Effects of 70-keV Electrons on Two Polyarylene Ether Ketones

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ABSTRACT: Films prepared from two polyarylene ether ketones with the repeat units [–PhC(O)PhC(O)-PhOPhXPhO–], where X = $C(CH_3)_2$ or CH_2 and Ph = C_6H_4, were bombarded with 70-keV electrons. The effects of irradiation were determined from the fraction of gel formed; the intrinsic viscosities, gel permeation chromatography, and NMR spectroscopy of the soluble portion of the irradiated films; and the changes in the IR spectra of the materials. In a Charlesby–Pinner analysis of the gel fractions of the polyarylene ether ketone with the isopropylidene group, the numbers of scission and cross-linking events per 100 eV (9649 kJ/mol) absorbed were found to be small with $G(S) = 0.002$ and $G(X) = 0.009$, respectively. Replacing the isopropylidene group by a methylene and changing the substitution on the phenylene linking two carbonyl groups from all meta to 75:25 meta/para led to larger values; viz., $G(S) = 0.015$ and $G(X) = 0.03_5$. The study took into account the variation of energy deposition with depth in the sample.

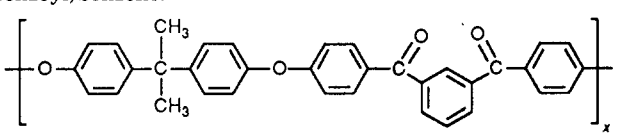
Introduction

Polymers undergo chemical changes when they are subjected to γ-radiation, energetic electrons, and other forms of ionizing radiation. The effects may include chain scission, cross-linking that can lead to gel formation, gas evolution, and double-bond formation. The susceptibility of macromolecules to such radiation and the extent of the effects depend on chemical structure. For example, aromatic groups generally provide good sinks for radiation energy and thereby impart radiation resistance to the macromolecule. Thus, polypropylene experiences $G(X) = 0.4$ chain scissions and $G(S) = 0.3$ cross-linkages for each 100 eV (9649 kJ/mol) of ionizing radiation;[1] the corresponding values for polystyrene are $G(X) = 0.03$ and $G(S) = 0.02$.[2]

In this study we have examined two polyarylene ether ketones, one of which has shown low sensitivity to ionizing radiation.[3] The two have structural features in common with one another and with several other polymers that have been studied previously. By comparing the effects of radiation on these systems, we have drawn conclusions about the contributions of certain chemical constituents to the polymers' susceptibility to radiation.

Experimental Section

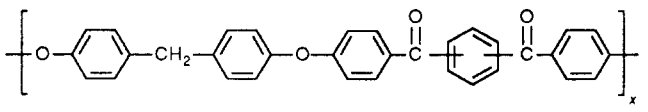
The two polymers studied were supplied by Hergenrother, Jensen, and Havens.[4,5] One, designated *m*-CBB/BIS-A, was synthesized by reacting Bisphenol A with 1,3-bis(4-chlorobenzoyl)benzene:



m-CBB/BIS-A

As reported earlier for material from the same batch,[4] it is amorphous with $T_g = 153$ °C, $\eta_{inh} = 0.61$ dL/g, and $\bar{M}_n = 29\,000$ g/mol.[6]

The second polymer, designated *m,p*-CBB/*p*-MDP, was synthesized[5] by reacting a 3:1 mixture of 1,3- and 1,4-bis(4-chlorobenzoyl)benzene with bis(4-hydroxyphenyl)methane:



m, p-CBB/*p*-MDP

† Now deceased.

The latter material is amorphous with $T_g = 145$ °C and $\eta_{inh} = 0.78$ dL/g.[5] Its molecular weight was not determined, but, on[5] the basis of closely related systems, $\bar{M}_n$ is estimated to be in the range 30 000–40 000 g/mol.

Dimethylacetamide and chloroform solutions of *m*-CBB/BIS-A and a 1,1,2,2-tetrachloroethane solution of *m,p*-CBB/*p*-MDP were cast into films. The films were mounted on an aluminum block inside a stainless steel vacuum chamber and irradiated at the NASA-Langley Research Center with 70-keV electrons from a Kimball Physics Inc. electron gun, usually at a rate of 4.5×10^{-9} A/cm^2.[7,8] This corresponds to 18 Mrd/h for 38-μm thick film. Ambient temperature was maintained by dissipating the heat in the aluminum block. After irradiations of up to 190 h, the films were exposed to nitrogen for at least 1 h in the closed chamber before being moved into the laboratory environment. The dosage was calculated for each polymer as a function of depth in the film using TIGER,[9] a one-dimensional, multilayer code for electron/photon Monte Carlo transport, based primarily on the ETRAN model.[10]

Some of the irradiated film was then mixed with chloroform, a good solvent for these polymers. Any gel that had formed was separated from the solution by filtration. Solvent was evaporated from both the gel and sol fractions by heating them in an oven until their combined mass was the same as that of the original sample. Intrinsic viscosities of the sol fractions in chloroform were measured with Ubbelohde viscometers.

Other portions of the film were dissolved in deuterochloroform for NMR studied with a Varian FT-80A instrument. Transmission infrared spectroscopic measurements were made on thin (<0.01-mm) films using a Nicolet Model 3600 FT-IR. Holes were cut in the films for the IR studies to match pins on the IR sample holder to ensure that the same portion of the film was viewed by the spectrometer before and after irradiation.

Results

Solubility Studies. The Charlesby–Pinner theory[11] is used to analyze radiolysis results for polymers in which cross-linking and scission apparently occur simultaneously and in proportion to the dosage. It predicts that the fraction S of film that remains soluble after gel has started to form is related to the radiation dose R by the equation

$$S + S^{1/2} = p_0/q_0 + 1/(q_0N_0)(1/R) \qquad (1)$$

Here, p_0 and q_0 are the probabilities per unit dose for scission and for forming a cross-linked unit, respectively, in a main-chain repeat unit, and N_0 is the number-averaged degree of polymerization. The derivation of eq 1 depends on the molecular weight distribution being the most probable, a condition presumably met in the step polymerizations of the two polyarylene ether ketones in this

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Table I
Comparison of Fractions of Sol Formed Using Different Charlesby–Pinner Parameters for the *m*-CBB/BIS-A Polymer

overall dose, Mrd	film thickness, μm	S_{obs}	S_{calc}					percentage of film calc to contain gel				
	$1/q_0N_0$ (Mrd)		1400	1480	1600	1800	2000	1400	1480	1600	1800	2000
	p_0/q_0		0.20	0.07	0.00	0.10	0.20	0.20	0.07	0.00	0.10	0.20
360[a]	38[b]	0.97[c]	1.00	1.00	1.00	1.00	1.00	0	0	0	0	0
710	58	1.00	0.91	0.89	0.91	0.98	0.99	48	50	48	25	15
720	38	1.00	0.94	0.92	0.95	1.00	1.00	55	55	52	0	0
810[a]	38[b]	1.00[c]	0.87	0.85	0.87	0.98	1.00	62	62	60	45	18
940	71	0.70	0.73	0.70	0.71	0.80	0.82	65	65	62	55	50
1090	33	0.76	0.71	0.68	0.70	0.81	0.83	75	78	72	65	60
1590[a]	38[b]	0.38, 0.32[c]	0.47	0.43	0.44	0.56	0.58	100	100	98	92	90
1610	43	0.37	0.46	0.42	0.42	0.55	0.57	100	100	100	92	90
1810[a]	38[b]	0.35, 0.30[c]	0.41	0.36	0.36	0.49	0.50	100	100	100	98	95
2170[a]	38[b]	0.29	0.33	0.28	0.28	0.38	0.39	100	100	100	100	100
3440[a]	38[b]	0.11, 0.15[c]	0.20	0.15	0.14	0.21	0.20	100	100	100	100	100
	$\sigma(S_{calc} - S_{obs})$		0.08	0.08	0.07	0.12	0.12					

[a] Values reported for these dosages in ref 8 were 10 times too great. [b] The thicknesses of these films were in the range 30–50 μm. Calculations were based on the intermediate value of 38 μm. [c] For these data the amount of sol was measured by injecting a solution of the sol fraction in a GPC and integrating the detector response.

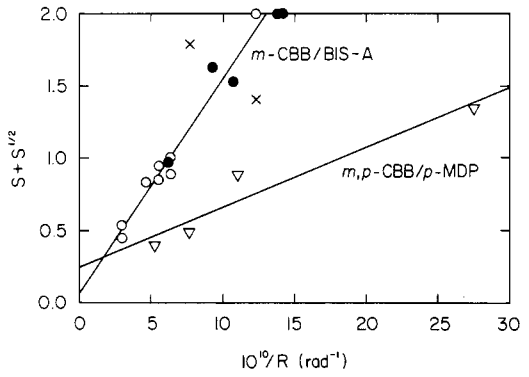


Figure 1. Charlesby–Pinner plot of $S + S^{1/2}$ against $1/R$ for *m*-CBB/BIS-A (○ and ×) and *m,p*-CBB/*p*-MDP (▽). Open circles represent data reported earlier;[7,8] filled circles show data obtained after the preliminary report.

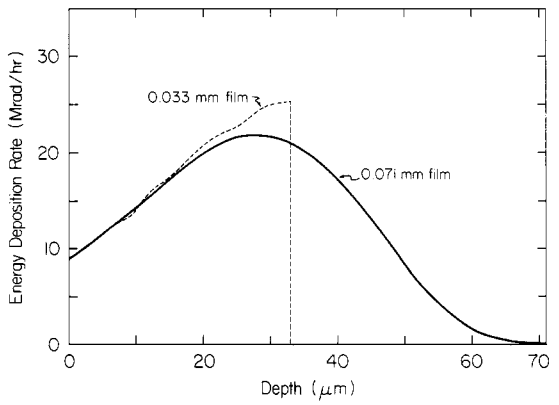


Figure 2. Energy deposition rate as a function of distance from the front face of the sample for films of *m*-CBB/BIS-A having two different thicknesses.

study. Figure 1 is a plot showing the left-hand side of eq 1 as a function of the reciprocal of the *overall* dosage for the two systems. The lines were determined with the method of least squares. In the case of *m*-CBB/BIS-A, two deviant points, shown with ×'s in Figure 1, were not included in the fit. The slopes $1/(q_0N_0)$ and intercepts p_0/q_0 were found to be 1480 Mrd and 0.07 for *m*-CBB/BIS-A and 410 Mrd and 0.25 for *m,p*-CBB/*p*-MDP.

The above analysis may not be fully satisfactory, however, since it does not take into account how the energy absorbed from the incident electrons varies with the depth in the sample. Because the energy deposition is nonuniform, gel forms in some layers of film before others. A correction can be made by calculating with TIGER[9] the energy-deposition profile from the energy of the incident electrons and the density, thickness, and elemental composition of the target. The curves in Figure 2, obtained with this program, are the profiles calculated for samples of *m*-CBB/BIS-A with thicknesses of 33 and 71 μm. The 70-keV electrons in these experiments gave up less energy near the front surface than in the interior of the sample where they were moving slower and where cascading secondary electrons and electromagnetic radiation had accumulated. The maximum deposition rate was calculated to occur at a depth of 28 μm for the thicker sample; whereas, a somewhat greater deposition rate appears near the back surface of the 33-μm sample. The difference can be attributed to radiation that passed through the thinner sample and was reflected off the aluminum sample holder back into the film.

A consequence of the nonuniform energy deposition shown in Figure 2 is that the simple scheme leading to Figure 1 using a dosage averaged over all depths may not yield a reliable calculation of the gel fraction, since the fraction of gel formed is not proportional to the dosage. A second consideration for the studies described here is that the films differed in their thicknesses, ranging from 25 to 71 μm.

To take account of the variation with depth of the deposition of the energy, each film was imagined to be sliced into 40 equally thick layers. The sol fraction S_i for layer i was computed using in eq 1 the dose R_i deposited in layer i, as determined from TIGER. The mean sol fraction S_{calc} for each film then is given by eq 2. The calculated sol

$$S_{calc} = (1/40)\sum_{i=1}^{40} S_i = (1/40)\sum_i [(1 + 4p_0/q_0 + 4/q_0N_0R_i)^{1/2} - 1]^2/4 \quad (2)$$

fractions depend on the values assigned to $1/q_0N_0$ and p_0/q_0; Tables I and II show S_{calc} for five different pairs of these parameters for 11 films of the *m*-CBB/BIS-A polymer (Table I) and for 5 films of the *m,p*-CBB/*p*-MDP polymer (Table II). Experimental values are given in the third column of each table. The last five columns of the tables list the percentages of layers in which gel is predicted to have been formed. As this shows, there can be intermediate doses in which some, but not all, layers contain gel. The bottom rows of Tables I and II show the

Table II
Comparison of Fractions of Sol Formed Using Different Charlesby-Pinner Parameters for the *m,p*-CBB/*p*-MDP Polymer

overall dose, Mrd	film thickness,[a] μm	S_{obs}	S_{calc}					percentage of film calcd to contain gel				
	$1/q_0N_0$ (Mrd)		350	380	410	410	450	350	380	410	410	450
	p_0/q_0		0.25	0.20	0.25	0.15	0.13	0.25	0.20	0.25	0.15	0.13
180	38	1.00	0.94	0.97	1.00	0.99	1.00	48	45	5	30	0
360	38	0.58	0.56	0.58	0.65	0.60	0.64	98	92	88	90	80
910	38	0.32	0.21	0.21	0.25	0.20	0.21	100	100	100	100	100
1310	38	0.13	0.15	0.14	0.18	0.13	0.14	100	100	100	100	100
1910	38	0.09	0.11	0.10	0.13	0.09	0.09	100	100	100	100	100
	$\sigma(S_{calc} - S_{obs})$		0.06	0.06	0.06	0.06	0.06					

[a] The thicknesses of these films were in the range 30–50 μm. Calculations were based on the intermediate value of 38 μm.

Table III
Results of the Gel Studies and Comparison with Other Polymers

polymer	G(S)	G(X)	temp, °C	ref
m-CBB/BIS-A	0.002 ± 0.002	0.009 ± 0.002	ambient	this work
m,p-CBB/*p*-MDP	0.015 ± 0.008	0.03_5 ± 0.01	ambient	this work
polycarbonate	0.09		ambient	16
poly(ether imide)	0.053	0.014	ambient	20
polysulfone I[a]	0.10[b]	0.10[b]	ambient[c]	17
	0.012 ± 0.003	0.051 ± 0.002	30	18
	0.03	0.04	35	19
	0.30	0.20	125	19
polysulfone II[d]	0.08	0.07	220	19

[a] T_g = 190 °C. [b] We calculated these values for G(S) and G(X) from the reported[17] gel fractions. The authors found G(S) = 0.08 and G(X) = 0.16. [c] Brown and O'Donnell[19] pointed out that the temperature of these samples may have been significantly above ambient, owing to the high dose rate (240 Mrd/h) employed in these studies. This accounts for the high values of G(S) and G(X). [d] T_g = 230 °C.

standard deviations of S_{calc} compared to S_{obs} for the different pairs of parameters.

For the *m*-CBB/BIS-A polymer, the values $p_0/q_0 = 0.07$ and $1/q_0N_0 = 1480$ Mrd obtained from the plot in Figure 1 lead to an underestimation of the minimum radiation dose for incipient gel formation

$$R_g = \frac{1/(q_0N_0)}{2 - (p_0/q_0)} \quad (3)$$

Our results for *m*-CBB/BIS-A can be accurately represented by $1/q_0N_0 = 1800 \pm 200$ Mrd, $p_0/q_0 = 0.1 \pm 0.1$, and $R_g = 950 \pm 150$ Mrd. Deviations of S_{calc} from S_{obs} at high dosages can be expected, owing to significant modifications in chemical structure.[12,13] This is supported by the change in the UV–vis spectrum that occurs with increased dosage.[3] The values $1/q_0N_0 = 400 \pm 50$ Mrd, $p_0/q_0 = 0.19 \pm 0.06$, and $R_g = 220 \pm 20$ Mrd were chosen to represent the solubility data in Table II for the *m,p*-CBB/*p*-MDP polymer.

The numbers of cross-linkages G(X) and chain scissions G(S) per 100 eV (9649 kJ/mol) absorbed are given in Table III for these and some related polymers (see discussion below). They were calculated as prescribed by Charlesby and Pinner;[11] i.e., $G(X) = 4.82 \times 10^5 q_0/w$ and $G(S) = 9.64 \times 10^5\ p_0/w$, where w is the mass of the repeat unit in atomic mass units.

Gel Permeation Chromatography. GPC measurements afford a different perspective on the effects of irradiation. Figure 3 shows the GPC response for chloroform solutions of six different films of *m*-CBB/BIS-A polymer that received overall dosages between 0 and 3440 Mrd. The area under each curve is proportional to the amount

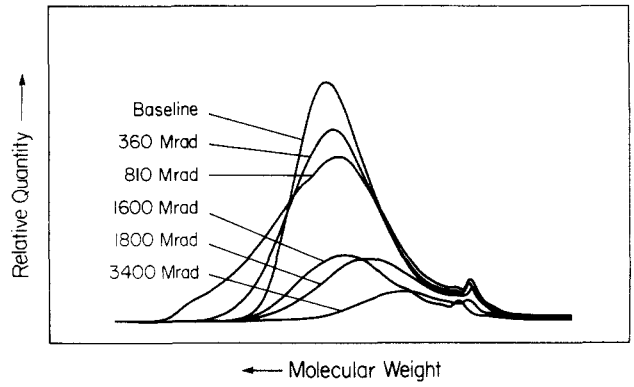


Figure 3. Gel permeation chromatograms for the soluble portions of samples of *m*-CBB/BIS-A films at different dosages.

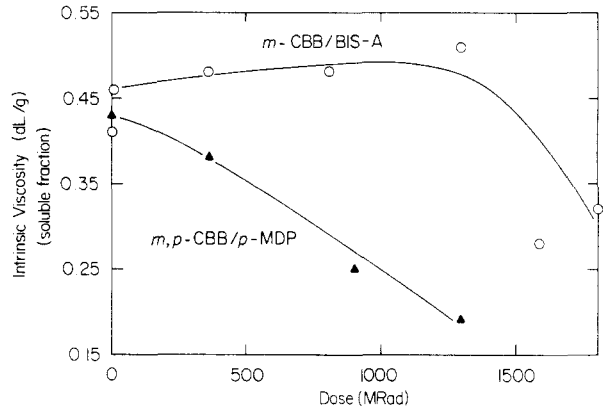


Figure 4. Intrinsic viscosities [η] for the soluble portions of *m*-CBB/BIS-A (○) and *m,p*-CBB/*p*-MDP (▲) as a function of overall dose.

in the sol fraction. At dosages below R_g the radiation had the effect of increasing the high molecular weight end (i.e., low retention volumes) of the distribution; that component then decreased at dosages above R_g because the longer chains were more likely to become part of the gel phase, which was removed from the sample before injection into the GPC. The maximum detector response for each film occurred at higher retention volume with increasing dosage. This is consistent with the loss of higher molecular weight material from the system and the increase in the number of lower molecular weight chains that are formed in the scission process. At long retention times, there appeared small peaks that probably resulted from low molecular weight cyclic material formed during synthesis.

Solution Viscosities. The intrinsic viscosities [η] of the sol fractions of *m*-CBB/BIS-A and *m,p*-CBB/*p*-MDP are compared in Figure 4 as a function of the overall dosages. Their dependencies on R were quite different. The viscosity of the former increased slowly until a dosage near $2R_g$, at which point it decreased sharply. The *m,p*-

CBB/p-MDP polymer with a larger $G(S)/G(X)$ ratio exhibited an intrinsic viscosity that decreases almost linearly with R over the range studied.

IR and NMR. The integrated proton magnetic resonance spectrum of the soluble fraction of m-CBB/BIS-A indicated a loss of alkyl hydrogens, relative to the aromatic, as the radiation dose was increased. Specifically, the ratio of the alkyl hydrogens to aromatic decreased by 2.9, 3.3, and 4.0% for overall doses of 360, 1590, and 2170 Mrd, respectively, compared to the unirradiated material. The NMR spectra of the irradiated films showed new resonances at 0.9 and 1.3–1.4 ppm, the latter appearing as a small shoulder on the methyl peak centered at 1.69 ppm. Although neither resonance has been assigned to a particular structure, their chemical shifts are characteristic of those that would originate from aliphatic hydrocarbons on adducts to the isopropylidene group.

Infrared absorbance by m-CBB/BIS-A varied slightly with radiation dose. Peaks at 1244, 1497, 1595, and 1658 cm^{-1} associated with vibrations involving the aromatic carbonyl and aromatic ether groups decreased in intensity. Funk and Sykes[14] found a similar decrease in IR absorption for aromatic carbonyl groups at 1650 cm^{-1} for the structurally similar poly(arylene ether ether ketone) (PEEK), –O–PhOPhC(O)Ph–, at high doses. However, in contrast with our measurements on m-CBB/BIS-A, absorption from the phenyl ether linkages at 1491 and 1225 cm^{-1} increased when PEEK was irradiated. Our studies showed a decrease in the absorption at 2968 cm^{-1} associated with the loss of methyl hydrogens that was evident in the NMR spectra. There was no evidence of hydroxyl formation in either the IR or NMR studies.

Comparisons

Some insight into the chemical changes occurring as the result of ionizing radiation can be obtained by comparing several macromolecules that have structural features in common. The two polyarylene ether ketones in this study are related to a polycarbonate, a poly(ether imide), and two polysulfones that have been studied in other radiation experiments. The repeat units of the last four polymers are drawn in Figure 5. Table III summarizes results for all six systems, giving the frequencies of scission and cross-linking per 100 eV. m-CBB/BIS-A, which shows the greatest resistance of the six to both scission and cross-linking, is compared below to each of the reamining five.

***m,p*-CBB/*p*-MDP.** m,p-CBB/p-MDP differs from m-CBB/BIS-A by (1) the replacement of an isopropylidene group in m-CBB/BIS-A by a methylene group in m,p-CBB/p-MDB and (2) 1,4-phenylene links between carbonyl groups in m,p-CBB/p-MDP in place of 25% of the 1,3 links in m-CBB/BIS-A. We attribute most of the difference in the radiation resistance of the two polymers to the $-CH_2-$ substituent in the m,p-CBB/p-MDP and believe that this linkage in the latter macromolecule is most susceptible to cross-linking and chain scission.

Polycarbonate. Golden and Hazell[15] found no evidence for radiation-induced gel formation in the phenylene polycarbonate shown in Figure 5. Films ($\bar{M}_n$ = ca. 14 000 g/mol) irradiated at dosages up to 1000 Mrd were completely soluble, and, unlike the findings reported here for m-CBB/BIS-A, the intrinsic viscosities of polycarbonate solutions were observed to decrease regularly with dosage over this range. Spectroscopic and gas evolution measurements[15] (98% of the volatile products from irradiation was CO and CO_2) indicated that main-chain scission took place at the carbonate positions. There was little evidence for degradation at the isopropylidene linkage. Similarly, Lyons, Symons, and Yandell[16] observed no evidence for rupture of the isopropylidene group in EPR studies on the model compound 2,2-diphenylpropane after it had been exposed to γ-irradiation. Thus, although the isopropylidene moiety might seem[17,18] to be a potential site for cross-linking, it apparently does not fulfill that role to a significant degree in this system or in m-CBB/BIS-A.

Polysulfone. Brown and O'Donnell[19] exposed two aromatic polyether sulfones to γ-irradiation from a cobalt-60 source. One, called polysulfone I and shown in Figure 5, has aromatic ether and isopropylidene linkages and therefore resembles the m-CBB/BIS-A under study here. The second polyether sulfone differs from the first by the replacement of the isopropylidene moiety in polysulfone I with another sulfone group.

Brown and O'Donnell[18,19] found that polysulfone I is more likely to cross-link and undergo chain scission than polysulfone II even though II has twice the concentration of the more vulnerable $-SO_2-$ linkages. They reported yields for scission and cross-linking for II only at an elevated temperature (220 °C), which is just below T_g. However, the temperature coefficients for $G(X)$ and $G(S)$ are presumably positive and the values at ambient temperatures would be lower than for polysulfone I. Since the only difference in structural components is the isopropylidene group in I, this substituent is the probable cause of I's greater sensitivity to ionizing radiation. This is in contrast to polycarbonate, m-CBB/BIS-A, and the poly(ether imide) represented in Figure 5 (see below), in which the isopropylidene unit is almost inert toward scission and cross-linking.

This apparently inconsistent behavior may depend on the hydrogen radicals generated during radiolysis. The concentration of $H^\bullet$ is greater in irradiated polysulfone I than in II, owing to the isopropylidene group in I. This is substantiated by the volatile-product yields measured[18,19] at 30 °C, which showed that 19% of the gas produced with I was H_2; whereas, it was only 7% with II. The total volatile-product yields were the same for the two polymers, namely, $G(\text{total gas}) = 0.04$.

Reactions proposed by Brown and O'Donnell[18,19] and by Lyons et al.[16] to describe part of the radiolysis mechanism can account for the role of hydrogen in causing polysulfone I to be the more susceptible:

$$-PhSO_2Ph- \xrightarrow{\text{radiation}} -PhSO_2^\bullet + {}^\bullet Ph- \quad (4)$$

$$-PhSO_2Ph- + H^\bullet \rightarrow -Ph-H + {}^\bullet SO_2Ph- \quad (5)$$

$$-PhSO_2Ph- + H^\bullet \rightarrow -PhSO_2H + {}^\bullet Ph- \quad (6)$$

$$-PhSO_2^\bullet + H^\bullet \rightarrow -PhSO_2-H \quad (7)$$

$$-Ph^\bullet + H^\bullet \rightarrow -PhH \quad (8)$$

$$-PhSO_2-H \rightarrow -PhH + SO_2 \quad (9)$$

$$-PhSO_2^\bullet \rightarrow -Ph^\bullet + SO_2 \quad (10)$$

$$-Ph^\bullet + -PhOPhSO_2PhO \rightarrow -Ph(Ph)OPhSO_2PhO- + H^\bullet \quad (11)$$

The hydrogen radicals, which are in greater supply in polysulfone I, promote scission in steps 5 and 6 and increase the production of stable scission products in steps 7 and 8. Combination of two radical-terminated chains is more likely to occur with polysulfone II, where the concentration of $H^\bullet$ is lower, than it is with polysulfone I. The end-linking reaction in step 11 can contribute to the eventual formation of a network.

As in the case of the polycarbonate, polysulfone I apparently does not undergo significant amounts of main-chain scission at the isopropylidene linkage. This is in

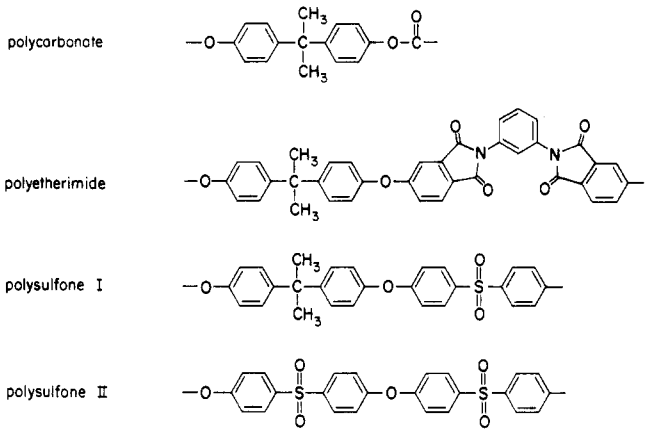
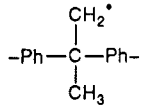


Figure 5. Structural formulas for the repeat units of polymers used for comparison.

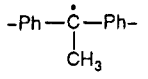
accord with the EPR studies at 77 K of Lyons et al.[16] in which no evidence of radical fragments that would have resulted from scission at that link was found.

Poly(ether imide). Basheer and Dole[20] irradiated the poly(ether imide) shown in Figure 5 with 9-MeV electrons. They found that high dosages were required to form a gel and that the polymer is more resistant to chain scission than most. Mass spectrometric analyses showed the dominant volatile products from the irradiation to be CO and/or N_2, water, and carbon dioxide. Methane was present only in small amounts; no analysis was made for H_2.

EPR studies have been performed on this poly(ether imide) by Basheer and Dole[20] and by Long and Long.[21] After γ-irradiation at 77 K, the former authors observed signals that they attributed to the radical derived from isopropylidene:

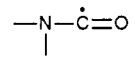


They did not observe either the expected phenoxy or the radical shown below, which would be formed by removing a methyl group from the isopropylidene link:



However, they suggested that the signals of these latter two species may have been superimposed on the spectrum of the isopropylidene radical.

After irradiating this polyimide with 100-keV electrons, Long and Long[21] observed EPR signals from the isopropylidene and phenoxy radicals as well as from cyclohexadienyl radicals and the amide carbonyl radical shown here:



Infrared studies by Long and Long showed increases in aromatic hydrogen atoms and monosubstituted benzenes and decreases in aliphatic hydrogen, aromatic ethers, and di- and trisubstituted benzenes for irradiations of up to 6000 Mrd.

As presented in Table III, radiation-induced cross-linking occurs in the poly(ether imide) with a probability that is very low, although larger than that of *m*-CBB/BIS-A. Scission of the poly(ether imide) might occur at the isopropylidene, the ether, and/or the imide linkages. However, since both the poly(ether imide) and *m*-CBB/BIS-A have the former two units but the *m*-CBB/BIS-A has a smaller propensity for scission, we conclude that the imide is the likely site for breaking the main chain in the poly(ether imide). Long and Long's observations of an imide carbonyl radical and Basheer and Dole's measurement of large proportions of CO_2 and probably CO in the product gas are consistent with this hypothesis.

Conclusions

The two polyarylene ether ketones studied here differed in their responses to bombardment with 70-keV electrons. Although both experienced cross-linking and chain scission, a Charlesby–Pinner analysis of the sol fractions remaining after radiolysis showed *m*-CBB/BIS-A to be less susceptible than *m,p*-CBB/*p*-MDP to both effects. Intrinsic viscosities of solutions of the sol components for the two irradiated polymers were found to be consistent with the solubility studies, which revealed that *m,p*-CBB/*p*-MDP probably has the greater ratio $G(S)/G(X) = 2p_0/q_0$. Accordingly, *m,p*-CBB/*p*-MDP, which is more likely to experience a scission event for each cross-linking, exhibits a solution viscosity that decreases monotonically with dosage (Figure 4). On the other hand, $[\eta]$ for *m*-CBB/BIS-A increases slowly with dosage to 1200–1400 Mrd before decreasing abruptly, owing to the removal of higher molecular weight material, which had been preferentially incorporated in the gel component above $R_g \approx 950$ Mrd. The change in the molecular size distributions in the sol fractions of *m*-CBB/BIS-A was evident in the GPC measurements described above.

The principal site for structural changes in *m,p*-CBB/*p*-MDP is probably the methylene linkage. The corresponding group in the *m*-CBB/BIS-A, i.e., the isopropylidene, is more stable and consequently this polyarylene ether ketone is less susceptible to scission and cross-linking. Both NMR and IR studies show evidence of changes in the isopropylidene, although the changes are not extensive and may in some cases be intramolecular rearrangements that do not result in scission or cross-linking. (For example, an isopropylidene linkage may have been converted to a propylene linkage or to an unsaturated derivative of a propylene linkage.) The carbonyl and ether linkages in the two polymers studied here are other possible sites for chemical changes. As with the isopropylidene, there is spectroscopic evidence that these substituents are affected, but again only to a small extent.

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Registry No. (*m*-CBB)(BIS-A) (copolymer), 100344-02-3; (*m*-CBB)(BIS-A) (SRU), 100344-94-3; (*m,p*-CBB)(*p*-MDP) (copolymer), 109521-10-0; (*m,p*-CBB)(*p*-MDP) (SRU), 104624-95-5.

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(7) This rate is $^1/_{10}$ the value reported in a preliminary account[8] of these studies. The larger value used previously was in error.
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Notes

Demonstration of the Inhibitory Role of Oxygen during the Room-Temperature Radical Polymerization of Styrene Initiated by a Cobalt(II)–Sodium Borohydride Redox System

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Oxygen plays two exactly opposite roles in radical polymerization reactions: it can either initiate or retard (or even inhibit) these reactions.[1] The unique case of high-pressure radical polymerization of ethylene, in fact, illustrates both these roles.[2] Unlike its role in initiation,[3,4] the retarding or inhibitory action of oxygen in such reactions is scarcely understood, notwithstanding the well-known peroxide scheme.[5] Furthermore, the peroxide-based inhibitory action of oxygen in radical polymerization is temperature dependent, owing to the fact[5] that the peroxides could decompose at higher temperatures, generating additional radicals that may initiate polymerization. In this context, the study of polymerization reactions wherein noninitiating, stable products are obtained in the presence of oxygen would be useful for better understanding of the inhibitory role of oxygen in radical polymerization.

With this background, attention was drawn to a recent report[6] regarding mimicking of enzyme activity; the reaction involves oxidation of styrene-like substrates to corresponding 1-phenylethanol derivatives via a 1-phenylethyl radical intermediate in the presence of various cobalt complexes (mostly square-planar type) and BH_4^-. It was realized that if this redox reaction is carried out in an oxygen-free atmosphere in the presence of excess monomer, the radicals produced could initiate a polymerization. This reaction system would thus provide an illustration of the inhibitory role of oxygen in the radical polymerization reactions. Hence we decided to carry out some experiments to prove the viability of the above theme, in the case of styrene polymerization. Further, this would also involve extending the versatility of square-planar Co^{2+}–BH_4^- systems to the tetrahedral complexes (Figure 1), hitherto unused in polymerization reactions.

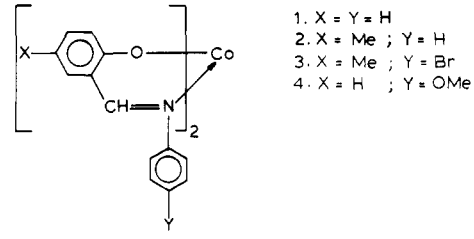

Figure 1. Tetrahedral Co complexes used as catalysts.

Styrene was washed with 10% NaOH and water and dried over anhydrous Na_2SO_4, prior to distillation under reduced pressure. Salicylaldehyde was vacuum distilled before use, and 5-methylsalicylaldehyde was prepared as described elsewhere;[7] these were subsequently used to prepare the tetrahedral cobalt complexes.[8] The new complexes (**2** and **3**) were characterized as follows: (a) **2**: IR (KBr) 2990 (w), 1610 (s), 1570 (s), 1480 (m), 1370 (m), 1300 (s), 1190 (m), 1150 (s), 810 (m) cm^{-1}; mp 201 °C. Anal. Calcd for $C_{28}H_{24}N_2O_2Co$: C, 70.13; H, 5.04; N, 5.84; Co, 12.30. Found: C, 70.13; H, 5.06; N, 5.64; Co, 12.28. (b) **3**: IR (KBr) 2990 (w), 1610 (s), 1580 (s), 1520 (s), 1480 (m), 1450 (s), 1370 (m), 1310 (s), 1200 (s), 1160 (s), 1140 (m), 1070 (m), 1000 (m), 820 (m) cm^{-1}; mp 262 °C. Anal. Calcd for $C_{28}H_{22}N_2O_2Br_2Co$: C, 52.77; H, 3.47; N, 4.39; Co, 9.26. Found: C, 52.61; H, 3.47; N, 4.33; Co, 9.25. The general procedures used for the aerial oxidation as well as the polymerization of styrene employing each of the tetrahedral complexes **1**–**4** are discussed below.

A mixture of freshly distilled styrene (17.5 mmol), cobalt complex (1.7 mmol), and $NaBH_4$ (1.7 mmol) in tetrahedrofuran (THF) (30 mL) was stirred magnetically for 16 h in air at room temperature (28 °C). The solvent was removed completely under reduced pressure, and the residue was extracted with chloroform (2 × 25 mL) and dried over anhydrous Na_2SO_4. The chloroform solution was concentrated to half its volume (25 mL). To this chloroform solution, acetyl chloride (3 mL) and triethylamine (3 mL) were added simultaneously. It was then left

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