Synthesis, characterization and thermal degradation studies of poly(ether ether ketone) copolymers

M. Rama Rao, V. L. Rao*, T. S. Radhakrishnan and S. Ramachandran*
*Propellants, Polymers and Chemicals and *Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695 022, India*
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Poly(ether ether ketone) copolymers (I–V) were prepared by the nucleophilic reaction of 4,4′-difluorobenzophenone with varying mole proportions of hydroquinone and resorcinol using sulpholane as solvent and in the presence of K_2CO_3. The polymers were characterized by different physico-chemical techniques. The glass transition temperature and crystallinity of the polymers was found to decrease with increase in concentration of the resorcinol units in the polymers. Thermogravimetric studies showed that all the polymers were stable up to 400°C with a char yield above 50% at 900°C in nitrogen atmosphere. The isomeric polymers (I and V) showed distinct differences in their thermal degradation behaviour and the pyrolysis-g.c. data indicated the random nature of the copolymers (II–IV). The amount of resorcinol evolved during pyrolysis at 800°C was correlated with the sequence distribution of the comonomers in the polymer.

(Keywords: poly(ether ether ketone) copolymer; i.r. spectroscopy; ^{13}C n.m.r. spectroscopy; thermogravimetry; X-ray diffraction; pyrolysis-gas chromatography)

INTRODUCTION

In recent years, tough high temperature low density thermoplastic resins have been rapidly gaining acceptance for use in high performance composite materials for aerospace structural applications. Poly(ether ether ketone) (PEEK), developed by ICI[1], is a semicrystalline polymer and is a very promising candidate because of its unique properties of toughness, stiffness, thermo-oxidative stability, chemical and radiation resistance and retention of physical properties at high temperatures[2]. In addition, the indefinite shelf life, suggested ease of fabrication, 'repairability' and reprocessing capability suggest that PEEKs have potential advantages over thermoset materials[3,4] in their various applications. Therefore, we have undertaken systematic studies on the evaluation of properties of copolyether ether ketones derived from various monomers. In this paper we report on the synthesis of copolymers based on 4,4′-difluorobenzophenone (DFBP) and varying mole proportions of hydroquinone (HQ) and resorcinol (RE). The copolymers were characterized by physical and spectral methods and their thermal behaviour was studied by pyrolysis-g.c. and thermogravimetry. Interestingly, the isomeric polymers show significant differences in the composition of their pyrolysates and these differences are discussed in relation to the sequence distribution of comonomers in the polymer chain.

EXPERIMENTAL

Materials

High purity DFBP (Aldrich) was used as received. Anhydrous K_2CO_3 (BDH) was dried under vacuum at 100°C for 2 days prior to use. HQ was crystallized from ethanol under nitrogen and dried under vacuum. RE was recrystallized from toluene and dried under vacuum. Sulpholane was stored over dried molecular sieves (type 4A) and distilled from NaOH pellets under reduced pressure. The middle fractions were collected and stored over molecular sieves.

Polymer synthesis

Ether ether ketone copolymers were synthesized by the nucleophilic substitution reaction of DFBP and HQ/RE using anhydrous K_2CO_3 in sulpholane medium under nitrogen atmosphere according to the general procedure of Roovers *et al.*[5]. 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 twice in methanol and boiled with water repeatedly, filtered and dried under vacuum at 100°C for 12 h.

Characterization

Elemental analysis was performed with a Perkin Elmer model 2400 CHN analyser. Inherent viscosities were obtained for 0.4% polymer solutions in 98% H_2SO_4 at 25°C using an Ubbelohde suspended level viscometer. Glass transition temperatures (T_gs) and melting points were measured using a Mettler thermal analyser 3000 coupled to a DSC 20 at a heating rate of 10 K min^{-1}.

The i.r. spectra of the polymers were run as KBr pellets (2%) using a Perkin Elmer 283 spectrophotometer. ^{13}C

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n.m.r. spectra were recorded on a 22.5 MHz Jeol FX-90Q Fourier transform n.m.r. spectrometer. Methanesulphonic acid (CH_3SO_3H) and $CDCl_3$ mixtures were used as solvents with tetramethylsilane (TMS) as the internal standard. Other relevant experimental parameters were: acquisition time, 1.6 s; pulse width, 18 μs (corresponding to a nuclear tip angle of 60°); data points, 8K; pulse delay, 2.5 s; sweep width, 5000 Hz; and number of pulses, 5000.

X-ray scattering data were obtained on pellets (13 mm diameter) of the polymer using a Philips PW 1729 X-ray generator with nickel-filtered Co Kα radiation at 30 kV and 20 mA and PW 1710 diffraction counting unit over a 2θ angular range of 10–40°.

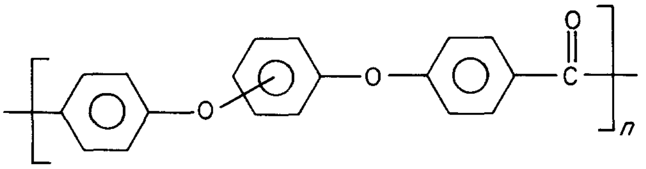
Thermal behaviour

Thermogravimetric analysis of the polymers was carried out under nitrogen atmosphere using a DuPont TA 2000 in combination with a 951 thermogravimetric analyser at a heating rate of 10 K min^{-1}.

Pyrolysis-g.c. of the polymers was carried out using a CDS 100 pyroprobe coupled to a Shimadzu GC-5A chromatograph. About 0.6–0.7 mg of the samples was pyrolysed for 20 s. The g.c. conditions used were: column, SE-30 (2 m × 3 mm i.d.); column temperature, 70–250°C programmed at a linear heating rate of 5 K min^{-1}; injection port, 300°C; detector, f.i.d.; and carrier gas, He (flow rate of 40 ml min^{-1}). A Shimadzu data processor C-R1A was used for the computation of peak areas.

RESULTS AND DISCUSSION

The ether ether ketone copolymers were synthesized by the aromatic nucleophilic displacement of fluorine from an activated substrate (DFBP) by HQ/RE. Copolymers I–V were obtained by varying the mole ratio of HQ to RE with the repeating unit:



Copolymer I contains no RE and corresponds to the PEEK developed by ICI. Feed ratios and some properties of the polymers are given in *Table 1*.

Characterization

The elemental analysis, i.e. C and H content, of copolymers I–V is listed in *Table 1*. The values are in agreement with theoretical values confirming the proposed structure.

The i.r. spectra of all the polymers show no absorption in the 3500–3000 cm^{-1} region indicating the absence of –OH group but all the spectra show characteristic bands at 1650 cm^{-1} (s, $\nu_{c=o}$) and 1250 cm^{-1} (s, ν_{c-o}). Further, absorption at 1250 cm^{-1} decreases in intensity from polymer I to IV and is absent in polymer V whereas the absorption at 970 cm^{-1} increases in intensity from polymer I to V, being very much less in polymer I. These differences are attributed to the varying proportions of *para* and *meta* linkages and may provide a means of estimating the mole fraction of HQ and RE moieties in the polymers. It was also observed that the ratio of the optical densities of the peaks at 1650 and 930 cm^{-1} is nearly constant ($I_{930}/I_{1650} = 1.3$) in all the polymers. Therefore, the ratio of the intensities of the peaks at 970 and 930 cm^{-1} (I_{970}/I_{930}) was considered to be a measure of the RE moiety concentration in the copolymers and is plotted in *Figure 1* against the mole per cent of RE in the feed. The linearity of the plot shows that the relative concentration of the two comonomers is close to the feed ratio. This was further confirmed by the ^{13}C n.m.r. spectrum of polymer III.

The ^{13}C n.m.r. spectra of polymers I, III and V were recorded at 22.5 MHz in CH_3SO_3H and $CDCl_3$ mixed solvents with $CDCl_3$ providing the internal lock signal and with TMS as the internal standard. The spectrum of polymer I is identical to the spectrum of the same polymer (and also commercial PEEK) reported earlier by Colquhoun and Lewis.[6]. The spectra of copolymers III and V are shown in *Figure 2* along with partial assignments. (Detailed studies at higher magnetic fields

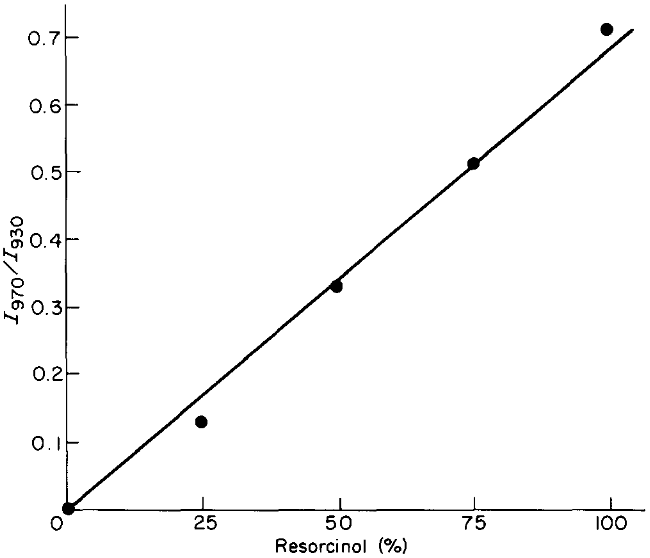


Figure 1 Plot of I_{970}/I_{930} *versus* percentage resorcinol

Table 1 Some properties of polymers I–V

Polymer	Feed ratio (mole fraction) DFBP	HQ	RE	Inherent viscosity (dl g^{-1})	Elemental analysis (%) C (79.2)	H (4.16)	T_g (°C)
I	0.5	0.5	0.0	0.96	78.6	3.95	155
II	0.5	0.375	0.125	0.75	78.8	3.99	152
III	0.5	0.25	0.25	0.65	78.5	3.98	145
IV	0.5	0.125	0.375	0.42	78.2	3.96	140
V	0.5	0.0	0.5	0.35	78.3	3.93	119

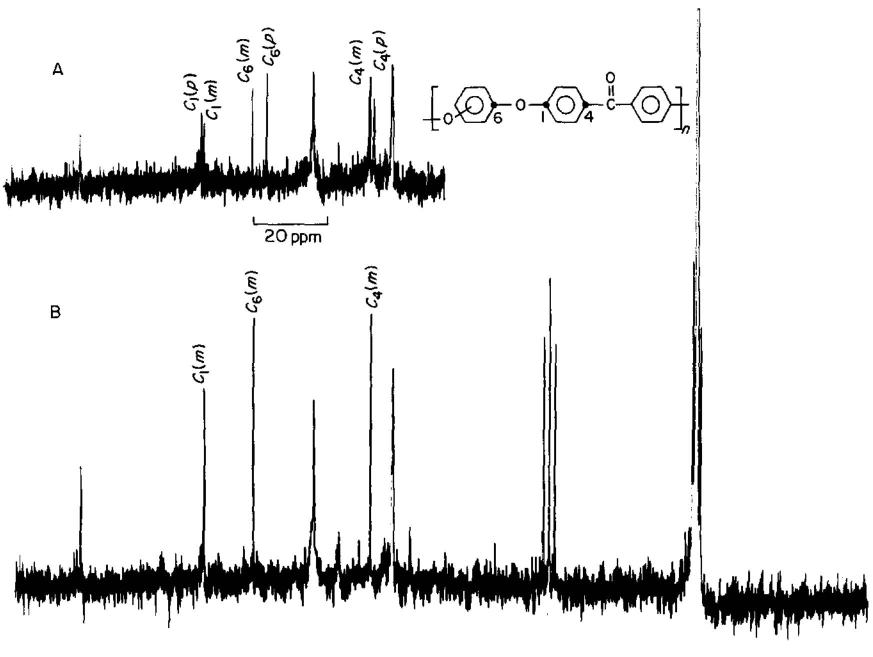


Figure 2 N.m.r. spectra of polymers (A) III and (B) V

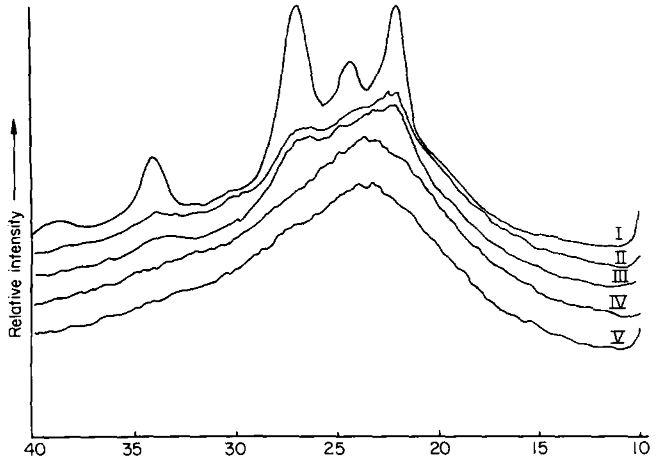


Figure 3 X-ray diffraction spectra of polymers I–V

are under investigation). The spectra of copolymers II and IV could not be recorded due to their poor solubility. The mole ratio of HQ and RE units in copolymer III can be readily obtained from its ^{13}C n.m.r. spectrum, because carbons 1, 4 and 6 show distinctly separate signals in the two moieties. This calculation yields a mole ratio of HQ to RE of 1.1 which is close to the value of 1 in the feed. Therefore, from i.r. and n.m.r. data, it can be presumed that for polymers II and IV the mole ratio of HQ to RE is close to that in the feed.

Thermal transitions

The T_gs of the copolymers were determined by d.s.c. and the results are given in *Table 1*. Samples were heated to 300°C at a rate of 10 K min^{-1} in static air, quenched and rerun to obtain the T_g. The T_g values of the copolymers decreased with increase in concentration of RE in the polymer. This gradual decrease can be attributed to the greater flexibility of the polymer chain due to the incorporation of *meta* linkages. Similarly,

Table 2 Thermal analysis of polymers I–V

	IDT	FDT	D_{max}	Char residue (%)			IPDT
Polymer	(°C)[a]	(°C)[b]	(°C)[c]	600°C	700°C	900°C	(°C)[d]
I	450	682	535	62	53	46	724
II	400	665	510	67	59	52	744
III	410	680	520	65	57	51	745
IV	415	685	510	67	61	55	752
V	425	700	555	72	63	58	768

[a] IDT, initial decomposition temperature
[b] FDT, final decomposition temperature
[c] D_{max}, maximum decomposition temperature
[d] IPDT, integral procedural decomposition temperature

X-ray diffraction data (*Figure 3*) indicate that polymer I with the all *para* units is semicrystalline whereas polymer V with all *meta* units is quite amorphous. Also, the crystalline transition temperature could be observed only for polymer I and not for the other polymers.

Thermogravimetric studies

Thermal degradation behaviour of copolymers I–V was studied by thermogravimetry in nitrogen atmosphere at a heating rate of 10 K min^{-1}. The results are given in *Table 2*. All the copolymers were stable up to 400°C and give a char residue of 50–60% at 900°C. The relative thermal stabilities of the copolymers can be assessed by their integral procedural decomposition temperatures (IPDT) proposed by Doyle[7]. IPDT values indicate that the thermal stability of the copolymers also increases with increasing *meta* linkages. Pyrolysis-g.c. data suggest this may be attributed to the nature of the non-volatile residue and is discussed later.

Pyrolysis-g.c.

About 0.6–0.7 mg of the copolymer samples were pyrolysed at 800 and 990°C and typical pyrograms are shown in *Figure 4*. The major products of decomposition were identified by comparison of their retention times with those of authentic compounds. The nature and composition of the major pyrolysates are given in *Table 3*. The results indicate that: (1) phenol is the major product for all the copolymers (>50%); (2) no benzaldehyde is found among the pyrolysates; (3) the isomeric polymers I and V show distinct behaviour. RE was obtained as one of the major products (13.6%) in the case of polymer V whereas correspondingly no HQ was evolved in the case of polymer I; (4) the amount of RE produced is not proportional to the amount of *meta* units present in copolymers II, III and IV, which probably indicates the influence of the sequence distribution of the comonomers in the polymer chain; and (5) other minor products observed were diphenyl, dibenzofuran, *p*-hydroxybenzophenone, 4,4′-dihydroxybenzophenone, diphenyl ether, etc.

These observations can be rationalized on the basis of the mechanism proposed by Hay and Kemmish[8] for the thermal degradation of commercial PEEK corresponding to polymer I. The mechanism involves random chain scission at either the ether or carbonyl links. The radicals generated do not depolymerize but undergo termination by either a hydrogen abstraction or by recombination or by internal cyclization as shown in *Scheme 1*.

The observation that in the case of polymer I phenol constitutes nearly 90% of the decomposition products at 800°C with minor amounts of benzofuran, *p*-hydroxybenzophenone and higher keto fragments suggests that both ether–phenylene and carbonyl–phenylene bond cleavages are quite facile. On the other hand, polymer V on pyrolysis gives considerable amounts of RE (13.6%), *p*-hydroxybenzophenone (10.9%) and higher keto fragments (5.5%) indicating that the cleavage of the ether–phenylene bond is much more facile than the carbonyl–phenylene bond. These differences in the degradation behaviour of isomeric polymers I and V may be attributed to conformational differences of the polymer chains rather than to electronic factors. As

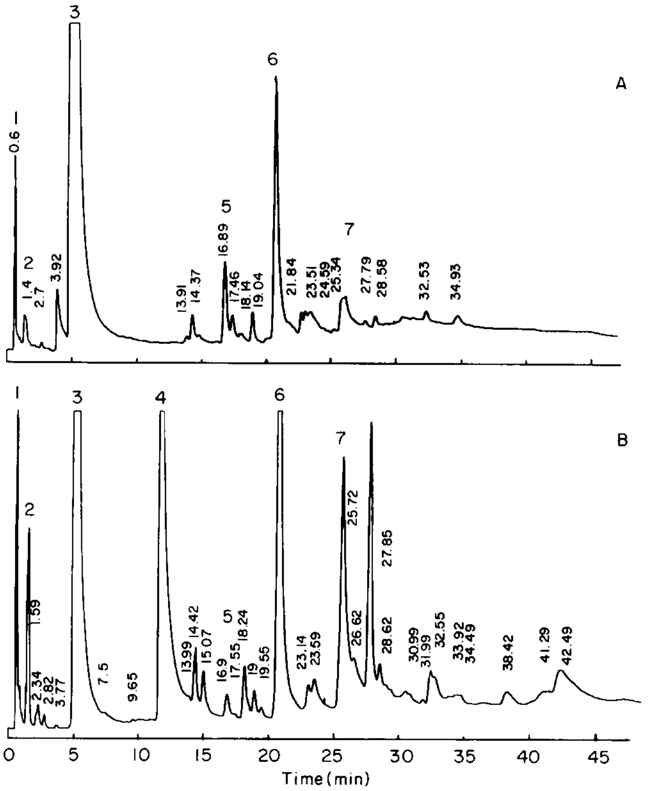
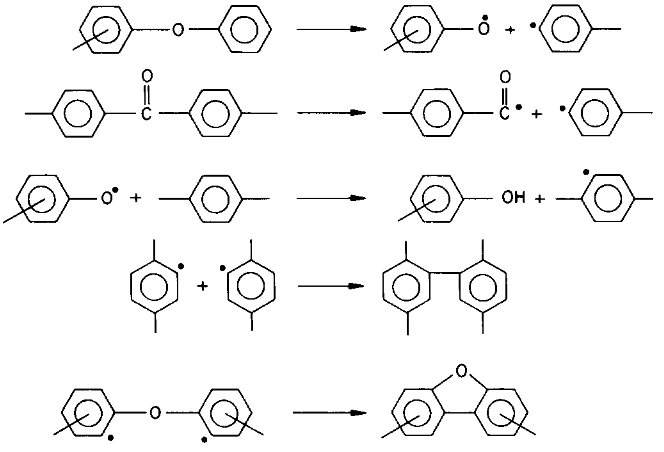


Figure 4 Pyrograms of polymers (A) I and (B) V. Pyrolysis temperature 800°C



Scheme 1

Table 3 Composition of major pyrolysates from polymers I–V

	Composition (wt%)					
Polymer	Benzene (2)[a]	Phenol (3)	Resorcinol (4)	Dibenzofuran (5)	*p*-Hydroxybenzophenone (6)	4,4-Dihydroxybenzophenone (7)
Pyrolysis temperature 800°C[b]						
I	0.2 ± 0.1	90.2 ± 1.3	–	0.7 ± 0.1	3.0 ± 0.2	1.2 ± 0.4
II	1.4 ± 0.2	83.3 ± 0.8	0.1	1.6 ± 0.3	1.6 ± 0.2	2.7 ± 0.9
III	0.6 ± 0.1	82.5 ± 3.1	1.0 ± 0.3	1.0 ± 0.2	3.2 ± 0.2	2.6 ± 0.2
IV	0.8 ± 0.2	78.6 ± 0.7	4.4 ± 0.8	0.8 ± 0.1	4.2 ± 0.2	2.8 ± 0.4
V	1.8 ± 0.1	50.2 ± 0.4	13.6 ± 1.0	0.3 ± 0.1	10.9 ± 0.1	5.5 ± 0.6
Pyrolysis temperature 990°C						
I	4.1	81.1	0.2	2.1	2.0	1.8
II	4.2	77.9	0.1	2.0	1.8	3.5
III	5.6	76.0	1.2	2.1	2.9	2.6
IV	4.3	69.8	4.4	1.6	5.2	4.0
V	8.1	45.9	6.1	2.3	8.0	4.8

[a] Peak numbers are shown in parentheses
[b] Average of three sets of experiments

Table 4 Composition of major pyrolysates from polymers I, IV and V on sequential pyrolysis

Pyrolysis	Concentration (wt%)						
temperature (°C)	C_2 (1)[a]	Benzene (2)	Phenol (3)	Resorcinol (4)	Dibenzofuran (5)	*p*-Hydroxybenzophenone (6)	4,4′-Dihydroxybenzophenone (7)
Polymer I							
700	3.0	–	90.4	0.0	0.4	2.2	0.3
800	0.1	0.2	92.4	0.0	0.9	2.8	0.8
900	0.4	2.5	81.6	0.0	3.2	2.7	2.7
990	6.0	16.8	49.0	0.0	10.5	2.3	1.7
Polymer IV							
700	2.2	1.0	81.1	6.9	0.9	2.5	2.0
800	0.1	0.6	83.4	3.3	0.9	4.1	2.0
900	1.6	11.1	64.4	1.1	4.1	4.2	2.0
990	10.2	29.6	37.3	0.0	7.6	2.8	0.5
Polymer V							
700	41.0	2.9	18.0	11.3	0.5	3.6	11.1
800	0.2	1.6	54.2	15.5	0.3	11.0	4.5
900	3.0	11.4	52.7	3.9	3.5	6.0	2.2
990	41.3	28.4	6.4	0.5	4.0	1.8	2.0

[a] Peak numbers are shown in parentheses

pointed out earlier, polymer I is semicrystalline whereas polymer V is completely amorphous with *meta* linkages serving as kinks, at which points the cleavage is more facile. Copolymers II, III and IV with varying compositions of HQ and RE units behave similarly to polymers I and V. However, the concentration of Re in their pyrolysates is not in proportion to their RE content and will be discussed in detail later. Similar trends were observed at pyrolysis temperature at 990°C.

The pyrolysis of the polymers leaves considerable residues as indicated by thermogravimetric studies. The non-volatile residue in the case of PEEK was found[8] to be insoluble, deficient in oxygen compared to the starting material and difficult to characterize. In order to gain greater insight into the structure of the non-volatile residue, sequential pyrolysis of the polymers was carried out in the temperature range of 600–990°C. The polymer was first pyrolysed at 600°C for 20 s and the chromatogram of the volatiles was recorded. The residue was then successively pyrolysed at 700, 800, 900 and 990°C, the pyrograms of the volatile being recorded at each temperature. The results of these analyses are shown in *Table 4* for copolymers I, IV and V. The amount of volatiles at the pyrolysis temperature of 600°C was too small for a satisfactory pyrogram to be obtained. In the case of polymer I, the results indicate that the concentrations of benzene and dibenzofuran increase with increase in pyrolysis temperature with a considerable amount of phenol being still present. No appreciable increase in components containing carbonyl groups was observed. Therefore, it can be inferred that the non-volatile residue consists of biphenylene crosslinked structures and dibenzofuran moieties. On the other hand, polymer V showed an increase in benzene, lower (C_2) hydrocarbons and a small increase in DBF with increase in pyrolysis temperature. This suggests that the non-volatile residue contains a preponderance of phenylene linkages and less dibenzofuran moieties. This implies that the non-volatile residue of polymer V is more graphitized in nature than the residue from polymer I. This is in agreement with the observation from t.g.a. studies on the greater thermal stability of polymer V compared to polymer I. The behaviour of copolymer IV is intermediate in nature and is in accord with the trends outlined for polymers I and V.

Further, as pointed out earlier, the amount of RE evolved on pyrolysis is not proportional to the concentration of RE units in the copolymers. Thus polymer V gives 13.6% RE whereas copolymer III, containing half the amount of RE units, gives only 1.2% RE. Copolymer IV behaves in a similar way. Therefore, an attempt was made to correlate the amount of RE evolved to the blocky, alternating or random nature of the copolymers. The fluoro compound (DFBP) which reacts with HQ (RE) at one end may have (1) a strong preference for HQ (RE) at the other end resulting in HQ (RE) blocks; or (2) a preference for RE (HQ) at the other end resulting in alternating nature; or (3) show equal reactivity towards HQ and RE giving random sequences.

If the copolymers were blocky in nature, the amount of RE produced is expected to be proportional to the *meta* linkages in the copolymers and if the copolymers were alternating in nature, the amount of RE should be proportional to the concentration of blocks of *meta* linkages in copolymer IV. However, the experimental values are substantially lower than expected (*Table 3*) ruling out the alternating or blocky nature and suggest the random nature of the copolymers. This is quite reasonable because it is rather unlikely that the electronic effects propagate through three aromatic rings separated by ether and carbonyl linkages.

Assuming the random nature of the copolymers, it is next attempted to correlate the concentration of RE evolved from the dyad and triad intensities calculated based on Bernoullian statistics. The results are shown in *Table 5* and show that an approximate correlation exists between the triad arrangements and the RE evolved. This

Table 5 Observed and calculated percentages of resorcinol in polymers II–V

Polymer	Resorcinol observed (%)	Resorcinol calculated (%)[a]			
		RK[b]	RKR	RKRKR	RKRKRKR
II	0.1	3.4	0.85	0.2	0.01
III	1.0	6.8	3.4	1.7	0.85
IV	4.4	10.2	7.65	5.7	4.28
V	13.6	–	–	–	–

[a] 13.6 × fraction of *n*-ad

[b] R, resorcinol moiety; K, ketone moiety

confirms that the differences in the pyrolysis behaviour of isomeric polymers I and V originate in the conformational differences of the polymer chains.

CONCLUSIONS

The main conclusions that can be drawn from this study are that the isomeric polymers I (DFBP-HQ) and V (DFBP-RE) show distinct differences in their pyrolytic behaviour. RE is one of the major products of decomposition in the case of polymer V whereas correspondingly no HQ was produced in the case of polymer I. Also, the amount of RE produced in the copolymers (DFBP-HQ-RE) II–IV can be correlated with the sequence distribution of the comonomers in the polymer chain.

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