

4.4 *The Radiation Chemistry of Poly(Arylene Ether Phosphine Oxide)s

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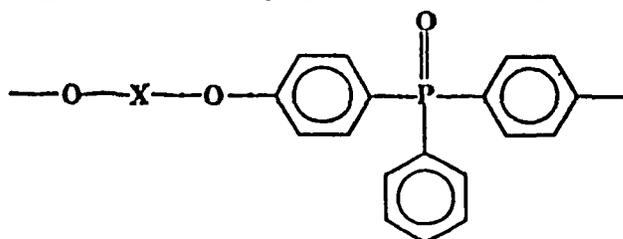
Abstract: Electron spin resonance spectroscopy has been used to study the radicals which are formed on the gamma radiolysis of selected poly(arylene ether phosphine oxide)s which have been irradiated either at 77 or 303 K. At 77 K both neutral and anionic radicals are formed, but the anionic radicals are unstable above 200 K. Two types of neutral radicals were observed. They were the phenyl and phenoxy radicals formed by homolytic scission of the backbone ether bonds. ^{31}P NMR spectroscopy showed that no new structures involving phosphorus were formed, but there was an indication that crosslinking may take place at aromatic rings adjacent to phosphorus atoms. Solution viscosity measurements indicated that the polymers undergo net chain scission on irradiation, but the net scission yield is very small.

INTRODUCTION

In general, highly aromatic polymers with phenyl groups in the backbone chain have been demonstrated to exhibit good thermal properties and to have a high resistance to degradation by gamma radiation. This is believed to be due to their propensity to degrade the absorbed energy to heat without the cleavage of bonds and to their ability to scavenge hydrogen atoms to form the less reactive cyclohexadienyl radicals. The radiation resistance of these polymers has resulted in their use in the structural components of space vehicles and as insulators in nuclear reactor applications.

The poly(arylene ether phosphine oxide)s, or PEPOs as they are commonly called, along with other aromatic polymers containing the phosphine oxide moiety, have two other desirable properties. First, the presence of the phosphorus imparts to the polymers an inherent flame retardancy. Second, under an oxygen atom flux the surface phosphorus is converted to phosphate, which renders the polymer surface resistant to further oxygen atom attack. These two properties are particularly useful for space applications in low earth orbits.

In this paper we report a study of the high energy radiation sensitivity of three PEPO polymers, using ESR spectroscopy to study the radical formation, ^{31}P NMR to probe cleavage of phosphorus carbon bonds, and solution viscosity to investigate the molecular weight changes. The generalized structure of the three PEPO polymers is given below. As well as the phosphine oxide groups, the polymers contain either hydroquinone, HQ, bisphenol-A, bis-A, or biphenol, BP, repeat units in the chains, which are indicated by the X in the generalized structure. The radiation chemistry of the poly(arylene ether sulfone), PSO, analogues of the three polymers has been reported previously (Hill, 1992).



EXPERIMENTAL

The PEPO polymers were synthesized in the laboratory of Professor J.E. McGrath at Virginia Polytechnic and State University. They possess glass transition temperatures in the range 200 to 250 °C, and they are thermally stable to approximately 500 °C. The M_n of the polymers was in the range 20–25 kg mol⁻¹ prior to irradiation.

Samples of the powdered polymers were irradiated under vacuum in pyrex ampoules or quartz ESR tubes using an AECL Gammacell facility. The ESR spectra were obtained on a Bruker X-band spectrometer, and the radical concentrations were determined by comparison with a Varian pitch reference standard. The NMR spectra were obtained in CDCl₃ solvent on a Bruker AC200F FT-NMR spectrometer, and the molecular weight changes were monitored by measuring the limiting viscosity numbers of the polymers in dichloromethane at 298 K.

RESULTS AND DISCUSSION

The 77 K ESR spectra, obtained after irradiation of the PEPO polymers at 77 K, are characterized by broad featureless singlets centered at approximately $g = 2.004$. The spectrum for bis-A PEPO is shown in Figure 1 as an example. The observed spectra are similar to those reported previously for the polysulfone (Lewis, 1989), polyketone (Heiland, 1994a) and polycarbonate (Hama, 1970) analogues of the polymers, and show no evidence for the presence of any phosphorus centred radicals. The spectra have been analysed in terms of the formation of both anion radicals and neutral phenyl and phenoxy radicals, the latter radicals being formed as a result of backbone scission.

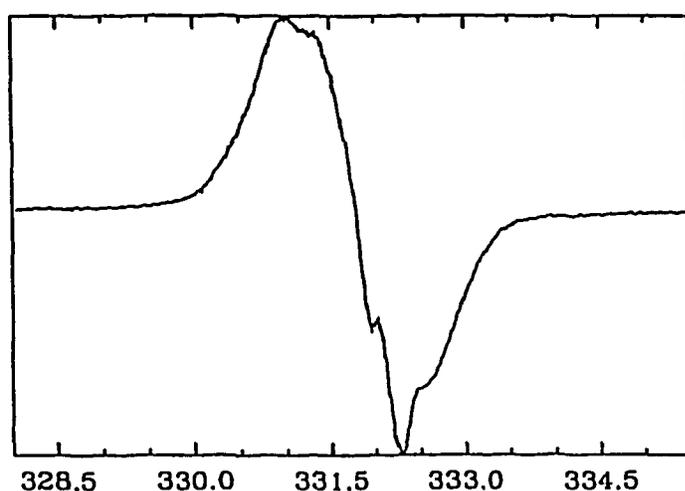


Figure 1: Radical spectrum of bis-A PEPO obtained at 77 K.

Photobleaching studies carried out at 77 K confirmed the presence of two anion radicals following radiolysis at this temperature. It is postulated that these two anions are located on the oxygen atoms of the phosphine oxide or on the aromatic rings of the main chain or the side chains. The anion radicals were shown to constitute approximately sixty percent of the total radical yield at this temperature.

The radical yield versus dose curves were determined at 77 K for low doses, and are shown in Figure 2. Dose saturation effects are clearly present, even at low doses. The dose curves are very similar for the three polymers, and the low dose G-values for radical

7MGy, indicating that while chain crosslinking takes place, the chain scission reaction dominates over crosslinking. This observation was confirmed by solution viscosity measurements. The limiting viscosity numbers for the polymers in dichloromethane were shown to decrease slowly with dose, as demonstrated in Figure 3 for HQ-PEPO. These observations indicate that the polymers are resistant to radiation damage but that the molecular weights of the polymers decrease slowly with increasing dose, indicating that $G(S)$ is only slightly greater than $4G(X)$.

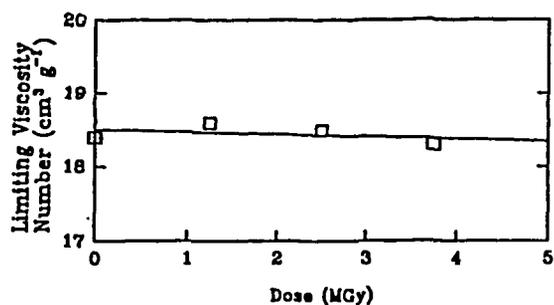


Figure 3: Limiting viscosity number versus dose plots for HQ-PEPO in dichloromethane.

It is of interest to compare the radical yields for the PEPO polymers with those for other polymers which contain the same comonomer back-bone groups. This has been done in Figure 4 for a range of polymers containing the bis-A and HQ comonomer groups. The figure shows that the radiation chemical yields for the PEPO polymers are very similar to those of their polysulfone analogues, but they are less resistant to radical formation than the polyketones and the polyimides, and they are significantly more resistant than Kevlar or bis-A polycarbonate, for which G -radical has been reported to be 1.8 at 77 K (Hama, 1970)

The relative sensitivity of the polymers shown in Figure 4 can be compared with the relative sensitivities as assessed by volatile gas formation, or on the basis of the changes in their tensile properties. Recently Hegazy et al. (Hegazy, 1992) reported that on the basis of the G -values for total gas formation on gamma radiolysis, the polymers could be ranked in terms of resistance to damage in the order Kapton > PEEK > bis-A PSO > bis-A polyester. In an earlier study of the tensile properties of many of the same polymers, Sasuga et al. (Sasuga, 1985) concluded that for e-beam irradiation the order of radiation resistance was PEEK > KAPTON > Ultem > bis-A PSO > PPO, based on a 50% decrease in tensile strength.

There is a great deal of correspondence between the order of radiation resistance as assessed by radical yield, gas formation and tensile property changes, except that on the basis of the radical yields the relationship is reversed for Kapton and PEEK compared to that found for the gas yields. The reason for this reversal in the order is not clear. However, the dose range used for the assessment based on radical formation is of the order of 10 kGy, while the dose required for measurement of the gas yields or the tensile property changes is much higher, being of the order of 10 MGy. Thus for the latter measurements the doses are one thousand times higher than for the radical measurements, and the damage to the polymer would be correspondingly much greater.

formation for the polymers was determined from the plot to be 0.58. This value is very similar to the values obtained for the polysulfones at low dose, which are HQ PSO 0.56, bis-A PSO 0.57 and BP PSO 0.51 (Heiland, 1994b).

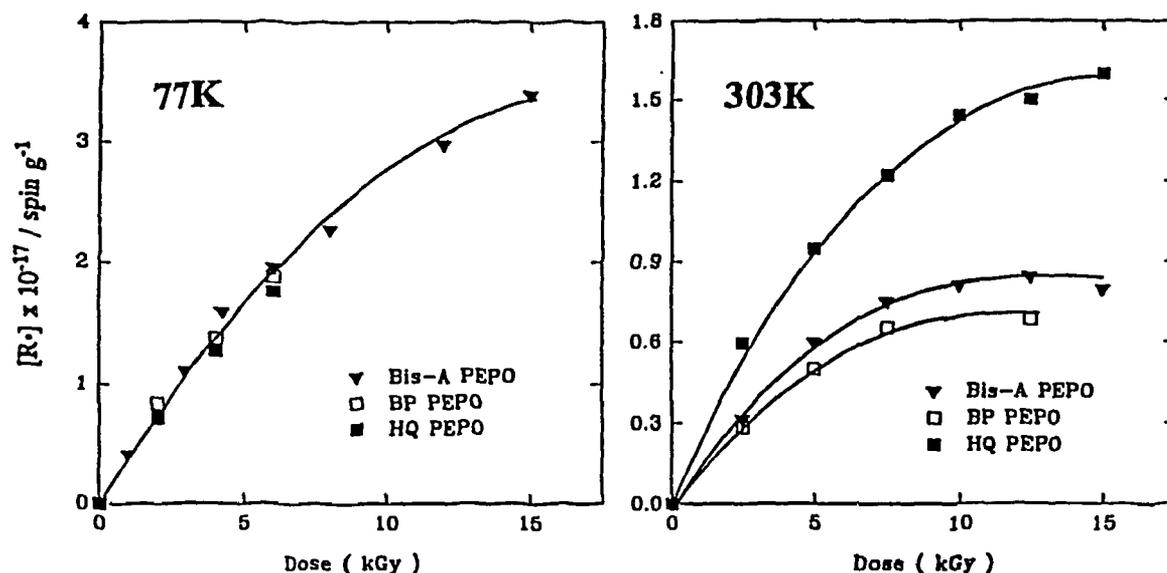


Figure 2: Radical yield plots for irradiation of the PEPO polymers at 77 and 303 K.

Thermal annealing of the samples after irradiation at 77 K demonstrated that radicals are lost over two thermal ranges. Over the temperature range 77 to 200 K the anionic species are lost, and above room temperature the phenyl and phenoxy radicals both begin to decay concurrently.

Radiolysis at room temperature (303 K) produced radical spectra identical to those observed by warming to this temperature. The radical yield plots are shown in Figure 2. At 303 K the radical yields for HQ PEPO are much greater than those for bis-A PEPO and BP PEPO, which are of similar magnitude. Dose saturation effects were also evident at this temperature. The low dose radical yields were calculated from the plots in Figure 2 to be 0.35 for HQ PEPO, 0.22 for bis-A PEPO and 0.19 for BP PEPO. The somewhat higher G-value for HQ PEPO could reflect the higher ether oxygen content of this polymer as compared to the other two.

The ^{31}P NMR spectra of samples of the PEPO polymers which had been irradiated to 6.9 MGy at room temperature have been investigated, and were found to show no new phosphorus resonances. The only major phosphorus resonance observed in the samples was that due to the triphenyl phosphine unit at 29.1 ppm, indicating that the phosphorus-phenylene bonds are not broken during radiolysis. However, the spectra did show evidence of significant broadening of this phosphorus peak in the irradiated polymers, particularly towards lower field, which would be consistent with some deshielding of phosphorus atoms. The broadening could also be indicative of a lowering of the mobility of the groups adjacent to phosphorus. Both of these effects would be consistent with chain crosslinking at the phenyl rings attached to the phosphorus atoms in the chain.

The irradiated PEPO polymers remained soluble in dichloromethane to doses greater than

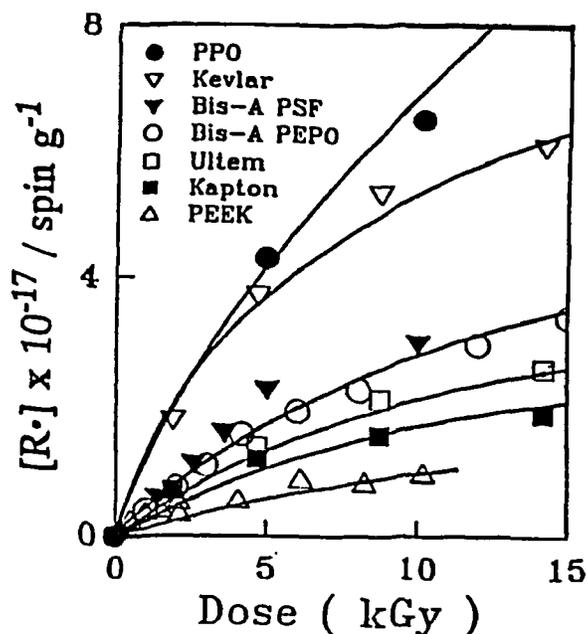


Figure 4: Comparison of the radiation chemical yields for related polymers at 77 K.

CONCLUSIONS

The radical yields on gamma radiolysis of HQ PEPO, bis-A PEPO and BP PEPO have been measured at 77 and 303 K. At 77 K both anions and neutral radicals are formed, but at room temperature only neutral radicals are observed. Two anion radicals were observed, one associated with the phosphine oxide units and one with the aromatic units. The neutral radicals were the mainly phenyl and phenoxy radicals formed by cleavage of phenyl-oxygen bonds. At 77 K the yield of radicals was similar for all three polymers, but at 303 K the yield of radicals from HQ PEPO was higher than that for the other two polymers. The radiation sensitivity of the PEPO polymers was found to be similar to that of their PSO analogues.

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