

Microstructure and Thermal Degradation of Poly(ether ketone sulfone) Copolymers: ^{13}C NMR and Thermogravimetry Studies

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ABSTRACT: Microstructure of poly(ether ketone sulfone) copolymers I–V, derived from varying mol proportions of dihydroxy diphenyl sulfone (DHDPS, A) and dihydroxybenzophenone (DHBP, C) with stoichiometric amounts of difluorobenzophenone (DFBP, B) was studied by ^{13}C nuclear magnetic resonance spectroscopy. The results were interpreted in terms of the compositional triads BBB, BBA, ABA, BAB, and AAB because B and C moieties become indistinguishable in the copolymers. Feed ratios calculated from the triad intensities agree well with experimental values, validating the chemical shift assignments. The presence of AAB and BBA triads in polymer II (A : C = 1 : 0) indicates the occurrence of transesterification reaction during its synthesis. Thermal decomposition characteristics of the copolymers were studied by thermogravimetry. Activation energies for thermal degradation were calculated using Coats-Redfern's method assuming the order of the reaction is 1 and was found to vary from 281 to 193 kJ mol^{-1} . A good linear correlation was obtained between activation energy values and BBB triad intensities. These observations were rationalized by consideration of their decomposition mechanisms. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3425–3431, 1999

Key words: polyether ether ketone; polyether ketone sulfone copolymers; ^{13}C nmr spectroscopy; thermogravimetry

INTRODUCTION

Thermoplastic polymers, which possess exceptional thermooxidative and dimensional stability, glass transition temperature (T_g) above 200°C , and T_m below 400°C , are extensively used as matrices in advanced composites for aerospace and microelectronic applications. Semicrystalline poly(aryl ether ketone) polymers meet most of these requirements but have the disadvantage of high T_m values and cannot be processed below

450°C without leading to degradation.¹ Therefore, attempts have been made to incorporate amorphous segments with the $-\text{SO}_2-$ group into the ether ketone chain by blending^{2,3} and block^{4–7} or random copolymerization.^{8,9}

In continuation of our earlier studies on synthesis and evaluation of properties of poly(ether ketone sulfone) copolymers from various monomers,^{10,11} we now report on microstructure and thermal degradation of copolymers derived from difluorobenzophenone (DFBP) and varying mol proportions of dihydroxybenzophenone (DHBP) and dihydroxy diphenyl sulfone (DHDPS) using ^{13}C nuclear magnetic resonance (NMR) and thermogravimetric techniques. The correlation be-

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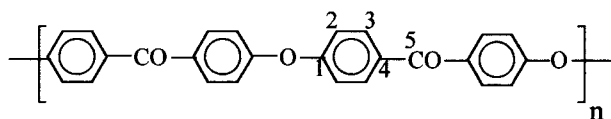


Figure 1 Chemical shifts of polymer I.

tween microstructure expressed in terms of compositional triads and activation energies (E_a) for thermal degradation is observed and rationalized in terms of the degradation mechanism of the polymers.

EXPERIMENTAL

Poly(ether ketone sulfone) copolymers I–V were synthesized by the nucleophilic substitution reaction of DFBP (Aldrich, USA) with varying mol proportions of DHBP (Lancaster, UK) and DHDPS (Aldrich): DHBP/DHDPS I = 1 : 0; II = 0 : 1; III = 1 : 1; IV = 3 : 1; and V = 1 : 3) using anhydrous K_2CO_3 in benzophenone and sulfolane medium (3 : 1 ratio) at 17% solid content under dry N_2 atmosphere as per the details described previously.^{12,16} The reaction mixture was slowly heated to 150°C and water was removed by azeotropic distillation with toluene. The polycondensation reaction was continued for 2 h at 230°C. The viscous reaction mixture was cooled to room temperature and precipitated in water. The product was refluxed with water repeatedly and subjected to Soxhlet extraction with acetone, filtered, and dried under vacuum at 100°C for 12 h.

^{13}C NMR spectra were recorded at 100 MHz using a Bruker AMX-400 spectrometer. A mixture of methane sulfonic acid and $CDCl_3$ was used as solvent with tetramethyl silane as the internal standard. Thermogravimetric analysis of the polymers was performed using a Dupont thermal analyser system 2000 in connection with a 951 thermogravimetric analyser at a heating rate of 20 K min^{-1} in dry N_2 atmosphere.

RESULTS AND DISCUSSION

Poly(ether ketone sulfone) copolymers I–V were synthesized by reacting stoichiometric amounts of

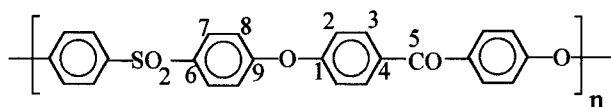


Figure 2 Chemical shifts of polymer II.

DFBP with varying mol proportions of DHBP and DHDPS (DHBP/DHDPS: I = 1 : 0; II = 0 : 1; III = 1 : 1; IV = 3 : 1; and V = 1 : 3).

^{13}C NMR Spectra

The mode of synthesis suggests that polymer I has the structure as shown in Figure 1. The ^{13}C NMR spectrum of I shows five absorptions corresponding to the five distinguishable carbons as indicated in the structure. The chemical shift assignments of the various carbons were based on the additivity constants for substituted benzenes and are in agreement with the values reported in the literature.

Similarly, II is expected to have the structure as shown in Figure 2 and should show nine different absorptions corresponding to the nine distinguishable carbons. However, ^{13}C NMR spectrum of II shows 10 additional lines. This obser-

Table I ^{13}C NMR Data for Polymers I–III

Sl. No.	Chemical Shift (ppm)	Relative Peak Intensities (%)		
		P-I	P-II	P-III
1*	164.04	8.20	0.0	2.13
2*	120.31	40.71	0.0	18.67
3*	138.09	35.56	0.0	6.53
4*	127.06	10.34	0.0	1.83
5*	201.31	5.14	0.0	2.22
6**	163.80	0.0	1.10	4.57
7**	(120.31)	0.0	4.45	—
8**	137.92	0.0	3.13	12.22
9**	127.66	0.0	1.27	4.27
10**	201.59	0.0	1.43	2.99
11+	166.08	0.0	3.61	2.39
12+	119.15	0.0	14.27	7.52
13+	138.68	0.0	11.57	7.13
14+	125.86	0.0	3.54	1.92
15+	201.21	0.0	2.29	2.22
16***	158.59	0.0	4.30	2.90
17***	121.52	0.0	14.27	8.93
18***	130.57	0.0	13.58	8.46
19***	136.78	0.0	4.34	3.03
20++	160.22	0.0	1.40	0.0
21++	(121.36)	0.0	—	0.0
22++	130.20	0.0	5.72	0.0
23++	136.97	0.0	1.66	0.0
24++	158.70	0.0	—	0.0
25++	120.06	0.0	—	0.0
26++	130.38	0.0	6.78	0.0
27++	135.30	0.0	1.23	0.0

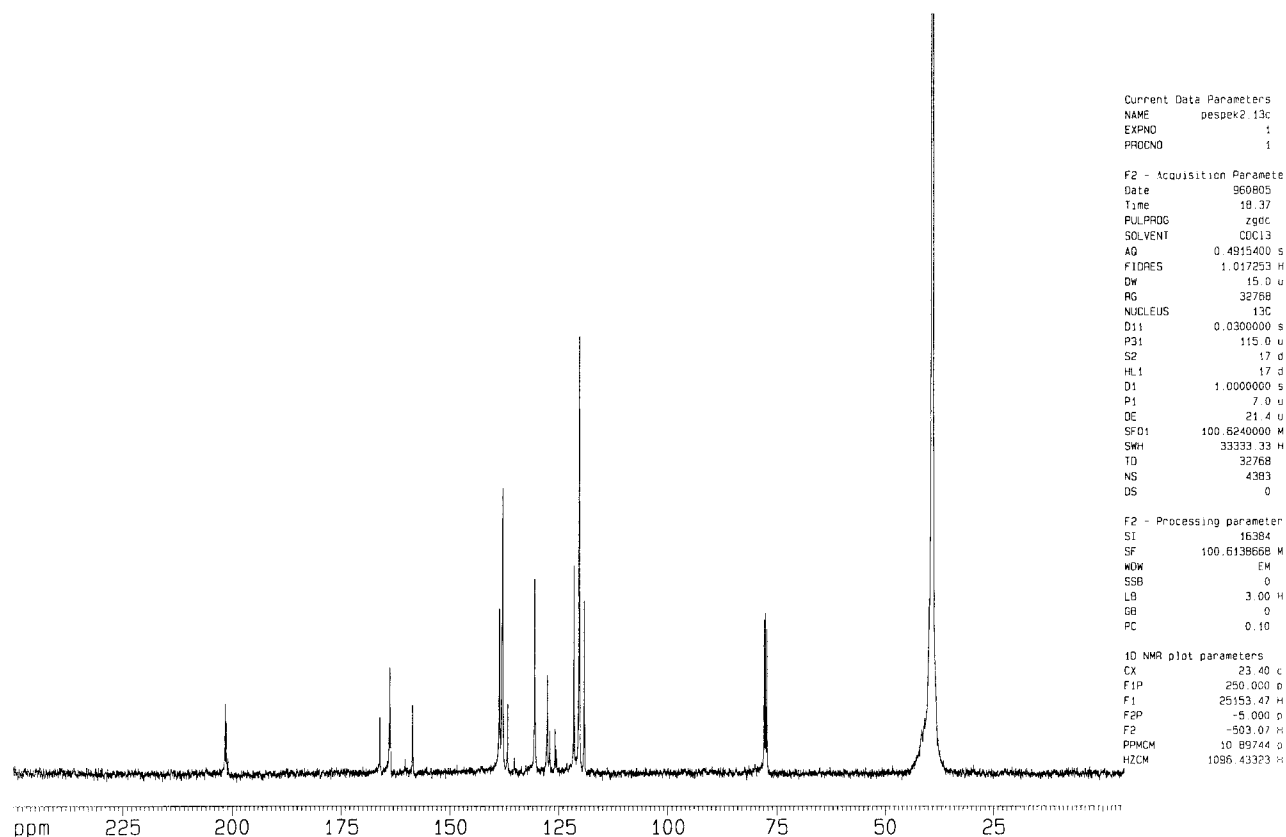


Figure 3 ^{13}C NMR spectrum of polymer III.

vation can be rationalized on the basis of the microstructure of the copolymers. Polymer I will have all the resonances indicated under the BBB triad for Polymer III. Polymer II will have additional resonances at 135.30 ppm, 130.20 ppm, 160.22 ppm, 136.97 ppm, and 130.38 ppm, corresponding to the AAB triad as described in our previous article.¹¹

MICROSTRUCTURE

The microstructure of polymers I–V can be interpreted in terms of the six possible compositional

triads BBB, BBA, ABA, BAB, AAB, and AAA ($A = -\text{OArSO}_2\text{ArO}-$; $B = -\text{Ar}-\text{CO}-\text{Ar}-$). It should be noted that DHBP and DFBP moieties become indistinguishable in ^{13}C NMR spectra of the polymers. Consequently, I contains only BBB triads and shows the expected five line absorption pattern. Polymer II is expected to show nine absorptions corresponding to the triads ABA and BAB. Therefore, the presence of 10 extra lines in the spectrum of II indicates the presence of additional triad structures of the type ABB and AAB because ^{13}C NMR chemical shifts are sensitive to the nearest neighboring units. This is confirmed by the presence of common absorptions observed

Table II Feed Ratios and Triad Intensities of Polymers I–IV

Polymer	Feed Ratio (mol fraction)			Triad Relative Intensities				
	DFBP	DHBP	DHDPS	BBB	ABA	ABB	BAB	AAB
I	0.5	0.5	0.0	1.00	0.0	0.0	0.0	0.0
II	0.5	0.0	0.5	0.0	0.12	0.40	0.43	0.05
III	0.5	0.25	0.25	0.19	0.21	0.35	0.25	0.0
IV	0.5	0.375	0.125	0.59	0.09	0.22	0.10	0.0

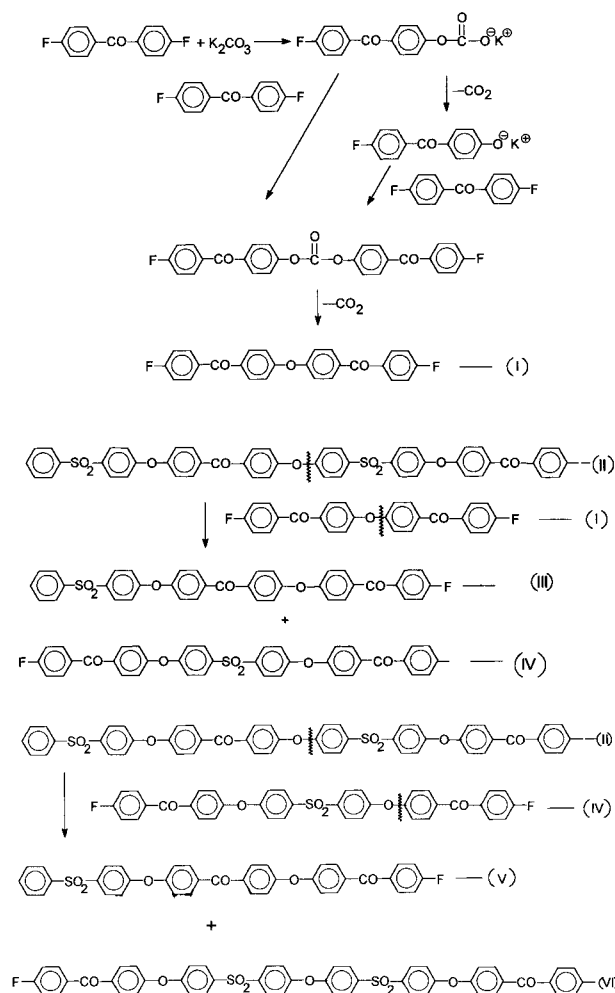


Figure 4 Transesterification of polymer II.

in the ^{13}C NMR spectra of II, and III and IV which should contain ABB triads as indicated by the mode of their synthesis. A complete list of chemical shift assignments for polymers I, II, and III are given in Table I and Figure 9 and the ^{13}C

NMR spectrum of polymer III is given in Figure 3. Relative intensities of the various triads in I–IV are given in Table II. The feed ratios calculated from these triad intensities agrees well with the experimental values as shown in Table II and validates the chemical shift assignments of the triads.

The presence of triads AAB and ABB in the structure of II can arise only if transesterification takes place during its synthesis, and can be represented as in Figure 4.

However, the absence of AAB triads in III and IV suggest that transesterification reaction does not occur when the sulfone monomer concentration is less than 50%. Furthermore, such transesterification reactions were reported earlier under similar experimental conditions for copolymer systems based on 4,4'-bis(4-fluorobenzoyl) biphenyl with 4,4'-dihydroxy diphenyl and 4,4'-dihydroxydiphenylsulfone.⁸

Thermogravimetric Studies

Thermal degradation behavior of copolymers I–V was studied by thermogravimetry in nitrogen atmosphere at a heating rate of 20 K min^{-1} . The initial decomposition temperature, the maximum decomposition temperature (D_{max}), and the char residue at 600, 700, and 900°C from the thermograms were determined and the values obtained are given in Table III. All polymers are stable up to 460°C and give a char residue of 45–55% at 900°C. The relative thermal stabilities of polymers can be assessed by their integral procedural decomposition temperature values proposed by Doyle.¹³ Integral procedural decomposition temperature values indicate that the thermal stability of the copolymers increases with increase in the ketone content in the polymers as observed previously.¹¹

Table III Thermal Analysis of Polymers I–V

Polymer	IDT (°C)	FDT (°C)	D_{max} (°C)	Char Residue (%), °C			IPDT (°C)
				600	700	900	
I	500	780	552	70	61	56	716
II	460	690	567	56	48	45	666
III	530	720	593	67	55	50	705
IV	530	750	580	67	58	52	710
V	510	770	567	60	53	44	689

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

Table IV Kinetic Parameters of Polymers I-V

Polymer	T (°C)	α Range	ΔE (kJ/mol)	Correlation Coefficient
I	460–580	0.0010–0.5300	280.9	0.9978
	600–690	0.6957–0.9849	80.5	0.9984
II	480–600	0.0117–0.7039	192.9	0.9975
	620–690	0.8486–0.9934	80.2	0.9977
III	470–620	0.0038–0.7406	202.9	0.9952
	640–690	0.8968–0.9907	87.0	0.9958
IV	470–610	0.0013–0.7370	247.0	0.9989
	630–680	0.8731–0.9787	70.9	0.9972
V	470–610	0.0025–0.7679	232.4	0.9994
	630–690	0.8937–0.9924	77.2	0.9964

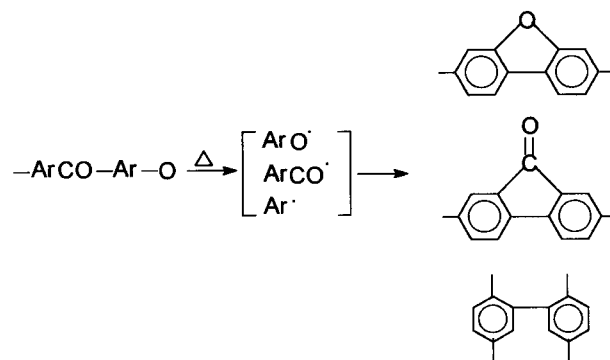
The overall E_a for decomposition was calculated using the Coats and Redfern equation¹⁴ assuming the order of the reaction is 1: $\ln[-\ln(1 - \alpha)/T^2] = \ln[AR/\Phi(1 - 2RT/E_a)]E_a/RT$, where α is the fraction decomposed at T , temperature; Φ , the heating rate; R , the gas constant; and A , the Arrhenius frequency factor. ΔE_a was calculated from the plot of $\ln[-\ln(1 - \alpha)/T^2]$ vs $1/T$. A typical Coats-Redfern plot for polymer is shown in Figure 10.

The Coats-Redfern plot indicates a two-stage decomposition. The first and main stage of decomposition occurs in the temperature range of 460–620°C and corresponds to a weight loss of approximately 30–44% of the active material decomposed. The overall ΔE_a calculated from these plots are given in Table IV. Polymer I, which contains carbonyl but not sulfonyl linkages, shows ΔE_a at a value of 281 kJ mol⁻¹ whereas the corresponding value is 193 kJ mol⁻¹ for polymer II which contains both carbonyl and sulfonyl linkages in equal proportion. Copolymers III, IV, and V, which contain varying proportions of carbonyl and sulfonyl linkages, show ΔE_a between these two extremes.

The ΔE_a values ($\Delta E_a = 78 \pm 9$ kJ mol⁻¹) for the second stage of decomposition suggest that it

Table V Activation Energy Vs Carbonyl Content of the Feed and Triad Intensities

Polymer	Carbonyl Content	BBB Triad Intensity	Activation Energy ΔE_a , kJ mol ⁻¹
I	1.0	1.0	281
II	0.5	0.0	193
III	0.75	0.19	203
IV	0.875	0.59	247

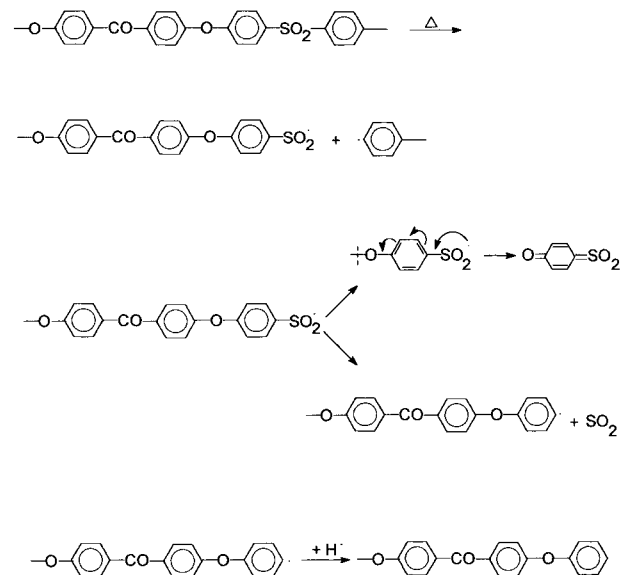
**Figure 5** Mode of thermal decomposition of polymer I.

is a physical process that involves the volatilization of the products formed during the first stage of decomposition.

Correlation of ΔE_a with Microstructure

Polymer I has the same structural units as poly(ether ether ketone) polymer whose mechanism for thermal degradation was reported by Hay and Kemmish.¹⁵ The mechanism involves random chain scission at either the ether (Ar—O) and/or carbonyl (Ar—CO) linkages. The radicals formed do not depolymerize but undergo termination by either H abstraction or by recombination or internal cyclization as shown in Scheme 1 of Figure 5.

In the case of polymer II, available bond energy data indicate that Ar—SO₂ is a weaker bond com-

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

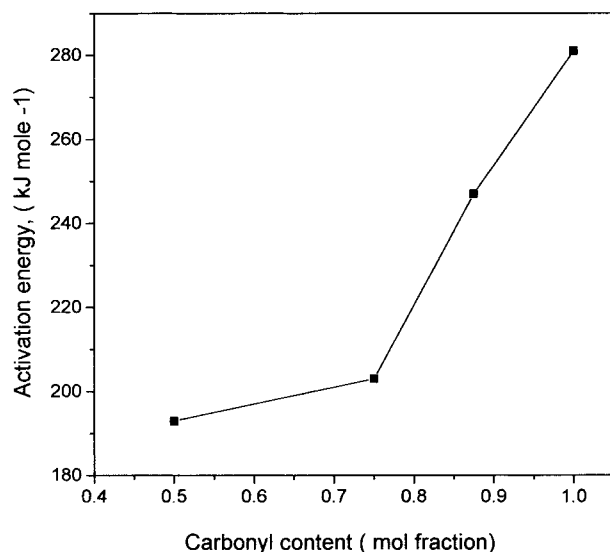


Figure 7 Plot of activation energy vs carbonyl content of the feed.

pared with Ar—O and Ar—CO bonds. Cleavage of this bond initiates its decomposition and results in the loss of small molecules and the remaining units being similar to the units in I but of much reduced chain length as shown in Scheme 2 of Figure 6. Consequently, ΔE_a for decomposition of II is lower than that of I.

Therefore, an attempt was made to correlate ΔE_a values with the carbonyl content of the polymer as shown in Figure 7. Although ΔE_a values increase with increasing carbonyl content (Table

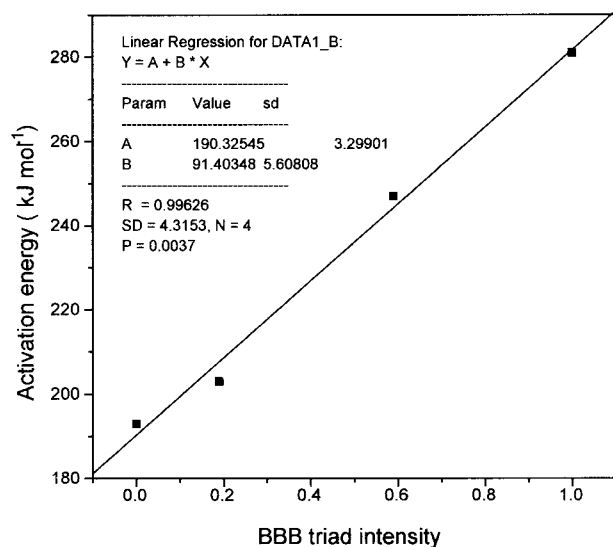


Figure 8 Plot of activation energy vs BBB triad intensities.

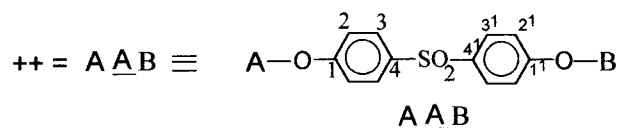
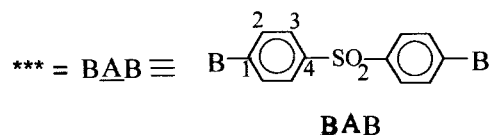
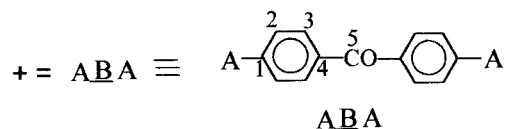
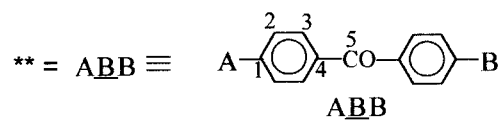
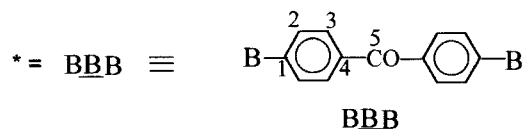


Figure 9 Chemical shift assignments for triads for polymers I, II, and III in Table I.

V), no linear correlation was observed as indicated in Figure 7. This observation suggests that the microstructure of the polymers may be influencing their degradation behavior due to the possible occurrence of microcrystalline domains depending on the triad structures, as we reported previously.¹² This is indeed found to be the case by the excellent linear correlation obtained between ΔE_a and BBB triad intensities as shown in Figure 8.

CONCLUSIONS

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

- ¹³C NMR spectra could be used to arrive at the relative intensities of compositional triads in the polymers.
- Transesterification was observed during the synthesis of II, and not III and IV for

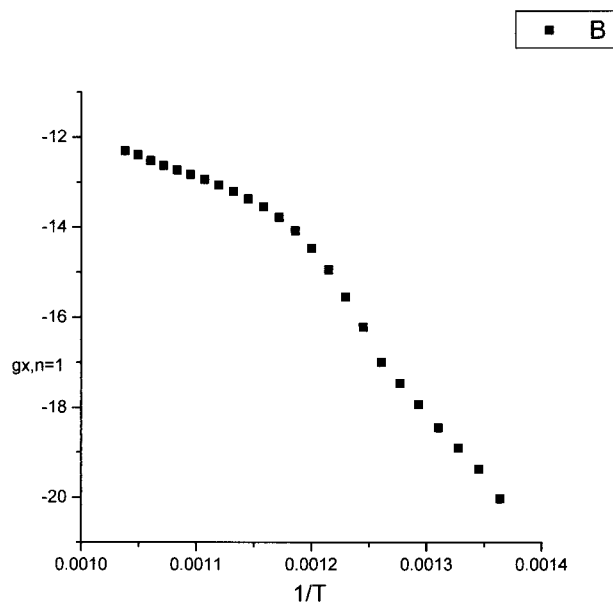


Figure 10 Typical Coats-Redforns plot for polymer I.

which the concentration of Ar—SO₂— units is less than 50% in the copolymer.

3. Thermal stability of the polymers increases with the carbonyl content of the copolymers.
4. A linear correlation exists between ΔE_a for decomposition and microstructure of the polymers.

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