PII: S0032-3861(96)00975-5

Polymer Vol. 38 No. 15, pp. 3927–3930, 1997

0032-3861/97/$17.00+0.00

Radiation-induced processes in poly(alkylene terephthalates) and diethyl terephthalate: evidence for formation of cyclohexadienyl-type radicals

A. Yu. Orlov* and V. I. Feldman
L. Ya. Karpov Institute of Physical Chemistry, Vorontsovo Pole Str. 10,
Moscow 103064, Russia
(Received 22 October 1996)

The low-temperature radiolysis of poly(butylene terephthalate), poly(ethylene terephthalate), and diethyl terephthalate was studied by electron spin resonance spectroscopy. The radiation-induced formation of radicals of the cyclohexadienyl type was observed for all the samples studied. It was shown that the radicals of the cyclohexadienyl type represented a considerable fraction of neutral radicals produced in the radiolysis of phthalates under consideration. The identification of the signals of various alkyl-type radicals is discussed. The kinetics of radical decay at room temperature was investigated. © 1997 Elsevier Science Ltd.

(Keywords: polyesters; radiolysis; e.s.r.)

INTRODUCTION

The cyclohexadienyl (CHD)-type radicals resulting from hydrogen atom addition to the aromatic ring were found to play an important part in the radiolysis of aromatic polymers (such as polystyrene) and corresponding prototype compounds[1–5]. The electron spin resonance (e.s.r.) spectra of these species exhibit large characteristic hyperfine coupling with two CH_2 protons ($a(CH_2) = 4.5$–5.0 mT) and additional splitting of ~ 1.0 mT due to *ortho* and *para* protons, and of ~ 0.3 mT due to *meta* protons (the last is usually unresolved)[6]. However, in the case of poly(ethylene terephthalate) (PET), no e.s.r. signals of the CHD-type radicals were detected in irradiated samples at room or higher temperatures (up to 433 K)[7–9]. A similar result was obtained for terephthalic acid[8]. The absence of these signals was interpreted as an evidence for sensitivity of hydrogen addition to the nature of ring substituents. Meanwhile, such a conclusion is in conflict with the observation of CHD-type radicals upon treating terephthalic acid with hydrogen atoms generated from microwave gas discharge at room temperature reported by Campbell *et al.*[10].

Recently, we examined the e.s.r. spectra of polycarbonate–poly(butylene terephthalate) (PBT) blends irradiated at 77 K and revealed that the signals of neutral radicals with comparatively large separation resulted from PBT moieties[11]. Although a detailed analysis of these components was not given by Orlov *et al.*[11], it is reasonable to ascribe the corresponding features to CHD-type radicals. From this point of view, it appears to be of interest to reinvestigate the radical formation in irradiated poly(alkylene terephthalates), paying special attention to the thermal stability of various species. In this work, we report the results of e.s.r. studies on the formation and annealing behaviour of paramagnetic species in PET, PBT and diethyl terephthalate (DET, taken as the model compound) irradiated at 77 K.

EXPERIMENTAL

The polymer samples used were commercial PBT (molecular weight 60 000; crystallinity 30%) and PET (molecular weight 20 000–25 000; crystallinity 25%). DET of 'pure' grade (polycrystalline powder) was used as received. All the samples were degassed in a vacuum line under a residual pressure of 0.13 Pa for 24 h at room temperature. SK-4B glass tubes, which gave no appreciable e.s.r. signal upon irradiation, were used. The samples were irradiated at 77 K up to a dose of 185 kGy using a K-120000 ^{60}Co γ source. The dose rate was 50 kGy h^{-1}. The e.s.r. spectra were measured at 77 K using a standard X-band spectrometer with a high-frequency modulation of 100 kHz. Low microwave power level (~5 μW) was used in order to avoid the saturation of the e.s.r. signal. The irradiated samples were annealed at the required temperature for 10 min using a variable-temperature nitrogen flow cryostat.

RESULTS

All the phthalates studied give rise to several kinds of paramagnetic species upon irradiation at 77 K. To make unambiguous identification, let us consider first the radical species trapped in irradiated DET. The e.s.r.

---

* To whom correspondence should be addressed

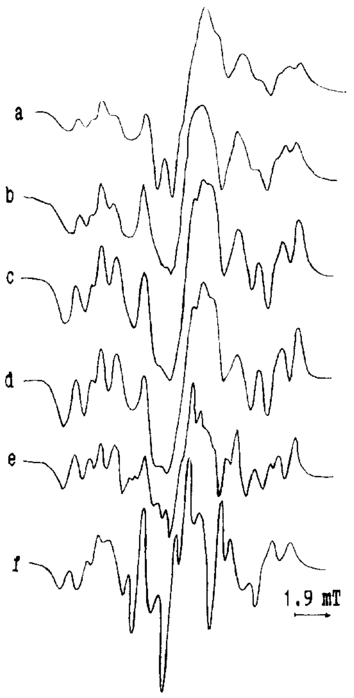

Figure 1 The e.s.r. spectra of DET irradiated at 77 K: (a) immediately after irradiation; (b) after annealing the sample at 200 K (10 min); after annealing the sample for (c) 5 and (d) 80 min at room temperature; (e) the spectrum recorded during annealing at room temperature. (f) Spectrum showing the simulated pattern for the mixture of CHD and alkyl-type radicals (see the text for parameters)

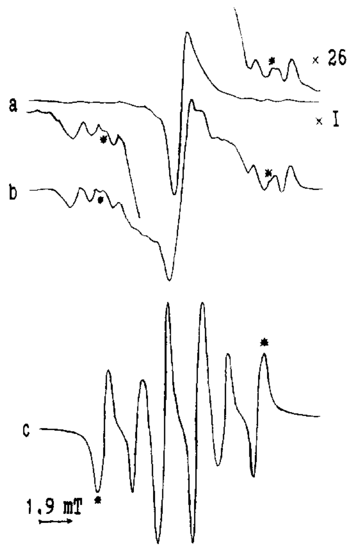

Figure 2 The e.s.r. spectra of PET irradiated at 77 K: (a) immediately after irradiation; (b) after annealing the sample at room temperature (6.5 min). (c) Spectrum showing the simulated pattern for the radicals $-OC^{\bullet}HCH_2-$ (see the text)

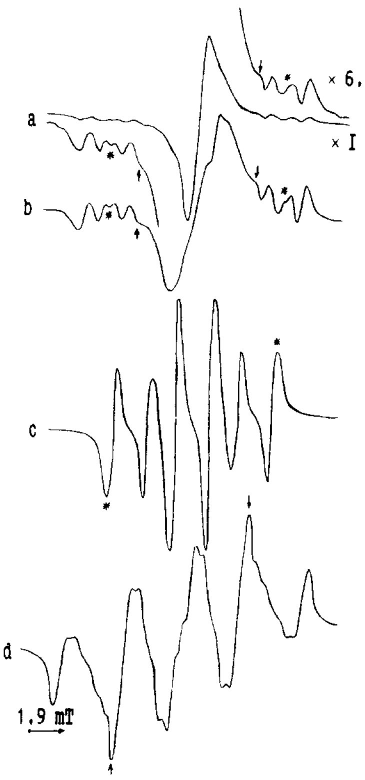

Figure 3 The e.s.r. spectra of PBT irradiated at 77 K: (a) immediately after irradiation; (b) after annealing the sample at room temperature (22 min). Spectra showing the simulated patterns for the radicals (c) $-OC^{\bullet}HCH_2-$ and (d) $-CH_2C^{\bullet}HCH_2-$, respectively (see the text)

spectrum of this sample exhibits a complex pattern resulting from lines of different radicals (*Figure 1a*). Nevertheless, the total width of the spectrum (~12.0 mT) bears clear evidence for the presence of signals of CHD-type radicals. The e.s.r. spectra of other radicals, which could result from the radiolysis of DET (substituted alkyl or phenyl radicals) show essentially a smaller total spread[6].

Upon annealing the sample at 200 K, the resolution of the outermost components improves to a certain extent. The main changes are observed in the central region of the spectrum (*Figure 1b*). This result is probably due to the reactions of charged species, which occur in small amounts in the irradiated DET. However, the total concentration of paramagnetic species increases by ~20%.

Annealing the sample at room temperature results in drastic improvement of the spectral resolution (*Figure 1c*). The peak intensities of the corresponding lines increase, whereas their widths decrease. An even better resolved spectrum was recorded at room temperature (*Figure 1e*). The improved spectral resolution makes it possible to make detailed analysis of the spectrum. In particular, one can observe well-determined features of CHD-type radicals and alkyl-type radicals of $CH_3C^{\bullet}HOCOR$ structure. This spectrum was simulated using the following isotropic hfs constants: $a(CH_2) = 4.75$, $a(o\text{-H}) = 1.0$, $a(p\text{-H}) = 0.8$, $a(m\text{-H}) = 0.3$ mT for CHD-type radicals; $a(CH_3) = 2.3$, $a(CH) = 1.7$ mT for $CH_3C^{\bullet}HOCOR$ radicals. The g factor of CHD-type radicals was considered to be greater by 0.0003 compared with the g factor of alkyl-type radicals, and the ratio of CHD to alkyl-type radicals was assumed to be 7:3 (*Figure 1f*). This simulation allows us to reproduce the features of CHD- and alkyl-type radicals, with the exception of the central region. The central part of the spectrum is not reproduced well, probably due to the presence of various phenyl-type radicals (involvement of phenyl-type radicals is also essential to meet the balance requirements).

The total concentration of paramagnetic species decreases as a result of annealing the sample at room temperature.

In order to estimate the effect of storage of the irradiated samples at room temperature on the concentrations of CHD-type radicals, we have carried out special kinetic studies. The samples were irradiated at 77 K and then annealed at room temperature for various periods of time (5 min to 3 days). A long storage time of irradiated samples at room temperature (up to several days) results in monotonous decrease of the integrated intensity of the total signal. This slow decay follows a second-order kinetic law for both alkyl and CHD-type radicals. However, for alkyl-type radicals, we also observed a region of initial faster decay (within the first several minutes). *Figure 1d* shows the e.s.r. spectrum of the sample annealed for 80 min at room temperature. One can see the change in the relative intensities of the lines due to CHD- and alkyl-type radicals. Slow decay at longer times does not result in further changes of this intensity ratio. Decay of alkyl radicals can be monitored by reduction of the intensity of all features ascribed to these species.

The e.s.r. spectra of PET and PBT irradiated at 77 K are shown in *Figures 2a* and *3a*, respectively. The lines of the CHD-type radicals with characteristic splittings are observed in both polymers. The concentration of the CHD-type radicals in PBT is higher than that in PET. The estimated ratio of the relative intensities of the outermost lines, which overlap with lines of other species only to a small extent, is 2.5. The features corresponding to alkyl-type radicals are also observed in the spectra of both polymers. We should note that the only kind of alkyl-type radical trapped in PET is the radical of structure $-OC^{\bullet}HCH_2-$, whereas in the case of PBT there are two possible structures: $-OC^{\bullet}HCH_2-$ and $-CH_2C^{\bullet}HCH_2-$. As will be shown later, the line marked with an asterisk results from the $-OC^{\bullet}HCH_2-$ radical for both polymers. Rough estimation shows that the intensity of this line in PBT is about three times greater than that in PET.

In contrast to DET, the spectra of polymers exhibit an intense central singlet. The signals for PET and PBT are characterized by approximately equal peak intensities and different linewidths (~0.93 mT for PBT and ~0.65 mT for PET).

The total concentration of the trapped paramagnetic species in PBT is 1.9 times greater than that in PET. This observation is in accord with the ratio of 1.8 for the dose of 1 MGy reported by Kroh and Pietrzak[12]. The concentration of paramagnetic species in DET is 1.33 times smaller than that in PBT. It should be noted that the ratio of integrated intensities of the e.s.r. signals for PBT and PET remains roughly constant when annealing the samples at 200 K or at room temperature.

After annealing the sample at 200 K, the shape of the central signal changes significantly for both polymers. The decrease in peak intensity of this signal is more pronounced in the case of PET. Annealing of the samples also results in a reduction of the total concentration of paramagnetic species in PET and PBT. In this case, the intensities of the outermost peaks of the CHD-type radicals increase by ~30% for both polymers.

The kinetic behaviour of the CHD- and alkyl-type radicals was examined at room temperature. A short (5 min) annealing time of the samples results in some (~20%) increase in the intensities of the outermost lines of CHD-type radicals (similarly to the result of annealing at 200 K). Analysis of the lineshape shows that this increase is due to line narrowing rather than to an increase in the concentration of CHD-type radicals.

Further annealing of the samples at room temperature ($t > 10$ min) results in monotonous decrease in the intensity of the outermost peaks of CHD-type radicals, the lineshape being virtually unchanged. The intensity of the lines of alkyl-type radicals also decreases. A rough estimation shows that this slow decrease follows a second-order kinetics for $-OC^{\bullet}HCH_2-$ and CHD-type radicals. The signals from $-OC^{\bullet}HCH_2-$ radicals become indiscernible after 80 min annealing of the sample at room temperature. The intensity of the lines of the CHD-type radicals decreases by an order of magnitude after storage for 24 h at room temperature; finally, these lines are not observed after 3 days of storage of the samples.

The shape of the central signal changes as a result of annealing the sample at room temperature. It should be noted that the spectra of annealed samples of PBT and PET exhibit different linewidths of the central signal (*Figures 2b* and *3b*).

The integrated intensity of the e.s.r. signal decreases strongly as a result of the sample storage at room temperature. The total concentration of paramagnetic species decreases by ~60–70% for PBT and PET after the first 5 min of annealing the sample at room temperature. Decay becomes slower at longer times.

DISCUSSION

Identification of paramagnetic species

The results obtained provide clear evidence for formation of the CHD-type radicals upon irradiation of DET, PET and PBT. These radicals have almost similar spectra characteristics for DET and polymers since the structures of the radical centres are quite similar. The CHD-type radicals make essential contributions to the e.s.r. spectra of the systems studied. Furthermore, these radicals are relatively stable at room temperature, and decay completely only after several days. Indeed, it is surprising that these radicals were not identified in the previous studies[7–9].

Identification of alkyl-type radicals is a more complicated problem. The spectra of these radicals have typically smaller spread, so their lines overlap with the signals from other species; in addition, the spectra of alkyl-type radicals depend crucially on the radical conformation, which is often not known. Nevertheless, we can make tentative interpretation of the spectra of these radicals using splitting constants reported for related species in the literature. Assuming the principal values of the hfs tensor for the α proton of the $-OC^{\bullet}HCH_2-$ radical to be 1.5, 2.6 and 1.5 mT[8], and taking an isotropic splitting constant of 3.3 mT for the two β protons (*trans* conformation of the CH_2 moiety), one may obtain the spectrum shown in *Figures 2c* and *3c*. The separation between the extrema of outermost peaks in this spectrum is about 9.0 mT. This result is in qualitative agreement with the observed separation between weak features in the spectra of irradiated PET and PBT marked with asterisks. Other lines of the simulated spectrum could barely be observed in the experimental patterns because of strong signal overlapping in the central region. However, in the spectra of irradiated PBT one can see two more distinct features separated by ~6.0 mT, which appear as 'shoulders' of the central signal (these features are marked with arrows). The corresponding lines are not observed in PET.

Considering the difference of the chemical structure of PBT and PET, we may assume that these features result from $-CH_2C^\bullet HCH_2-$ radicals, which can be generated in PBT, but not in PET. Indeed, the conformation of the methylene sequence for PBT crystallites was reported to be $GT\bar{G}$[13]. This structure implies that there are three protons with dihedral angles between the p-orbital axis and C–H bonds of $\Theta = 30^\circ$, and the corresponding coupling constants should be about 3.3 mT (as in the case of polyethylene[14]). The fourth proton is positioned in the nodal plane ($\Theta = 90^\circ$), and the coupling constant is close to zero. Furthermore, we may assume the principal values of the hfs tensor for the α proton to be 2.59, 1.21 and 3.41 mT as reported for the $-CH_2C^\bullet HCH_2-$ radical in polyethylene[14]. The spectrum simulated using these parameters is shown in *Figure 3d*. It has relatively weak outermost lines separated by 13.1 mT (in the spectrum of PBT they should overlap with the outermost peaks of the CHD-type radical) and more intense lines separated by 6.6 mT (marked with arrows). These lines may correspond to the 'shoulders' observed in the experimental spectrum of irradiated PBT. The agreement seems to be reasonable taking into account the signal overlapping in the experimental spectrum and the uncertainty of the conformation of the radicals associated with amorphous regions of PBT.

As was mentioned above, the central parts of the spectra of irradiated polymers exhibit strong signals, which are not observed in DET. These signals are probably due to charged paramagnetic species trapped in amorphous regions of the polymers. Apparently, these species are not stabilized in irradiated polycrystalline DET; this is an obvious trend for electron trapping in molecular glasses and polycrystals[15]. We can suggest tentatively that in the case of DET, electrons are trapped by radicals yielding diamagnetic ions. Annealing of the irradiated sample at 200 K results in reactions of these diamagnetic ions, which may give, at least partially, neutral radicals. Such reactions may explain the increase in the concentration of paramagnetic species in DET as a result of annealing. However, this effect requires more careful examination.

Mechanism of radical formation and decay

The general scheme for formation of the CHD-type radicals is concerned with hydrogen atom addition to the aromatic ring. Indeed, formation of the CHD-type radicals was observed upon bombarding terephthalic acid with hydrogen atoms generated in microwave discharge[10]. This may be also the case in the radiolysis of phthalates. Nevertheless, one should not ignore the possibility of combination of electrons with protonated aromatic rings, i.e. reactions of the type

$$e^- + RH_2^+ \rightarrow RH_2^\bullet$$

It was shown[5] that reactions of this type accounted for CHD-type radical formation in the radiolysis of PS. This reaction may also occur in DET, PET and PBT. The role of this process should increase with increasing irradiation dose.

In the cases of PET and PBT, we can separate fast decay (within the first 5 min of annealing the sample at room temperature) and slow decay. Averaged efficiency of radical decay in DET is higher than that in polymers; however, fast decay is not observed in this case. Probably, fast decay in polymers is mainly due to a combination of ionic paramagnetic species, which are not trapped in DET.

An apparent second-order kinetics of decay of the CHD-type radicals and $-OC^\bullet HCH_2-$ type radicals at room temperature implies that the radical decay is mainly due to combination. This may result in formation of various kinds of cross-links in polymers. In particular, one should take into account the possibility of cross-linking of CHD-type radicals yielding specific structures. It is to be noted that the results obtained provide new arguments concerning the relative importance of cross-linking and main chain scission in the radiolysis of PET. Indeed, comparison of the yields of gaseous products reveals that the yields of scission product (CO and CO_2) are higher than that of molecular hydrogen[16], which could be interpreted as an evidence for predominating main chain scission. However, taking into consideration formation of CHD-type radicals, one can see that the role of cross-linking may be underestimated from this comparison since the CHD-type radicals result in cross-linking, which is not accompanied by hydrogen formation.

ACKNOWLEDGEMENTS

The authors are indebted to E. V. Konyukhova and N. P. Bessonova for providing the polymeric samples. This work is a part of the IAEA Coordinated Research Program 'Stability and Stabilization of Polymers under Irradiation' (Research Agreement No. 7547/RUS). It was also supported by the Russian Foundation for Basic Research (grant No. 96-03-32949).

REFERENCES

1. Buben, N. Ya. and Chkheidze, I. I., *Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva im. D. I. Mendeleeva*, 1966, **11**, 228.
2. Campbell, D. and Turner, D. T., *Can. J. Chem.*, 1967, **45**, 881.
3. Chernova, I. K., Leshchenko, S. S., Golikov, V. P. and Karpov, V. L., *Vysokomolek. Soedin., Ser. A*, 1980, **22**, 2175.
4. Ohnishi, S., Tanei, T. and Nitta, I., *J. Chem. Phys.*, 1962, **37**, 2403.
5. Zezin, A. A., Feldman, V. I. and Sukhov, F. F., *Vysokomolek. Soedin., Ser A*, 1994, **36**, 925.
6. Pshezhetskii, S. Ya., Kotov, A. G., Milinchuk, V. K., Roginskii, V. A. and Tupikov, V. I., *EPR Svobodnykh Radicalov v Radiatsionnoi Khimii* [*ESR of Free-Radicals in Radiation Chemistry*], Khimiya, Moscow, 1972.
7. Araki, K., Campbell, D. and Turner, D., *J. Polym. Sci. B*, 1965, **3**, 993.
8. Campbell, D., Araki, K. and Turner, D. T., *J. Polym. Sci. A-1*, 1966, **4**, 2597.
9. Turner, D. T., in *The Radiation Chemistry of Macromolecules*, Vol. II, ed. M. Dole. Academic Press, New York, 1973, p. 137.
10. Campbell, D., Symons, M. C. R. and Verma, G. S. P., *J. Chem Soc. A*, 1969, 2480.
11. Orlov, A. Yu., Feldman, V. I. and Sukhov, F. F., *Khim. Vys. Energ.*, 1995, **29**, 274.
12. Kroh, J. and Pietrzak, M., *Khim. Vys. Energ.*, 1970, **4**, 246.
13. Wings, N. and Trafara, G., *Die Ang. Makromol. Chem.*, 1994, **217**, 91.
14. Shimada, S., Kashiwabara, H., Sohma, J. and Nara, S., *Jap. J. Appl. Phys.*, 1969, **8**, 145.
15. Dole, M. (ed.), *The Radiation Chemistry of Macromolecules*, Vol. I. Academic Press, New York, 1972.
16. Burow, S. D., Turner, D. T., Pezdirtz, G. F. and Sands, G. D., *J. Polym. Sci A-1*, 1966, **4**, 613.