

Effect of phase condition on the low-temperature radiation-induced degradation of polycarbonate as studied by spectroscopic techniques

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Abstract

Effect of phase condition (crystallinity) on the low-temperature radiation-induced degradation of polycarbonate was studied by electron spin resonance (ESR) and infrared (IR) spectroscopy. Semi-crystalline polycarbonate exhibits lower relative yields of radiation-induced degradation in comparison with amorphous polycarbonate, as evidenced by monitoring of both CO and CO₂ formation (IR spectroscopy), and radical pair formation (ESR spectroscopy). On the basis of results obtained, the mechanism of electron stabilisation in polycarbonate, and reasons of variation in radical pair inter-spin distance are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Radiolysis; Crystallinity effect

1. Introduction

In general, it is well known that the radiation-induced effects in polymeric materials are essentially affected by the polymer structure and morphology [1,2]. However, direct evidences for the effect of phase conditions and crystallinity on the primary processes in degrading heterochain polymers are quite limited.

The studies of radiation-induced damage in bisphenol-A-based polycarbonate (PC) are of considerable interest from both practical and modelling points of view. First, the variety of fields of the application of PC is known, including those associated with its exposure to high-energy radiation. On the other hand, the study of the radiation chemistry of PC provides an insight into basic mechanisms of the radiation-induced degradation of polymers, which exhibits predominant main-chain scission.

There are a lot of works concerning exposure of PC to either electron beams, or γ -radiation. However, the research was often governed by practical needs, so PC was irradiated at the room temperature, sometimes in the air. Owing to the occurrence of diverse secondary reactions under these circumstances, one cannot obtain conclusive evidence on

the primary radiation chemistry of PC in this case. The early stages of the radiolysis of PC were studied in Refs. [3–5], where the irradiation and subsequent measurements of the radiation-induced effects by ESR spectroscopy were carried out at liquid nitrogen temperature. It is worthwhile noting that using spectroscopic tools allows one to study not only the very radiolysis products, but also their environment, which may more substantially characterise the effect of radiation on PC, and which may, in turn, determine this effect to some extent. However, the results obtained are not complete since the analysis of stable products of the low-temperature radiolysis of PC is lacking. Furthermore, no specific attention was paid to the effect of phase condition and polymer microstructure on the product formation.

Recently, we applied a combination of the low-temperature ESR and IR spectroscopy to the investigation of the radiation-induced effects in amorphous PC and PC/poly(alkylene terephthalate) blends [6,7]. Using this approach made it possible to characterise both paramagnetic and diamagnetic products of the radiation-induced processes. Moreover, such a combination has proved to be helpful in studying details of radiation effects in these complex polymeric systems, including spatial distribution of the products as a function of system physical and chemical structure. Here, we report the application of the spectroscopic “diagnostics” to analysis of the effect of phase condition and microstructure on the low-temperature radiation-induced degradation of polycarbonate.

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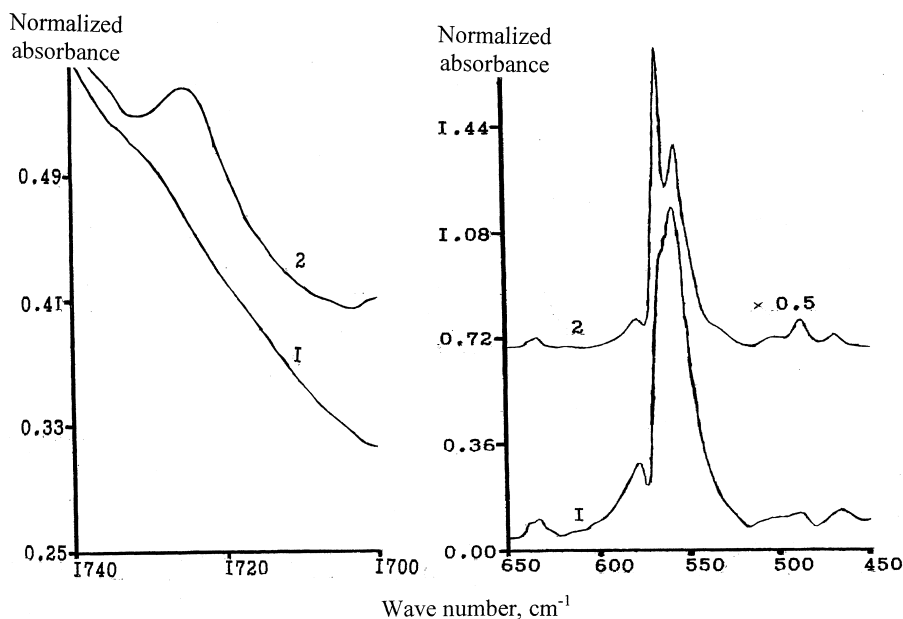


Fig. 1. Effect of PC structure on the IR spectrum of the sample: (1) spectrum of hot-pressed PC sample; (2) spectrum of cast PC sample. The spectra were taken at room temperature.

2. Experimental

Commercial grade PC (molecular weight 30 000) was used. The samples of PC were either hot-pressed, or cast from solution. Before hot-pressing the polymer was evacuated under the residual pressure of 0.13 Pa at least for 24 h at room temperature. The temperature of hot-pressing was 234–242°C. The sample was kept for 5 min without pressure application, and after that for 10 min under the pressure of 150 atm. Then the sample was cooled in the mould under the pressure of 150 atm. Amorphisation of samples of poly(ethylene terephthalate) (PET) (molecular weight 20 000–25 000, initial crystallinity 25%) and poly(butylene terephthalate) (PBT) (molecular weight 60 000, initial crystallinity 30%) was achieved through rapid quenching the mould with a sample from the melting point of the polymer to liquid nitrogen temperature. The resulting decrease in crystallinity of the samples was confirmed by IR spectroscopy [8]. The cast samples of PC were prepared on a KBr plate from a dilute solution of PC in CH_2Cl_2 ($\sim 0.1 \text{ g ml}^{-1}$). The film was dried for several hours in the air and then evacuated for 72–96 h (0.13 Pa). Removal of the solvent was checked by IR spectroscopy (CH_2Cl_2 absorption band at 744 cm^{-1}). In the case of ESR spectroscopy, SK-4B glass tubes, which gave no appreciable ESR signal upon irradiation, were used. The cryostat described in detail in Ref. [9] was used for IR spectroscopic studies. The cryostat makes it possible to irradiate the sample under the pressure of less than 0.13 Pa and at the temperature of 77 K, and to measure its IR spectrum afterwards. Before irradiation, all the samples were degassed in a vacuum line under a residual pressure of 0.13 Pa for at least 24 h at room temperature. The samples for ESR were irradiated at 77 K using a

K-120000 ^{60}Co γ -source. The dose rate was 50 kGy h^{-1} . In case of IR investigation, the samples were irradiated at 77 K with fast electrons (1.5 MeV) using an EG-2.5 Van-de-Graaf accelerator. The dose rate was 1200 kGy h^{-1} . The ESR spectra were measured at 77 K using a standard X-band spectrometer with a high-frequency modulation of 100 kHz. Low microwave power level ($\sim 5 \mu\text{W}$) was used in order to avoid the saturation of the ESR signal. The irradiated samples were annealed at the required temperature for 10 min using a variable-temperature nitrogen flow cryostat. The IR spectra were measured by FTIR spectrometer "Perkin Elmer-1710" in the region of 450–4000 cm^{-1} , the resolution being 2 cm^{-1} . Relative yields of radiolysis products obtained in PC and measured by IR spectroscopy were normalised by the intensity of the PC IR band with the maximum at 1774 cm^{-1} (absorption band of C=O moiety of PC), using appropriate reference to other PC IR bands not changed owing to PC crystallisation, when necessary. To measure crystallinity of the samples, calorimetric measurements were conducted by DSC using the instrument DSC-30 ("Mettler", Switzerland). The heating rate was $10^\circ\text{C min}^{-1}$.

Unlike PC films obtained by hot-pressing, PC films obtained from a solution exhibit a high degree of crystallinity, which can be revealed by IR spectroscopy. In particular, the appearance of a distinct peak with the maximum at 1724 cm^{-1} can be used as a spectroscopic indicator of PC crystallinity (Fig. 1, left). In addition, there is a splitting of the peak with the maximum at 557 cm^{-1} for a crystalline fraction of PC (Fig. 1, right). These features are also characteristic of the spectrum of crystalline PC (in comparison with the spectrum of amorphous PC), which was shown, but not analysed in this respect in Ref. [10]. DSC data were used to obtain the calibration dependence

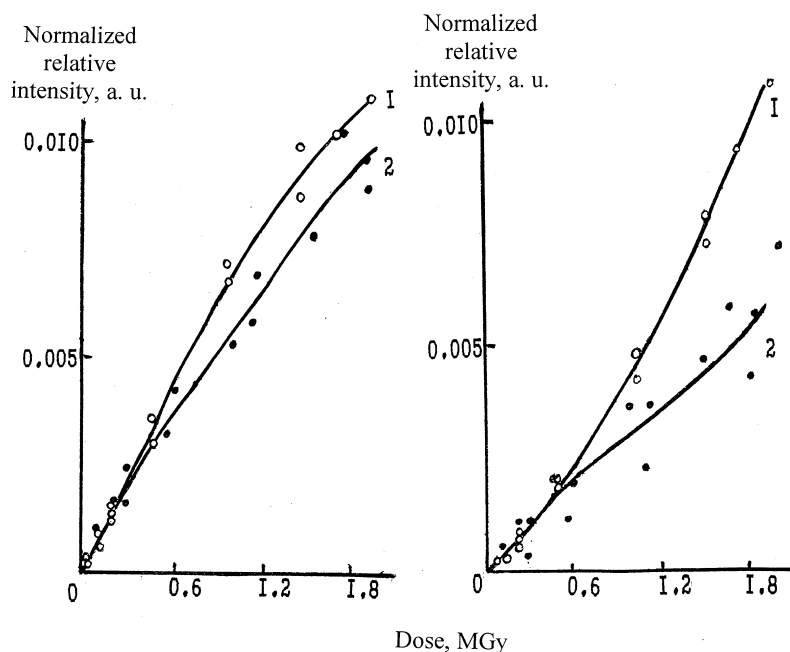


Fig. 2. Dose dependence of the relative intensity of CO absorption bands with a maximum at 2132 cm^{-1} (left) and with a maximum at 2113 cm^{-1} (right) for: (1) amorphous (○), and (2) semi-crystalline PC (●).

of normalised absorbance of the band with the maximum at 1724 cm^{-1} on the degree of PC crystallinity. For the study of the effect of phase condition on the low-temperature radiation-induced degradation of PC as studied by spectroscopic techniques, the semi-crystalline PC with crystallinity of ca. 75% was used.

3. Results and discussion

As we have shown previously [6], the radiolysis of amorphous PC at 77 K predominantly results in the formation of chain scission products, that is CO and CO_2 . The product composition for semi-crystalline PC is qualitatively the same.

3.1. Formation of CO

The IR band of CO radiolytically generated in amorphous PC exhibits two maxima: at 2132 and at 2113 cm^{-1} . According to our previous analysis [6], the former component results from CO molecules trapped in the PC matrix after radiation-induced degradation of the PC moiety. In view of peak position, dose dependence and thermal stability, the latter peak was ascribed to CO molecules localised in the vicinity of negatively charged ion of PhO^- type [6]. Low-frequency shift is characteristic of partial electron donation to CO, and the interaction energy necessary for such a shift of the CO vibration band from the fundamental frequency of CO is estimated [11] to be 20 kJ mol^{-1} .

The positions of the maxima of this doublet are the same for both amorphous and semi-crystalline samples, that is,

phase state negligibly affects spectroscopic characteristics of the CO molecules formed upon radiolysis at 77 K.

According to Ref. [12], the molar absorption coefficient of CO decreases rapidly when going from the fundamental frequency of CO found [13] to be 2143 cm^{-1} to lower frequencies. This means that the concentration of species absorbing at 2113 cm^{-1} is much smaller than the concentration of “non-disturbed” CO molecules absorbing at 2132 cm^{-1} .

The yield of “non-disturbed” CO (maximum at 2132 cm^{-1}) for PC films obtained from a solution is about 85% of the yield of corresponding species in hot-pressed films (Fig. 2, left), which indicates some decrease in the CO yield in the crystalline phase (as compared to the amorphous phase). This result is in general accord with the expected increase in the probability of cage recombination of a primary radical pair in the rigid crystalline phase.

As we have shown [7], the formation of the “non-disturbed” CO is accompanied by the formation of correlated radical pairs separated by the CO molecule: at the “wings” of the main signal distinct features of the signal of the radical pairs separated by the CO molecule were observed (Fig. 3). The perpendicular component of dipole–dipole splitting $D_{\perp} = 14.8\text{ mT}$ was observed for amorphous PC. According to the well-known equation [14] $D_{\perp} = 2.78/r^3$, this value corresponds to the inter-spin distance of 0.573 nm between the radicals in the pair. Unlike the spectrum of amorphous PC, the signal of radical pairs separated by CO in the spectrum of semi-crystalline PC sample exhibits dipole–dipole splitting $D_{\perp} = 17.8\text{ mT}$. This value corresponds to the inter-spin distance of

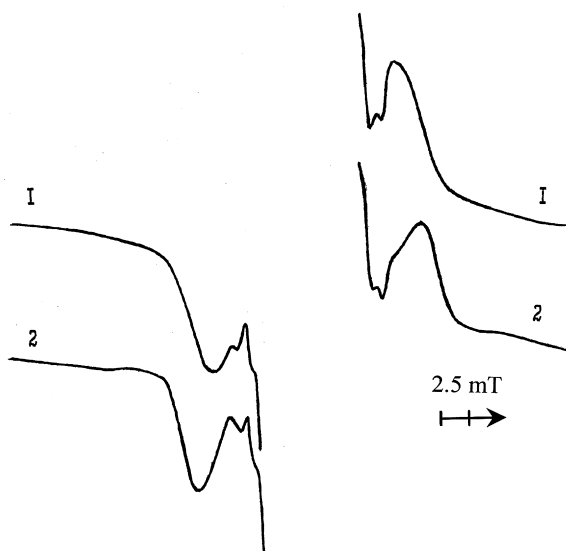


Fig. 3. ESR spectra of: (1) amorphous, and (2) semi-crystalline PC irradiated at 77 K to the dose of 165 kGy.

0.538 nm between the radicals in the pair. Actually, different values of the dipole–dipole splitting (15.0 and 18.1 mT) for the radical pairs in irradiated PC were reported previously in Refs. [4,5], respectively; however, to the best of our knowledge, this difference was not explained or even discussed. We shall address later the discussion concerned with the inter-spin distance in the pair. Now, we should note that the yield of the radical pairs separated by the CO molecule is less by ca. 15% in semi-crystalline samples in comparison with the amorphous ones. This result is in good accord with the IR spectroscopic data concerning the effect of the PC crystallinity on the CO yield (see above). In addition to the signal arising from allowed transition ($\Delta M_s = 1$, i.e. in the region of $g \approx 2$), we also detected a characteristic signal resulting from forbidden transition in the spectrum of radical pairs ($\Delta M_s = 2$, $g \approx 4$) for both types of PC. It is well known [15] that the intensities of the signals corresponding to forbidden and allowed transitions for disordered samples are related by the equation:

$$I(\Delta M_s = 2)/I(\Delta M_s = 1) = 4/15(D_{\parallel}/2H_0),$$

where $I(\Delta M_s = 2)$ is intensity of the signal corresponding to forbidden transition; $I(\Delta M_s = 1)$ is intensity of the signal corresponding to allowed transition; $D_{\parallel} = 2D_{\perp}$ is a parallel component of dipole–dipole splitting; H_0 is the external magnetic field strength.

Using this ratio, one can estimate the contribution from radical pairs into the total concentration of paramagnetic species trapped in PC. The calculated value of $I(\Delta M_s = 2)/I(\Delta M_s = 1)$ for amorphous PC is 6.53×10^{-4} , which agrees well with the published data [5]. In view of this, it turns out that the integrated intensity of the signal of the radical pairs at $\Delta M_s = 1$ amounts to ca. 66% of the total integral intensity of the signal observed in the region of $g \approx 2$. Assuming the equal probability of the transitions for

doublet and triplet states (isolated radicals and radical pairs, respectively) [16], that is assuming $J \ll kT$ (J — the singlet–triplet splitting for a radical pair), we can estimate the ratio of the number of radicals in pairs to the number of isolated radicals directly from the ratio of the integrated intensities of corresponding signals in the region of $g \approx 2$. This means that the fraction of radicals trapped as correlated radical pairs separated by the CO molecule is ca. 66% of the total amount of paramagnetic species observed in amorphous PC irradiated at 77 K. The same procedure gives the value of 57% for semi-crystalline PC. Both these values are high enough. This means that the homolytic PC-chain scission that resulted in the formation of radical pairs separated by the CO molecule is the predominant way of radiation-induced processes in PC.

Absorption bands with the maximum at 2113 cm^{-1} show similar dose dependence for the spectra of amorphous and semi-crystalline samples in the region of small doses (Fig. 2, right). As the dose increases, the build-up of this component reveals an essential difference. This means that the probability of CO trapping in the proximity of a negative ion is smaller for semi-crystalline samples than for amorphous ones in the region of large doses. While annealing a sample at 200 K, decay of the band with the maximum at 2113 cm^{-1} is less efficient for semi-crystalline samples than for amorphous ones (by 10 and 60%, respectively), i.e. disappearance of the negative ions in the crystalline region occurs at higher temperatures.

To explain the mechanism of the formation of a CO molecule in the proximity of negatively charged PhO^- -type ions, we should turn to the ESR results. According to ESR data [7], amorphous PC irradiated to the dose of ca. 10 kGy exhibits a strong narrow singlet signal. The origin of this singlet is still under discussion. According to Ref. [3], this feature in irradiated PC results from electrons stabilised in inter-molecular traps. However, the origin of a similar-type signal observed in low-molecular-weight carbonates is not clear [17–22]. In particular, detailed study of the spectrum of simple dialkyl carbonates using ^{13}C -labelling of the carbonate moiety revealed that the signal under consideration should rather originate from intramolecular stabilisation of the excess electron (radical anion) [18]. Comparison of the ESR spectra of PC samples with different crystallinity after the irradiation to the dose of 9 kGy shows that the fraction of the narrow singlet ascribed to trapped electrons is less by ca. 1/3 for semi-crystalline films of PC than for amorphous ones (Fig. 4). This result bears evidence for electron stabilisation in the inter-molecular traps predominantly existing in amorphous domains of PC. The process of electron trapping is known to be very sensitive to the phase state of the matrix; actually, excess electrons are trapped in glasses, but not in crystals [1]. The signals from monomeric radical anions of organic aliphatic carbonates (unlike trapped electrons) are characterised by considerable anisotropic hyperfine coupling with ^{13}C nuclei ($a_{\perp}(^{13}\text{C}) = 12.78 \text{ mT}$ for radical anions of ^{13}C -enriched dimethyl carbonate [18]). Obviously, using a high gain of the signal, one can

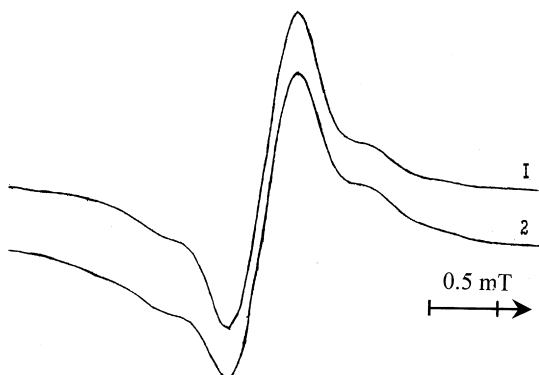


Fig. 4. ESR spectra of: (1) amorphous, and (2) semi-crystalline PC irradiated at 77 K to the dose of 9 kGy.

observe corresponding lines for the natural abundance of the ^{13}C isotope (1.1%). Such satellites were really detected for irradiated propylene carbonate [17]. In the case of diarylcarbonates and PC, ^{13}C -splitting is expected to be somewhat lower due to spin density delocalisation on to the benzene rings. Nevertheless, using even high enough gain, we failed to detect the doublet with a similar splitting in the case of PC (Fig. 5). The failure to detect the satellite lines of isotopic nature for both types of PC samples can result from electron stabilisation in inter-molecular-type traps (in this case the electron is not localised at one carbonate moiety, so the characteristic coupling with ^{13}C nuclei should not be observed).

Assuming the electron stabilisation in the inter-molecular-type traps, the formation of the negatively charged species in close proximity of CO molecule with the growth of irradiation dose can be explained by electron transfer from structural traps to PhO $^{\cdot}$ -type radicals in the pair separated by the CO molecule. This process is highly exothermic because of the considerable affinity of the PhO $^{\cdot}$ -type radicals towards the electron (i.e. the radicals are deeper traps). The probability of such a transition increases as a result of increasing concentration of the radicals as the dose grows. Lower efficiency of the build-up of CO associated with

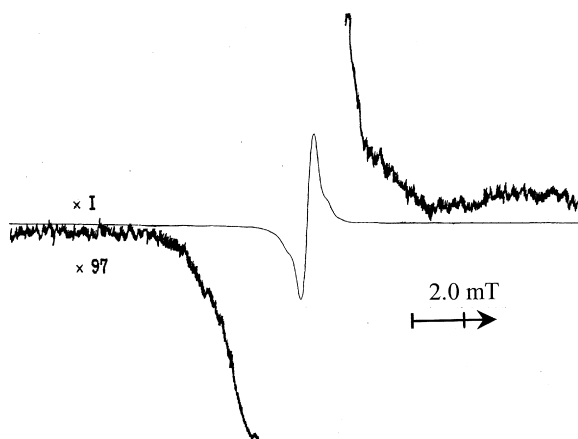
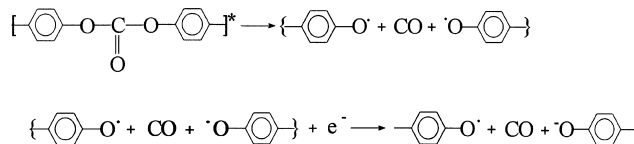


Fig. 5. ESR spectrum of PC irradiated at 77 K to the dose of 9 kGy.

Table 1
Splittings D_{\perp} (mT) for signals of radical pairs separated by CO molecule and observed in the spectra of PC irradiated at 77 K to the dose of 165 kGy, and in the spectra of PC/PBT blends irradiated at 77 K to the dose of 140 kGy, and corresponding distances between radical centres in a pair r (nm)

Blending time	D_{\perp}	r
Amorphous PC	14.8 ± 0.2	0.573
5 min	14.9 ± 0.2	0.571
1 h	16.1 ± 0.2	0.557
6 h	~ 17.2	0.545
Semi-crystalline PC	17.8	0.538

negative ions in semi-crystalline PC (Fig. 2, right) is likely because of predominant electron localisation in amorphous domains of the polymer. The electron transport at 77 K occurs rather via tunnel mechanism. So, the most probable mechanism of the CO localisation in the proximity of a negative ion may be described as follows:



Returning to the inter-spin distance, one can say that the smaller inter-spin distance in semi-crystalline samples witnesses that the equilibrium conformation corresponding to the crystalline phase features the minimum inter-spin distance. It is worthwhile noting that the definition “inter-spin distance” cannot be understood as the distance between two ether oxygen atoms because there is a considerable delocalisation of the spin density in the PhO $^{\cdot}$ -type radicals on to the aromatic ring [23]. In the amorphous sample, there is likely a variety of non-equilibrium (stressed) states with greater inter-spin distances. Such an explanation is in good agreement with irreversible decrease of the inter-spin distance as a consequence of matrix relaxation while annealing an irradiated sample at 200 K. This phenomenon was observed both by us, and in Ref. [5]. We also studied

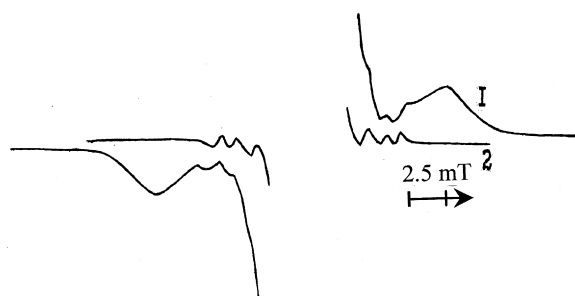


Fig. 6. ESR spectra of: (1) semi-crystalline PC irradiated at 77 K to the dose of 140 kGy; (2) amorphous PC irradiated at 77 K to the dose of 140 kGy and subsequently annealed to room temperature.

the formation of radical pairs in the blends of amorphous PC and PBT [7] with various blending times in the melt at 260°C, irradiation of PBT itself not giving any radical pairs, which may be mistaken for pairs produced from PC [7,24]. As the blending under the above circumstances advances, the degree of transesterification between components of the blend increases, going from negligible transesterification (5 min blending time) through block-copolymer (1 h blending time) to statistical copolymer with essential destruction (6 h blending time) [6,7]. Increasing the blending time results in a discernible increase in D_{\perp} for radical pairs separated by CO molecule originated from PC (Table 1). This implies that the effective spin–spin distance in the pair decreases. As was stated above, PC crystallisation results in decrease in the distance between radical centres in a pair, probably as a result of PC-chain relaxation. One may suggest, that PBT fragments penetrate into the PC phase in the course of blending, thus acting as PC plasticisers. The effect of PBT plasticiser is much more expressed for blends, where transesterification has taken place, because in this case rigid sequences of PC backbones, which prevent PC chains from being mobile, would be interrupted by more flexible PBT sequences. Such an increase in PC-chain mobility in the blend with PBT, which results in a rapid enough crystallisation of PC under circumstances of appropriate annealing as contrasted to failure of crystallisation of pure PC under the same circumstances, was reported, for example, in Refs. [25,26]. Thus, increase in the mobility in a melted blend leads to relaxation processes. This structure relaxation is detected after irradiation of the blends through the change of the inter-spin distance in the radical pairs.

The “wings” of the ESR spectrum of irradiated PC exhibit a number of lines of small intensity. The interpretation of these features is easier for semi-crystalline PC because of less overlap with lines of radical pairs separated by the CO molecule. After short-term annealing the sample at the room temperature the radical pair signals vanish, and the appearance of the spectrum “wings” becomes consistent with spectrum of the cyclohexadienyl-type radicals (Fig. 6) in accordance with Ref. [5]. For this reason, and in view of the above-mentioned, we can note that our previous assignment of a pair of these lines to the signal of ^{13}C -substituted radical anion [7] was probably incorrect. In the present work the analysis of saturation behaviour of the lines ascribed to the cyclohexadienyl-type radical reveals a different degree of saturation of the components before annealing the sample. The utmost lines separated by 12.5 mT saturate more readily than other pairs of these lines. According to Ref. [5], the signal of radical pairs separated by the CO_2 molecule with $D_{\perp} = 9.0$ mT (i.e. inter-spin distance is 0.676 nm) was detected in the spectrum of irradiated diphenylcarbonate. Supposing the similarity of g -factors for both kinds of radical pairs (separated by CO and CO_2 , respectively), one can assume that the signal of

pairs separated by CO_2 can contribute to the middle line of the low field triplet, and to the inner line of the high field triplet of cyclohexadienyl-type radical signal, these lines of the triplets being separated by 8.8 mT. Therefore, the observed difference in saturation may be explained by the presence of these pairs (the signals from the radical pair show saturation at higher microwave power than the signals from isolated radicals).

3.2. Formation of CO_2

The single band with the maximum at 2336 cm^{-1} was observed [6] for amorphous PC irradiated at 77 K. The same band maximum of the radiolytically produced CO_2 was detected for semi-crystalline PC.

The CO_2 build-up curve (integrated intensity versus dose) for semi-crystalline samples resembles qualitatively that for amorphous samples (Fig. 7). However, efficiency of the CO_2 formation is less in the case of semi-crystalline samples. The integrated intensity of the CO_2 absorption band for semi-crystalline PC is approximately equal to 75% of that in the spectrum of an amorphous sample within the dose range studied.

While going from the amorphous samples to semi-crystalline ones, the CO_2 formation, which probably requires larger activation volume, may be inhibited to a greater extent than the formation of CO monitored by the band with the maximum at 2132 cm^{-1} (see above).

The half-widths of the absorption band of CO_2 for both types of the PC samples remain virtually unchanged in the course of the irradiation and diminish a bit (by 0.2–

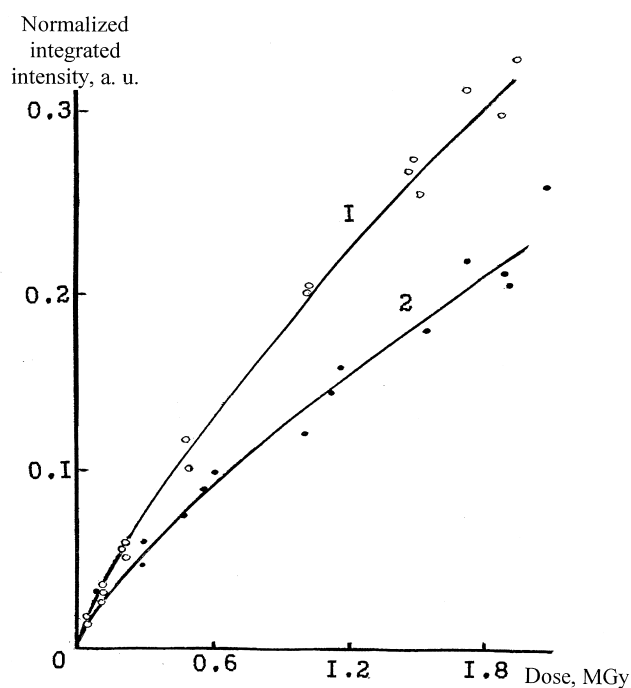


Fig. 7. Dose dependence of integrated intensity of CO_2 absorption band for: (1) amorphous (○), and (2) semi-crystalline PC (●).

Table 2
Half-widths (cm^{-1}) of bands of CO_2 molecules in the spectra of samples irradiated at 77 K to the dose of 1.0 MGy

Sample	Amorphous PC	Semi-crystalline PC	Amorphised PET	PET as received	Amorphised PBT	PBT as received
Half-width	5.0 ± 0.4	5.5 ± 0.4	6.7	7.6	7.2	7.6 ± 0.8

0.3 cm^{-1}) during the annealing of an irradiated sample at 200 K (Table 2). The half-width of the absorption band of CO_2 for semi-crystalline PC is somewhat larger than that for amorphous samples. The similar difference in half-widths of the absorption band of CO_2 was also detected for a pair of samples of PBT and PET studied by us. Within each pair of samples, one sample having greater degree of crystallinity has greater half-width of the absorption band of CO_2 . The cause of this difference is likely a smaller free volume in the samples having greater degree of crystallinity. This results in a possibility of “fixation” of CO_2 molecules in some unrelaxed states. The small decrease in half-width as a result of annealing PC samples at 200 K may be a result of thermal relaxation of disturbed CO_2 molecules.

4. Conclusions

The low-temperature spectroscopic studies allow one to assign rather “subtle” effects in the composition, distribution and local environment of the products of radiolysis of complex polymeric systems. Such a possibility is illustrated well by detailed investigation of the spectroscopic characteristics of the products of radiation-induced destruction for PC and PC-based systems.

Generally speaking, both ESR and IR spectroscopic data manifest that the yields of primary degradation products in irradiated semi-crystalline PC are somewhat lower than those in amorphous polymer. This is just what was expected from simple qualitative considerations taking into account the “cage effect”. However, even more significantly, the results obtained show directly the variations in the spectroscopic parameters of the radiolysis products with variations in the sample microstructure. This implies that the spectroscopic probing may reveal fine details of both radiolysis mechanism and sample microstructure.

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