

Synthesis and Characterization of Poly(ether sulfone) Copolymers

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ABSTRACT: Poly(ether sulfone) copolymers **I–V** were synthesized by the nucleophilic substitution reaction of 4,4-dichlorodiphenyl sulfone with varying mole proportions of 4,4-isopropylidene diphenol (bisphenol A) and 4,4-dihydroxydiphenyl sulfone (bisphenol S) using sulfolane as the solvent in the presence of anhydrous K₂CO₃. The polymers were characterized by different physicochemical techniques. The glass transition temperature was found to decrease with increase in the concentration of bisphenol A units in the polymers. All polymers were found to be amorphous. Thermogravimetric studies showed that all the polymers were stable up to 400°C with a char yield of about 36% at 900°C in a nitrogen atmosphere. ¹³C-NMR spectral analysis reveals that bisphenol S-based triads are preferentially formed compared to bisphenol-A triads, indicating greater reactivity of bisphenol S toward dichlorodiphenyl sulfone. The overall activation energy for the thermal decomposition of bisphenol A-based polymer (**I**) is much higher than that of bisphenol S-based polymer (**II**). This was attributed to the modification of the backbone of polymer **I** during the initial cleavage of the C—CH₃ bond of the isopropylidene group. Polymer **II** decomposes by cleavage of the C—SO₂ bond. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 743–750, 1998

Key words: PES copolymer; ¹³C-NMR; DSC; thermogravimetry; activation energy

INTRODUCTION

Engineering thermoplastics are becoming potential candidates for many special-purpose applications in aerospace, military aircraft, automobiles, telecommunications, and missile technologies. The major advantages of using these materials as composite matrices, compared to currently used thermosetting resins, are their increased toughness and better impact resistance. Poly(ether sulfone) (PES) is one such useful engineering thermoplastic¹ because of its high thermal stability² and easy processability in the melt or in solution.³ Modification of epoxy resins with poly(ether sul-

fones)^{4–7} show improved mechanical properties and good interfacial adhesion without phase separation.^{6,7}

Nucleophilic displacement polymerization has been recognized as a convenient route to synthesize a variety of polyethers.^{8–10} Johnson et al.² reported for the first time the details of the synthesis of high molecular weight PES by reacting 4,4-dichlorodiphenyl sulfone (DCDPS) with bisphenol A in the presence of a NaOH/dimethyl sulfoxide medium. With 100% caustic or slightly less, high molecular weight PES could be made. However, a slight excess of NaOH leads to cleavage of the polymer chains *para* to the sulfone groups and results in the formation of low molecular weight polymers. Later, various researchers realized high molecular weight PESs by using excess K₂CO₃ in the presence of dipolar aprotic sol-

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vents.¹¹ However, the reaction times were too long. Recently, we succeeded in developing high molecular weight poly(arylene ether)s by employing K_2CO_3 in excess in high boiling solvents such as sulfolane, benzophenone, and diphenyl sulfone with relatively shorter reaction times.¹²⁻¹⁴

Further, polysulfones can be tailored to obtain optimum properties of toughness, strength, melt viscosity, and glass transition temperature by incorporating various substituents in the polysulfone backbone. Therefore, we have undertaken systematic studies on the synthesis and evaluation of properties of copoly(ether sulfone)s derived from various monomers. In this article, we report on the synthesis of copolymers based on DCDPS and varying mol proportions of bisphenol A (Bis A) and sulfonyl diphenol (Bis S) in the presence of K_2CO_3 and sulfolane medium. The copolymers were characterized by physical and spectral methods. Composition and sequence distribution of the comonomers in the copolymers were studied by ^{13}C -NMR spectroscopy. Thermal characterization of the polymers was carried out by thermogravimetry and activation energies for decomposition were evaluated.

EXPERIMENTAL

Materials

High-purity DCDPS (Chemical & Engineering Co., Bombay, India) was used as received. Anhydrous K_2CO_3 (BDH) was dried at 400°C for 8 h prior to use. Bisphenol A (Bis A) was recrystallized from hot toluene and dried under a vacuum. Sulfolane (Aldrich, Milwaukee, WI) was distilled from NaOH pellets under reduced pressure and the middle fractions were collected and stored over molecular sieves. High-purity sulfonyl diphenol (Bis S) obtained from Aldrich was used as received.

Polymer Synthesis

PES copolymers were synthesized by the nucleophilic substitution reaction of DCDPS and varying mol proportions of Bis A/Bis S using a slight excess of anhydrous K_2CO_3 in sulfolane medium at 30% solid content under a nitrogen atmosphere as per the procedure described in our earlier article.¹²

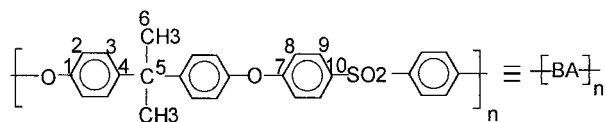


Figure 1 Chemical shifts of polymer I.

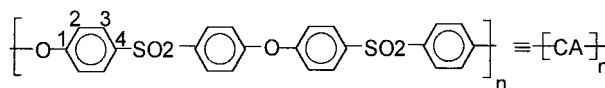


Figure 2 Chemical shifts of polymer II.

Characterization

Elemental analysis was performed using a Perkin-Elmer Model 2400 CHN analyzer. Inherent viscosities were obtained for 0.4% polymer solutions in NMP at 25°C using an Ubbelohde suspended level viscometer. Glass transition temperatures (T_g 's) were measured using a Mettler thermal analyzer 3000 coupled to a DSC 20 at a heating rate of 10 K min⁻¹. The IR spectra of the polymers were run as KBr pellets (2%) using a Perkin-Elmer 283 spectrophotometer. ^{13}C -NMR spectra were recorded at 100 MHz using a Bruker AMX-400 spectrometer. DMSO- d_6 was used as a solvent with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analysis of the polymers was carried out under a nitrogen atmosphere using a DuPont TA 2000 in connection with a 951 thermogravimetric analyzer at a heating rate of 20 K min⁻¹.

RESULTS AND DISCUSSION

PES copolymers were synthesized by the aromatic nucleophilic displacement of chlorine from an activated substrate (DCDPS) by Bis A/Bis S. Polymers I-V were obtained by varying the mol ratio of Bis A to Bis S. Polymer I, as shown in Figure 1, contains Bis A and 4,4'-dichlorodiphenyl sulfone and is similar to the UDEL® polysulfone offered by Amoco Polymers, Inc. Polymer II, as shown in Figure 2, contains Bis S and 4,4'-dichlorodiphenyl sulfone and corresponds to Victrex PES developed by ICI. Copolymers III-V are represented by Figure 3. Feed ratios and some properties of the polymers are given in Table I.

Characterization

Elemental Analysis

C and H contents of polymers I-V are listed in Table I. The values are in reasonable agree-

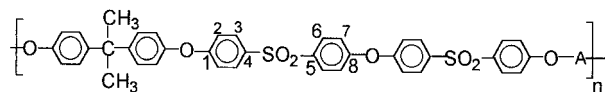


Figure 3 Chemical shifts of polymer III.

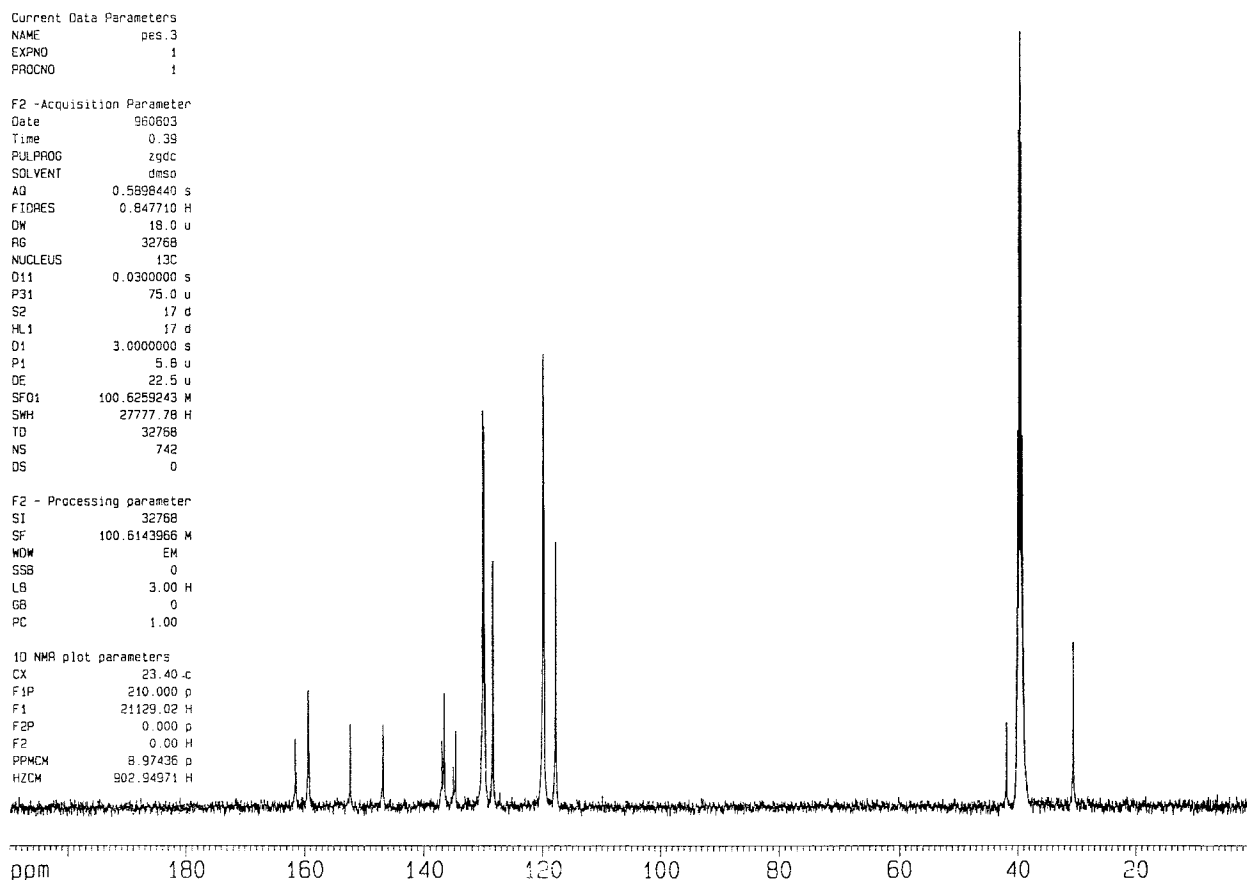
Table I Some Properties of Polymers I-V

Polymer	Feed Ratio (Mol Fraction)			Inherent Viscosity (dL/g)	Elemental Analysis (%)		T_g (°C)
	DCDPS	BPA	DHDPS		C	H	
I	0.5	0.5	0.0	0.45	71.5 (73.3)	4.3 (4.97)	180
II	0.5	0.0	0.5	0.80	60.70 (62.06)	3.3 (3.44)	232
III	0.5	0.25	0.25	0.62	65.9 (67.54)	4.0 (4.19)	198
IV	0.5	0.375	0.125	0.27	69.9 (70.39)	4.4 (4.58)	192
V	0.5	0.125	0.375	0.36	66.2 (64.77)	3.8 (3.81)	210

ment with theoretical values, confirming the proposed structures. The slightly lower values observed for the carbon content may be due to graphitization and consequent incomplete combustion.

IR Spectra

The IR spectra of all the polymers show no absorption bands in the 3500–3000 cm^{-1} region, indicating the absence of the —OH group but all the

**Figure 4** ^{13}C -NMR spectrum of polymer **III**.

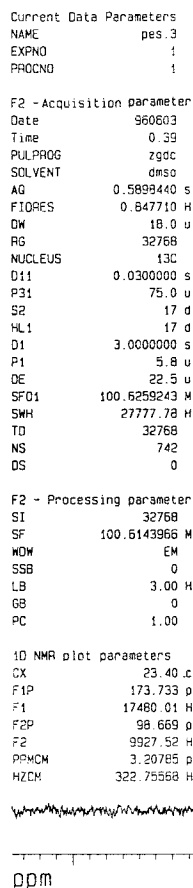


Figure 4 (Continued from the previous page)

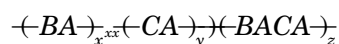
spectra show characteristic bands at 1300–1350 cm^{-1} (SO_2 , *as*) and 1140–1160 cm^{-1} (SO_2 , *s*) due to the sulfonyl group and a band at 1250 cm^{-1} due to phenylene ether stretching vibrations (*s*, $\nu\phi-\text{O}$). In addition, all polymers show a characteristic band at 1380–1360 cm^{-1} due to the gem dimethyl doublet except for polymer **II**, where gem dimethyl groups are absent.

¹³C-NMR Spectra

The ¹³C-NMR spectra of polymers **I–IV** were recorded at 100 MHz in $\text{DMSO}-d_6$ with TMS as the internal standard on a Bruker AMX-400 spectrometer. The spectrum of polymer **III** is shown in Figure 4.

The mode of synthesis of polymers **I** and **II** indicates that the polymers have the structures shown in Figures 1 and 2. This was confirmed by elemental analysis (Table I) and also by the ¹³C-NMR spectra of the polymers. The chemical-shift assignments of various carbons in polymers **I** and **II** were based on the additivity constants for substituted benzenes and are in agreement with the values reported in the literature.

Copolymers **III–V** can be represented by the following structure:



where *A* is the sulfone moiety; *B*, the Bis A moiety; and *C*, the Bis S moiety. The sensitivity of ¹³C chemical shifts to the environment enables one to distinguish the possible triad structures. In the copolymers, *B* units exit only as *ABA* compositional triads. Hence, carbons in *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 ¹³C chemical shifts. Similarly, carbons of *C* units in the copolymers will have the same chemical shifts as those of the corresponding carbons in polymer **II**.

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* units in *BAB* and *CAC* triads will be the same as those of the corre-

Table II Assignment of ^{13}C -NMR Chemical Shifts for Polymer III

Peak No.	Chemical Shift ^a (δ ppm)	Assigned Carbon ^b
1	161.56	III-1
2	161.38 (161.41)	I-7
3	159.37 (159.38)	II-1
4	159.24	III-8
5	152.29 (152.31)	I-1
6	146.85 (146.85)	I-4
7	137.05	III-5
8	136.66 (136.64)	II-4
9	135.16 (135.09)	I-10
10	134.77	III-4
11	130.15 (130.16)	II-2
12	129.97	III-2 + III-7
13	129.78 (129.81)	I-8
14	128.41 (128.42)	I-3
15	119.89 (119.71) 119.91)	I9 + II-3 III-3 + III-6
16	117.81 (117.80)	I-2
17	41.91 (41.90)	I-5
18	30.48 (30.46)	I-6

^a Values in parentheses represent chemical shifts for **I** or **II**.

^b **I**, **II**, and **III** refers to structures of polymers **I**, **II**, and **III** and the number represents the carbon designated therein.

sponding carbons of the A units in **I** and **II**, respectively. Thus, the ^{13}C -NMR spectra of the copolymers will show all resonance absorptions present in **I** and **II**. This was indeed found to be the case as shown by the chemical shift data of **III** given in Table II.

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 **II**. Thus, the carbon 1 in Figure 3 will show resonance at $\delta = 161.56$ ppm compared to the corresponding carbon **I-7** ($\delta = 161.38$). Similarly, carbons 4, 5, 7, and 8 show chemical shifts close to the shifts of the corresponding carbons of **I** and **II**. A complete list of chemical-shift assignments is given in Table II and the ^{13}C -NMR spectrum of **III** is given in Figure 2.

Further, the populations of A-centered triads can be estimated by considering the relative intensities of the appropriate carbons as given in Table III. Taking into consideration the statistical weighting of different carbons, the following relationships between triad populations and their relative intensities are obtained:

$$[BAB] = I_2/2I_1 \quad (1)$$

$$[BAC] = I_9/2I_{10} \quad (2)$$

and

$$[CAC] = I_3/4I_4 \quad (3)$$

$$[CAB] = I_8/4I_7 \quad (4)$$

where I_i is the intensity of peak i . It is assumed that nuclear Overhauser effects (NOE) are minimum since the intensities of the same carbon in only marginally different environments are considered. The results obtained are shown in Table IV. The close agreement obtained for the same triad ratio from different sets of carbon atoms validate this assumption. Also, since

$$[BAC] = [CAB]$$

and

$$[BAB] + [BAC] + [CAC] = 1,$$

the population of individual triads can be estimated and the results obtained for **III** and **IV** are also given in Table IV. Furthermore, the monomer ratios calculated from the triad population are in close agreement with the feed ratios and confirms the ^{13}C spectral data analysis.

Although statistical considerations dictate that *CAC* and *BAB* triads should be of equal intensity for polymer **III**, the observed values indicate preference for *CAC* triads. Similar is the case with polymer **IV**. This observation can be rationalized in that Bis S is more acidic than is Bis A. Bis S is more acidic because of the resonance stabilization as shown in Figure 5. Bis S and Bis S-type end groups probably react with potassium carbon-

Table III Relative Intensities of Some Peaks in ^{13}C -NMR Spectra of Polymers III and IV

Peak No.	No. Carbons	Relative Intensity (%)	
		Polymer III	Polymer IV
1	1	11.90	10.32
2	2	6.46	26.46
3	4	18.99	5.16
4	1	11.39	5.99
7	1	11.65	6.66
8	4	19.11	5.83
9	2	7.34	28.79
10	1	13.17	10.82

Table IV Triad Populations in Polymers III and IV

Sample No.	Triad Population	Polymer III			Polymer IV		
		Eq. (1)	Eq. (2)	Av	Eq. (3)	Eq. (4)	Av
1	[BAB]/[BAC]	0.271	0.279	0.275	1.282	1.330	1.306
2	[CAC]/[CAB]	0.417	0.410	0.413	0.215	0.219	0.217
3	[BAB]	—	—	0.163	—	—	0.518
4	[BAC]	—	—	0.592	—	—	0.396
5	[CAC]	—	—	0.245	—	—	0.086
6	[B]/[C]	—	—	0.85 (1.0)	—	—	2.97 (3.0)

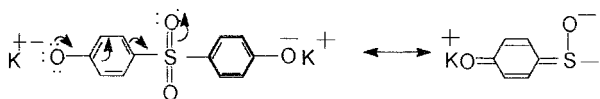
ate more readily to form phenoxide. The polymer-forming reaction with DCDPS takes place only with phenoxides and, hence, the preference for phenoxide formation could lead to a slight preference for CAC triads. Bis A phenoxide is harder to form but probably reacts faster with DCDPS in the absence of free Bis S or its type of phenolic end groups. In the presence of the Bis S type of phenolic groups, Bis A phenoxide might react to form Bis S phenoxide (due to pK_a differences) and the unreactive Bis A type of phenolic groups. Bis A phenoxide can also undergo an ether interchange reaction with the polymer backbone to displace the more acidic Bis S phenoxide, which again leads to a decrease in BAB triads.

Solubility

All polymers were soluble in dipolar aprotic solvents such as DMAc, DMSO, and NMP. The solubility of the polymers in common organic solvents such as THF decreases with increase in Bis S units in the polymer as shown in Table V.

Thermogravimetric Studies

The thermal degradation behavior of polymers I–V was studied by thermogravimetry (TG) in N_2 at heating rate of 20 K mn^{-1} . From the 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 VI. All polymers were stable up to 400°C . The maximum decomposition temperature was observed

**Figure 5** Resonance structures of Bis S.

between 535 and 580°C . All polymers gave a char residue of about 37% at 900°C . The relative thermal stabilities of the polymers can be assessed by their integral procedural decomposition temperature (IPDT) proposed by Doyle.¹⁵ IPDT values indicate that the thermal stability of the polymers increases with increase in Bis S units, as expected.

The overall activation energy (E_a) for decomposition was calculated from the weight loss–temperature profile by the equation of Coats and Redfern¹⁶:

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

where α is the fraction decomposed at temperature T ; Q , the heating rate; R , the gas constant; and A , the Arrhenius frequency factor. E_a was calculated from the plot of $\ln\{-[\ln(1-\alpha)]/T^2\}$ versus $1/T$.

The results obtained are given in Table VII and indicate that the activation energy increases with increase in the Bis A units in the copolymer. Further, the Coats–Redfern plots indicate that polymer I decomposes in two stages ($E_1 = 72$ and $E_2 = 214 \text{ kJ mol}^{-1}$), whereas polymer II decomposes in a single stage ($E = 132 \text{ kJ mol}^{-1}$). The large

Table V Solubility Characteristics of Polymers I–V

Polymer	DMAc	DMSO	NMP	CHCl_3	THF
I	+	+	+	+	+
II	+	+	+	+–	–
III	+	+	+	+	+
IV	+	+	+	+	+
V	+	+	+	+	–

+, soluble; +–, partly soluble; –, insoluble.

Table VI Thermal Analysis of Polymers I–V

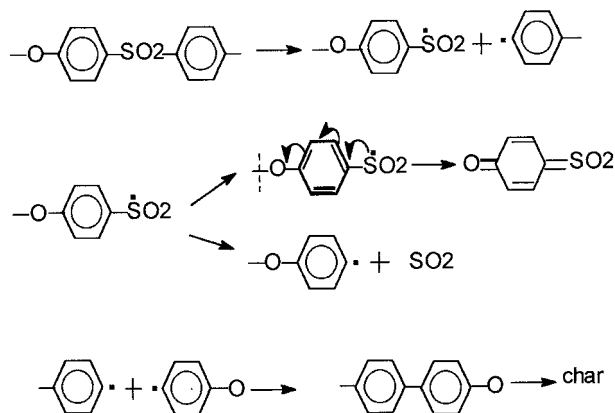
Polymer	IDT (°C)	D_{\max} (°C)	Char Residue (%)			IPDT
			600°C	700°C	900°C	
I	455	554	46	39	30	635
II	460	576	47	40	36	653
III	420	548	43	39	37	644
IV	440	553	42	39	36	639
V	430	527	42	37	34	632

IDT, initial decomposition temperature; D_{\max} , maximum decomposition temperature; IPDT, integral procedural decomposition temperature.

difference in the activation energies for decomposition for the two polymers may be rationalized as follows: According to available bond dissociation energies,^{17,18} the C—S bond of the diphenyl sulfone moiety is the weakest bond in polymer **II** and the probable mode of decomposition is shown in Figure 6. The observed char yield (36%) at 900°C for polymer **II** is in agreement with the loss of the —O—Ar—SO₂ moiety in each repeating unit (—O—Ar—SO₂—Ar—) of the molecule and the char may have polyphenylene-type structures.

In the case of polymer **I**, the weakest bond is the C—CH₃ bond of the isopropylidene group. The bond dissociation energies for C—CH₃ and C—SO₂ bonds are only marginally different (250 and 270 kJ mol⁻¹, respectively)¹⁸ and cannot account for the large difference observed in the E_a values for polymers **I** and **II**. A plausible explanation for this behavior is that the initial cleavage of the C—CH₃ bond results in the modification of the polymer backbone as indicated in Figure 7.

Thus, the initial cleavage of the C—CH₃ bond may result in the formation of extended conjugated and/or cyclic structures. The intact part of

**Figure 6** Mode of thermal decomposition of polymer **II**.

the repeat unit of polymer **I** still contains the less stable sulfone groups and provides a pathway for further decomposition. However, the E_a value (214 kJ/mol) observed is higher than the corresponding E_a value (132 kJ/mol) for polymer **II**. This observation can be rationalized on the following grounds:

1. Polymer **I** contains only half the amount of sulfone groups as in polymer **II**.
2. Loss of sulfone-containing moieties leaves behind larger fragments in the case of polymer **I** compared to polymer **II**.
3. The presence of alternating sulfone groups in polymer **II** may provide a synergistic effect for its decomposition.

The thermal degradation behavior of copolymers **III–V** is also in agreement with this behavior. Polymer **IV**, rich in Bis A units, shows two-stage decomposition and is similar to polymer **I**. Polymer **V**, rich in Bis S units, is similar to polymer **II**.

Table VII Kinetic Parameters of Polymers I–V

Polymer	T (°C)	α Range	ΔE (kJ mol ⁻¹)	Correlation Coefficient
I	420–490	0.0083–0.5458	71.7	0.9947
	510–550	0.039–0.5206	213.7	0.9890
II	470–610	0.0255–0.5458	132.1	0.9985
III	400–470	0.0174–0.069	73.7	0.9984
	470–550	0.069–0.439	125.3	0.9986
IV	400–460	0.0103–0.0451	93.8	0.9983
	520–560	0.1292–0.4598	195.7	0.9981
V	400–570	0.0042–0.5227	131.3	0.9983

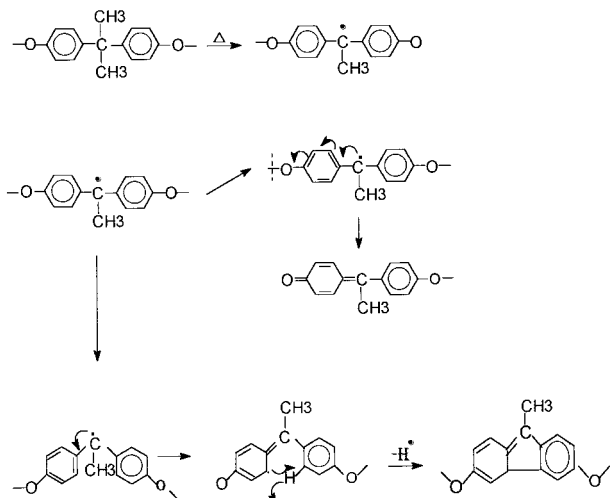


Figure 7 Mode of thermal decomposition of polymer I.

CONCLUSIONS

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

1. High molecular weight PES polymers can be synthesized by a nucleophilic displacement reaction of (A) DCDPS with (B) bisphenol (Bis A) and/or (C) sulfonyl diphenol (Bis S) in sulfolane medium using K_2CO_3 as the catalyst.
2. In the copolymers, the CAC triads are preferentially formed, indicating greater reactivity of Bis S compared to Bis A toward nucleophilic substitution.
3. Incorporation of Bis S into the copolymers increases the glass transition temperatures and also improves the thermal stability of the polymers.
4. The overall activation energy for thermal decomposition of the Bis A-based polymer (I) is 214 kJ mol^{-1} and is much higher than that of the Bis S-based polymer (II). This was attributed to the modification of the backbone of polymer I during the initial cleavage of the C—CH₃ bond of the isopropylidene group. Polymer II decomposes by cleavage of the C—SO₂ bond.

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