmosphere. The glass transition temperature was found to increase and the activation energy and inherent viscosities were found to decrease with increase in concentration of the 4,4′-dihydroxydiphenylsulfone units in the polymer. Trimerization reactions are found to be favorable with increase in concentration of methyl hydroquinone units in the polymer. Crystallinity of the polymer was also studied using wide angle X-ray diffraction. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1303–1309, 2006

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

INTRODUCTION

In the recent past, engineering thermoplastics have been 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 T_g, 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 arylene ether nitrile[4] (PEN, Idemitsu) exhibits superior solvent resistance due to its crystalline nature. Owing to its crystalline/semicrystalline nature, PEN exhibits high tensile strength and a melting point that qualify 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, and 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. In addition, high price and insolubility in common organic solvents limits its widespread application.

Various attempts have been made by several researchers and in our laboratory to improve the solubility of PEN type polymers by 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 polyether nitriles containing sulfone groups and pendant alkyl groups within the polymeric chain have not been studied in detail in open literature. They are expected to have the advantages of both polyether nitriles and PES in their properties, 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)

Correspondence to: V. L. Rao (rao_vl@rediffmail.com).
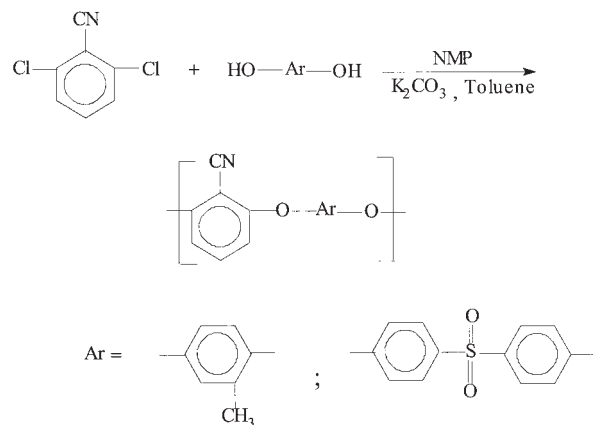
Scheme 1

with pendant methyl groups derived from various 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 FTIR technique. Thermal characterization of the polymers was carried out by thermogravimetry, and the activation energy for decomposition was evaluated.

EXPERIMENTAL

Materials

High purity 2,6'-dichlorobenzonitrile [Fluka], methyl hydroquinone [Lancaster], and 4,4'-dihydroxydiphenylsulfone [Aldrich] were used as received. Anhydrous K_2CO_3 [BDH] was dried in vacuum at 100°C before use. N-methyl pyrrolidone [SRL, India] was distilled under vacuum over phosphorous pentoxide and stored over 4 A molecular sieves.

Polymer synthesis

Poly ether nitrile and poly ether nitrile sulfone copolymers with pendant methyl groups were prepared, as shown in Scheme 1, by nucleophilic substitution reac-

tion of 2,6'-dichlorobenzonitrile [DCBN] with methyl hydroquinone [MeHQ] and varying mole proportions of MeHQ and 4,4'-dihydroxydiphenylsulfone [DH-DPS] using anhydrous K_2CO_3 in N-methyl pyrroli-done [NMP] medium with 28% solid content at 200°C under N_2 atmosphere as per 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 vacuum at 100°C for 15 h.

Instruments

Elemental analysis was performed with a Perkin–Elmer model 2400 CHN analyzer. Inherent viscosities were obtained for 0.2% polymer in p-chlorophenol at 60°C using an Ubbelhode suspended level viscometer. Glass transition temperature (T_g) and melting points were measured using a TA instrument DSC-2920 modulated differential scanning calorimeter operated at 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. ^{13}C-NMR spectra were recorded at 75.4 MHz using a Bruker Avance-300 spectrometer using deuteriated DMSO as 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 diffractometer with Cu-K∝ radiation at 40 kV and 30mA. The diffractograms were recorded at room temperature over the 2θ range 10–40θ. Thermogravimetric analysis of the polymers was carried out using a TA instrument model SDT-2960 thermal analyzer at a heating rate of 20Kmin^{-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 nucleo-

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 0.2 % polymer solution at 60°C.

philic displacement of chlorine from an activated substrate 2,6'-dichlorobenzonitrile [DCBN] by methyl hydroquinone [MeHQ]/4,4'dihydroxydiphenylsulfone [DHDPS]. Polymers I–V were obtained by varying the mole proportion of MeHQ to DHDPS. Feed ratios and some properties of the polymers are given in Table I. Inherent viscosity values reveal that the incorporation of the DHDPS unit into the polymeric chain lowers the viscosity of the polymers, indicating the lower reactivity of DHDPS towards the nucleophilic substrate. This may be due to the presence of electron withdrawing sulfone groups, which reduce the nucleophilicity of DHDPS. On the other hand, the electron releasing methyl groups (+I effect) in MeHQ enhances the nucleophilicity of MeHQ. However, 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% of MeHQ content, as shown in Table II.

Characterization

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

FTIR

FTIR technique was used for polymer characterization and for semi quantitative information of copolymer composition. The FTIR spectra of all polymers show characteristic bands at 2230cm^{-1} 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 the −OH and ϕ−Cl stretching vibrations at 3444cm^{-1} and 783cm^{-1}, respectively. The peak at 1150cm^{-1} is due to the stretching vibrations of the S=O group, and the peaks in the region between 1100–1250cm^{-1} are due to ϕ−O skeletal vibrations.
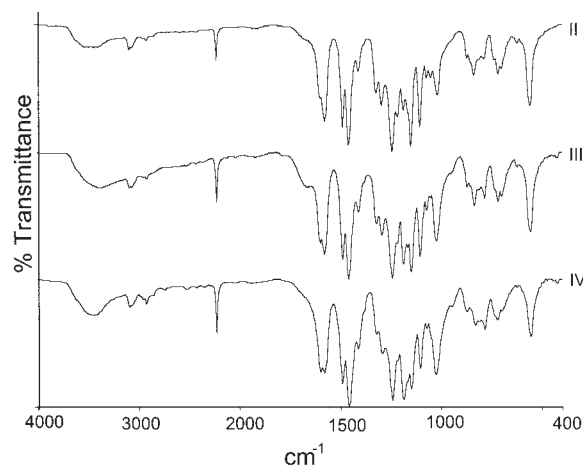

Figure 1 FTIR spectra of polymers II, III, and IV.

The formation of the product can be confirmed by the shift in the ring vibrations from 1490cm^{-1} to 1450cm^{-1} in the polymer, indicating a change in the substitution pattern. The peak at 1600cm^{-1} is assigned to the C=C stretching of the benzene ring where oxygen is ortho to CN. In polymer V, a weak band at 2924cm^{-1} is due to the stretching vibrations of the CH$_3$ group. The peak at 1450cm^{-1} due to the −CH$_3$ bending vibration overlaps with the C=C stretching vibration of the benzene ring, and the peak at 1187cm^{-1} is attributed to the ether linkages ortho to MeHQ. The presence of bands at 2924cm^{-1} and 1187cm^{-1} and the increase in intensity of 1459cm^{-1} peaks with respect to methyl content confirm the presence of MeHQ in the polymer.

The formation of the copolymers is confirmed by the characteristic peaks at 1150cm^{-1} and 1187cm^{-1}, corresponding to [$\nu\phi$ −S=O (DHDPS)] and [$\nu\phi$−O−(MeHQ)], respectively. An attempt has been made to obtain semiquantitative information on the relative amounts of DHDPS and MeHQ in the copolymers using integral intensities of the peaks νCN, $\nu\phi$−S=O (DHDPS), and $\nu\phi$−O (MeHQ). The intensities $\nu\phi$−O (MeHQ) and $\nu\phi$−S=O (DHDPS) are ratioed with respect to ν CN (DCBN) and then normalized to one so as to get the approximate information of the components present in the copolymers with different feed ratios. The percentage composition computed from

TABLE II
Solubility Behavior of Polymers I–V

| Polymer | Solvents | | | | |
	DMSO	DMF	NMP	CHCl$_3$	THF
I	++	++	++	−	−
II	++	++	++	−	−
III	++	++	++	−	−
IV	+−	+−	++	−	−
V	−	−	−	−	−

++ = Soluble; +− = Partially soluble; − = Insoluble.

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
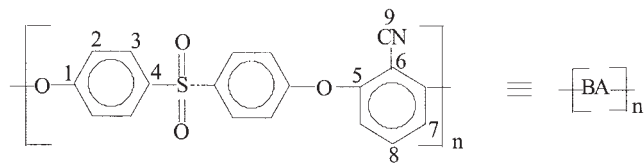
Figure 2 Chemical shifts of polymer I.
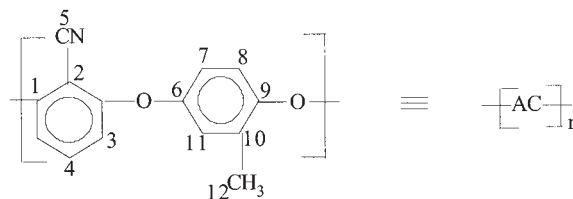
Figure 4 Chemical shifts of polymer V.

^{13}C-NMR

The ^{13}C-NMR spectra of polymers I, II, and III were recorded at 75.4MHz in DMSO-d6 with TMS as internal standard on a Brucker 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 also by the ^{13}C-NMR spectra of polymer I. However, the ^{13}C-NMR spectra of polymer V could not be recorded due to 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 following structure:

$$\left(BA\right)_x\left(CA\right)_y\left(BACA\right)_z$$
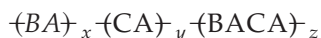
where A is the nitrile moiety, B is the sulfone moiety, and C is the methyl moiety. In the copolymers, the B unit exists only as ABA compositional triads. Hence, carbons in the B units in the copolymers will have the same chemical shifts as those of the corresponding carbons of the B units in polymer I. This is based on the reasonable assumption that only the nearest neighboring units affect the ^{13}C chemical shifts. Similarly, carbon C units in the copolymers will 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, namely, BAB, BAC or CAB, and CAC. The chemical shifts of carbons of the A unit in BAB and CAC will be 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 will 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 III given in Table IV.

The carbons of the A moiety in BAC or CAB, as is shown in Figure 3, will 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 will show resonance at δ = 159.9 ppm compared to the corresponding carbon 5 in Figure 2 (δ = 158.4 ppm). Similarly, 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. Due to 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 the characteristic peak at 16.1ppm confirms the incorporation of the methyl unit in the copolymer.

Thermal transition

The T$_g$s 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 10Kmin^{-1} in N$_2$ atmosphere quenched to −50°C and rerun to obtain T$_g$. The T$_g$ values of the copolymers increases with increase in concentration of DHDPS in the polymers. This gradual increase can be attributed to the greater polarity of the polymer chain due to incorporation of sulfonyl groups.

X-ray diffractograms in Figure 6 reveal that the tendency towards amorphous nature increases with
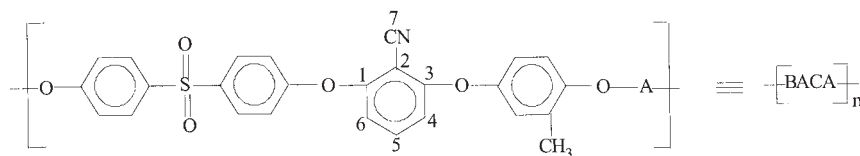

Figure 3 Chemical shifts of polymer III.

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

Peak no.	Chemical shifts[a] (δ ppm)	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] Values in parentheses represent chemical shifts for polymer I.

[b] I, V, & III refer to structures of polymers I, V, and III in Figs. 2–4, and the number represents the carbon designated therein.

increase in concentration of DHDPS in the polymer, which is further confirmed from the DSC studies where all polymers failed to show melt crystallization temperatures, except for polymer V (Table I). Similar observations were made in our earlier papers.[18,19]

Thermogravimetric analysis

Thermal degradation behavior of polymers I–V was studied by thermogravimetry (TG) in a N$_2$ atmosphere at a heating rate of 20Kmin^{-1}. From the TG trace, the initial decomposition temperature (IDT) and the char
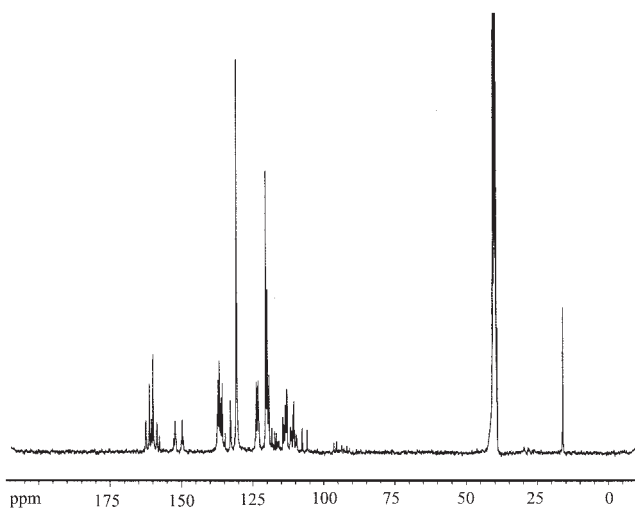

Figure 6 X-ray analysis of polymers I–V.

yield at 500, 700, and 900°C were determined, and the values are given in Table V. All polymers are 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) proposed by Doyle.[20] 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 Coats and Redfern's[21] equation assuming the order of reaction is 1:

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

TABLE V
Thermal Properties of Polymers I–V

Polymer	IDT	Char residue, %			IPDT
		500 °C	700 °C	900 °C	
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.
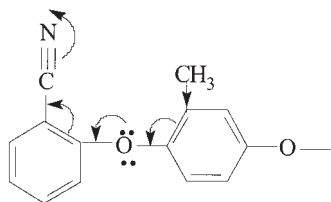
TABLE VI
Kinetic Parameters of Polymers I–V

Polymer	T (°C)	α-Range	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

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

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. E was calculated 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 temperature range 410–560°C and corresponds to a weight loss of $\sim$ 20–35% of the active material decomposed. The overall activation energy (E) for polymer V, which contains only MeHQ units, is 335 kJmol^{-1}, whereas the corresponding value is 103 kJmol^{-1} for polymer I, which contains only DHDPS units. Copolymers II, III, and IV, which contain varying mole proportions of methyl hydroquinone and DHDPS units, show a synergic effect, that is, with increase in MeHQ units, the activation energy increases. This may be due to the electron releasing (+I effect) of the methyl group, which activates the nitrile group in cyclization reaction for trimerization as per scheme 2.

To confirm the trimerization reaction, polymer V was heated at 350°C in inert atmosphere at various time intervals and IR spectra were recorded. The IR spectra (Figure 7) showed that there is a gradual decrease in the intensity of the characteristic nitrile peak at 2230cm^{-1} with time, confirming that the trimerization reaction has taken place. This was further con-
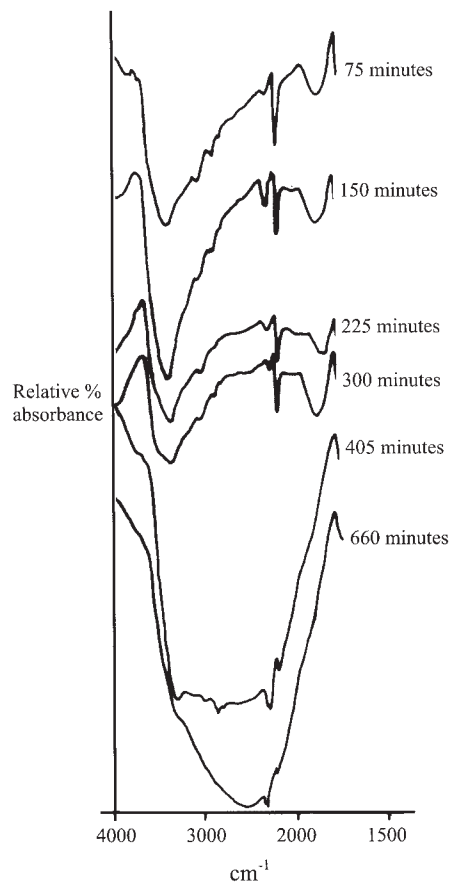

Figure 7 Trimerization behavior of polymer V at 350°C.

firmed by nitrogen analysis for the above said heated polymer V (350°C, N$_2$, 660min) 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 VII). However, the low values of C and H may be explained on the basis of degradation of the pendant alkyl groups or due to the degradation of the alkyl phenoxy groups after the cyclization of the nitrile groups. But for polymer I no appreciable change was observed in the intensity of the nitrile group at 2230cm^{-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 due to the presence of the electron withdrawing sulfone groups.

Scheme 2 Trimerization.

TABLE VII
Elemental Analysis of Polymer V Annealed at 350 °C in N$_2$ Atmosphere

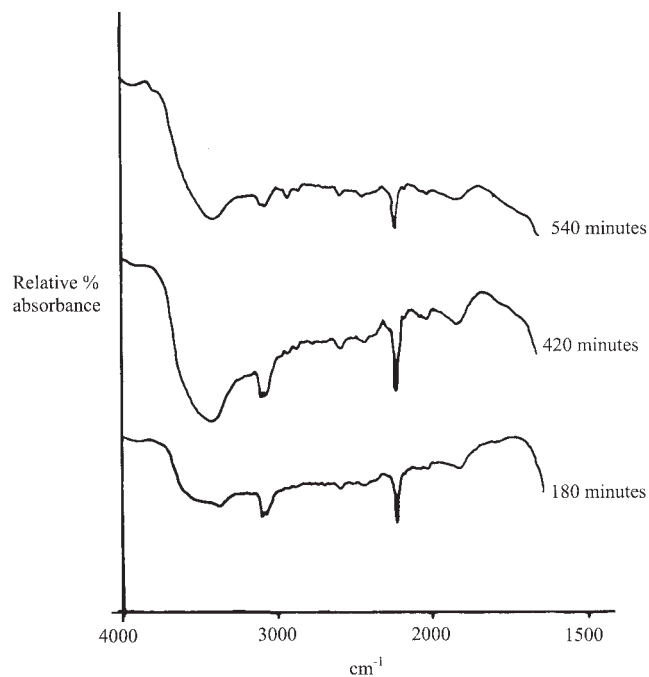| Polymer	Annealing time (in minutes)	Elemental analysis, %		
		C	H	N
V	405	59.5 (75.3)	2.7 (4.03)	5.8 (6.2)
"	660	50.8 (75.3)	2.3 (4.03)	5.9 (6.2)

Figure 8 Trimerization behavior of polymer I at 320°C.

The E values for the second stage of decomposition suggest that it is a physical process that involves volatilization of the products formed during the first stage of decomposition.

CONCLUSIONS

The following important conclusions can be drawn from the present study:

1. As sulfone content increases in the feed, the viscosity of the polymer decreases, confirming the low reactivity of DHDPS towards DCBN compared to that of MeHQ.
2. The glass transition temperature increases with increase in the sulfone content in the copolymer.
3. As sulfone content increases, crystallinity decreases in the copolymer, and thus failed to obtain a melt crystallization temperature due to amorphous nature.
4. The overall thermal stability and activation energy for thermal decomposition increases with increase in MeHQ content, which may be due to the presence of the electron releasing (+I effect) methyl group, which activates the nitrile group in the cyclization reaction for trimerization.

5. The infrared spectrum of the MeHQ-DCBN-DHDPS system shows the presence of two characteristic peaks at $1187 cm^{-1}$ $[\nu\phi-O-(MeHQ)]$ and $1150 cm^{-1}$ $[\nu\phi-S{=}O$ (DHDPS)]. This indicates that both MeHQ and DHDPS are incorporated in the copolymer chain.
6. Kinetic analysis shows a two stage thermal decomposition process, with the second stage having very low activation energy, indicative of physical process.

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