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Relaxation processes in poly(butylene terephthalate) studied by the spin probe spectroscopy

RAPID COMMUNICATION

Summary: The results of investigations of relaxation processes in an amorphous part of poly(butylene terephthalate) (PBT) are presented. Electron paramagnetic resonance (EPR) measurements in the version of a spin probe method (ESR) were performed in the temperature range of 4–380 K. The study has revealed that in the low temperature range the spin probe behavior reflects the relaxation process (γ) identified previously by other methods. The microwave power dependence of the ESR signal intensity indicates the usefulness of the saturation transfer method in the investigations of PBT and other polymers.

Key words: poly(butylene terephthalate), electron spin resonance (ESR), spin probes, relaxation processes.

Poly(butylene terephthalate) (PBT) has aroused a wide interest not only because of its interesting properties but because it is also used as a basic component of polymer materials, including multiblock elastomers [1–4]. There is a need of studying this compound by various dynamical physical methods using different frequencies [1–5]. The electron spin resonance (ESR) measurements in the version of spin probe method belongs to those which allows to study the mobility of polymer chain fragments and *e.g.* the behavior of stabilizer molecules in the polymers [6–8]. Nitroxide spin probe or spin label method have been used to study the motional effects in polymers in the three frequency ranges:

Fast (*F*): 10^{-11} – 10^{-9} s,

Slow (*S*): 10^{-9} – 10^{-7} s,

Very slow (*VS*): 10^{-7} – 10^{-3} s.

Hence, a direct comparison of the obtained results with those from NMR, a dielectric and ultrasonic measurement is possible. As a method of dynamics investigation of polymer systems it was usually applied to the fast and slow rotations and seldom to very slow rotations because the mobility in that range is studied by ESR spectrometers with large microwave powers. Besides, low temperatures were generally necessary in these studies.

Review of the literature [6–8] indicates that there is no *a priori* possibility of correlating the properties of macromolecules with the movement of the spin probe, *i.e.* no correlation of the spin probe movement with a specific type of the relaxation process (glass transition, segmental motion, local motion) of the polymer matrix in a wide range of temperature and frequency could be established.

A version of the spin probe method in which the ESR spectrum of a radical (paramagnetic center) depends on the applied microwave power is called the saturation method. To the best of our knowledge PBT was not studied by the ESR technique. This paper presents the measurements done in the *F* and *S* ranges. Preliminary investigations were also carried out in the *VS* range. These relaxation processes require investigations in the temperature range of 4–380 K, that is *ca.* 330 K below the polymer glass temperature and *ca.* 50 K above this temperature T_g (\approx 330 K), in order to obtain information on methodological aspects of that type of studies. One can hope that the results obtained for PBT may help in a proper interpretation of the measurements for more complex systems, *e.g.* multiblock elastomers.

EXPERIMENTAL

PBT with molecular weight $M_w \approx 35\,000$ was synthesized in the Department of Chemical Fibers and Physical Chemistry of Polymers, Technical University of Szczecin, Poland (see [9]).

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2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl [nitroxide radical $C_9H_{18}NO$ — Tempo, see Formula (I); $m = 156$] was used as a spin probe in concentration smaller than 0.01 wt. %. ESR measurements were carried out using a standard X-band Bruker E500 spectrometer with a variable microwave power in the 0–100 mW range. Oxford Instruments helium flow cryostat was used to study temperature dependence of the ESR spectra in the 4–380 K range. From the obtained, complete and — to a high degree — typical ESR spectra, the parameters which appear in equations (1) and (2) (see further text) were selected. The choice of parameters is illustrated in Fig. 1 and their meaning is given in explanation to eqs. (1) and (2).

RESULTS AND DISCUSSION

Figure 1. presents some representative ESR spectra with the parameters used for the calculation of the correlation times (τ). One can see that the studies in 4–380 K temperature range correspond to the above mentioned three mobility ranges (*F*, *S* and *VS*) of the spin probe. At low temperatures the ESR spectra exhibit a saturation effect related to the microwave power. At temperature around 70 K (depending on the microwave power) an apparent disappearance of ESR signal and an increase of the background noise is observed. The remaining low intensity and complicated ESR spectrum resemble a powder spectrum (see Fig. 1f).

Very similar results are obtained in a computer simulation of powder spectra for standard values of *A* and *g* tensors [6, 7] by using *e.g.* Bruker simulation program "Simfonia". Spectra, similar in the appearance to that in Fig. 1f, consisting of many narrow lines, are easily obtained assuming the linewidth of 0.01 mT for an individual line and several hundred of different orientations of radical in a sample. An increase of radical orientations to several thousand or an increase of the linewidth leads to the smoothing and changing appearance of the resultant spectrum.

In these studies the last type of spectrum was not investigated in details, so it will be not discussed further. However, it seems that the effect of spectrum change could be considered as a contribution to the discussion on "polymer powder" definition, *i.e.* in a sense of possibility of approximate estimation of sample coarseness.

In the fast rotation ranges, assuming isotropic mobility of the spin probe, the following relation was used [6]:

$$\tau(in\ s) = 6,65\Delta H_{(+1)} \cdot \left[\left\{ I_{(+1)} / I_{(-1)} \right\}^{\frac{1}{2}} - 1 \right] \cdot 10^{-10} \quad (1)$$

where: $\Delta H_{(+1)}$ — the linewidth of the low-field line, $I_{(+1)}$, $I_{(-1)}$ — the amplitude of the low- and high-field lines, respectively.

In the slow rotations range study of the motional effects, the following relation was used [6–8]:

$$\tau = a(1 - S)^b(32/A_{zz}^*) \quad (2)$$

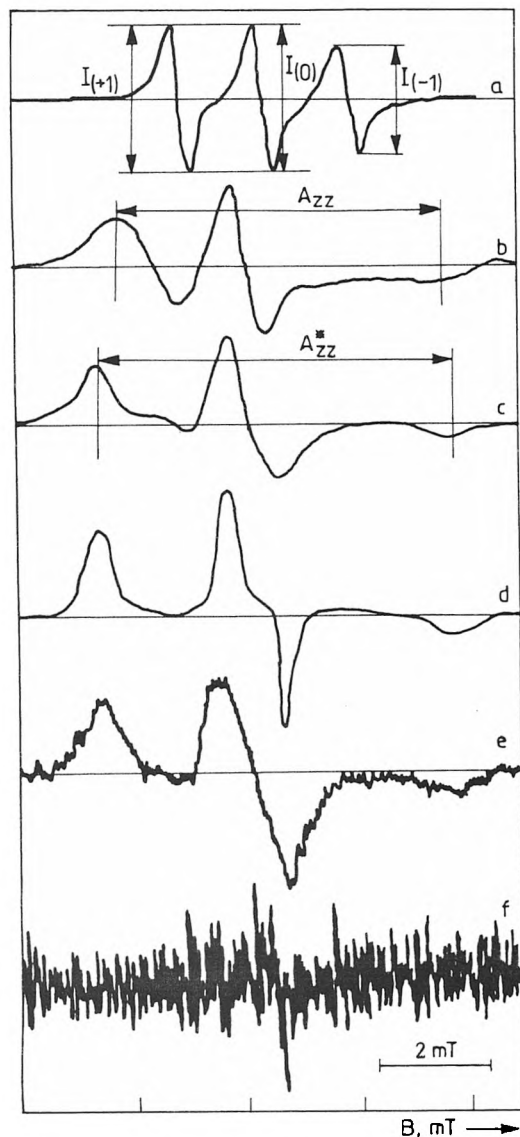


Fig. 1. The spectra of Tempo in the regime of fast (a), slow (b), and very slow rotations (c), as well as in conditions of partial saturation ($T = 130$ K; 15 dB attenuation) (d), higher saturation ($T = 70$ K; 29 dB attenuation) (e) and powder spectrum at 4 K and 20 dB (f)

where: $S = A_{zz}(\tau) / A_{zz}(\tau \rightarrow \infty)$; $A_{zz}^* = 3,34$ mT [6]; *a* and *b* are constants [6, 7].

The A_{zz} parameter is defined in Fig. 1 (spectra a and b) as separation of outer extremes of the spectrum. The dependence of A_{zz} on the temperature is presented in Fig. 2. Equation (2) could be used assuming the isotropic rotations of the spin probe and the application of a specific spin probe movement model, *e.g.* by using dimensionless parameter *R* described in [6, 7], characterizing the shift of the outer ESR lines.

Unfortunately, more detailed study of its variations is not possible based on these measurements. The obtained approximate value of $R \sim 1.5$ indicates the possibility of description of the spin probe motion by the free diffusion model which is an intermediate case between usu-

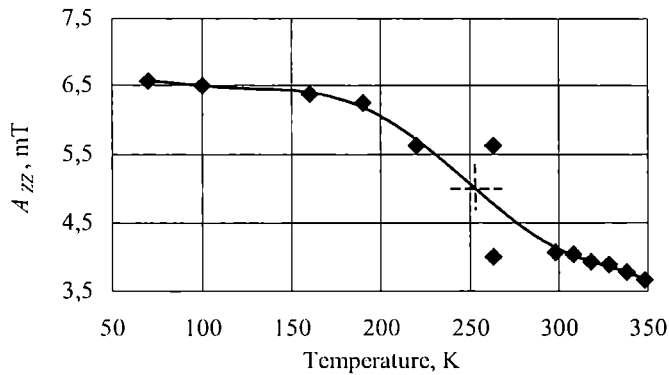


Fig. 2. Dependence of the outer extrema separation A_{zz} on temperature T . The dotted cross indicates the value of T_{50G} . The solid line is the guide to the eyes only

ally applied Brownian and strong diffusion models [6, 7]. Taking into account that in the high temperature range (≈ 380 K) the linewidth of the $m = +1$ line is approximately 0.3 mT, based on the papers [6, 7], the following pair of numbers $a = 1.1 \cdot 10^{-9}$ s; $b = -1.0$ can be used. The results of the correlation time calculations in F and S ranges (after conversion to frequency: $f = \frac{1}{2}\pi\tau$) [8] are presented in a condensed form in the relaxation diagram of PBT (Fig. 3). This diagram was prepared using the results of our own dielectric measurement [3], the dielectric studies of others [10–12] and NMR results [5].

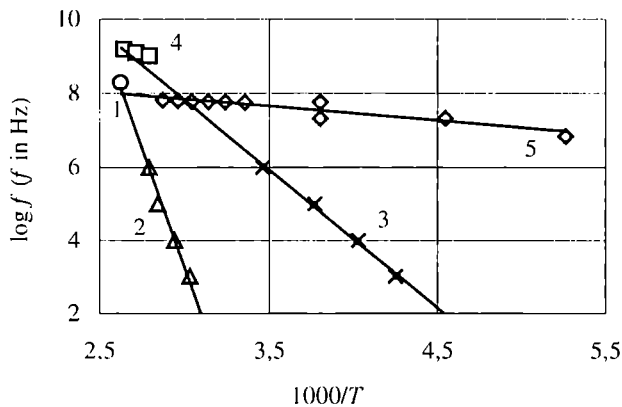


Fig. 3. Diagram of relaxation of PBT; 1— α -relaxation, NMR data [4]; 2— α -relaxation, dielectric data [3, 10–12]; 3— β -relaxation, dielectric data [3, 10–12]; 4— $\alpha + \beta$ -relaxation, ESR data calculated from eq. (1); 5— γ -relaxation, ESR data calculated from eq. (2)

As one can see in Fig. 3 for PBT in the high temperature region, i.e. for $T \approx 360$ – 380 K, the behavior of small Tempo-type probes corresponds to the merged relaxation named $\alpha + \beta$, where α denotes the glass transition and β denotes the segmental motion of an amorphous part of PBT. At lower temperatures the spin probe traces probably the β -relaxation in a narrow temperature range, which is typical for small probes below T_g [8].

At still lower temperatures the spin probe reflects the low temperature γ -relaxation. This relaxation was often attributed to the rotations of methylene groups [8, 13]. From the ESR studies, the activation energy of 11.4 kJ/mol was calculated which according to the data of other authors [8, 12] might be regarded as a typical value for such a process.

It is remarkable, that in the dielectric measurements carried out in the recent years [3, 10–12], this process was not detected. However it was found in polycesters and polyamides [7, 13]. That is in the systems containing $(-\text{CH}_2)_n$ sequences.

Illers and Breuer [14] reported an asymmetry of the 0.1 Hz dynamic mechanical β -peak, which they attributed to the superposition of a lower temperature component involving the motion of $-\text{CH}_2$ groups and a higher temperature component involving the $-\text{COO}$ motions. This is to be expected as the $-\text{CH}_2$ component will not contribute significantly to the dielectric loss peak but this component might, due to the collisions, influence the spin probe motion. Another additional suggestion, that γ and not β process is involved, comes from the temperature dependence of A_{zz} parameter (Fig. 2). As it was reported in details in [8], there is a correlation between the T_g temperature, determined usually from the low frequency measurements, and T_{50G} parameter determined as temperature at which the separation of the outer spectra extremes is equal to 50 Gs. From the discussed correlations it follows that $T_{50G} \approx T_g + 50$ K. The position of the dotted cross in Fig. 2 indicates clearly, that the above relation is not even approximately fulfilled for PBT because for our measurements $T_{50G} (\approx 250 \text{ K}) < T_g (\approx 330 \text{ K})$.

Saturation studies may conceivably confirm Illers's and Breuer's [14] proposal because these studies allow to determine the very slow correlation times.

We have found in the saturation experiments that:

— An increase of the microwave power results in the line broadening and decrease of the line amplitude. The characteristic curves are presented in Fig. 4. The inten-

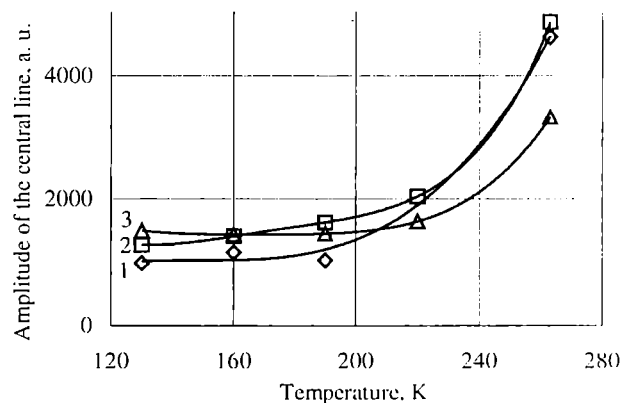


Fig. 4. The dependence of the amplitude of the central-spectrum line ($m = 0$) on the temperature at various attenuations: 1—5 dB, 2—8 dB, 3—15 dB

sity around 263 K is several times stronger than at 70 K and several tens times stronger than at 4 K (practical disappearance of the signal). This effect is clearly visible at around 100 K; at lower temperatures the spectrum changes to powder spectrum.

— An increase of the temperature (at a constant microwave power) results in an abrupt signal amplitude increase as is shown in Fig. 5.

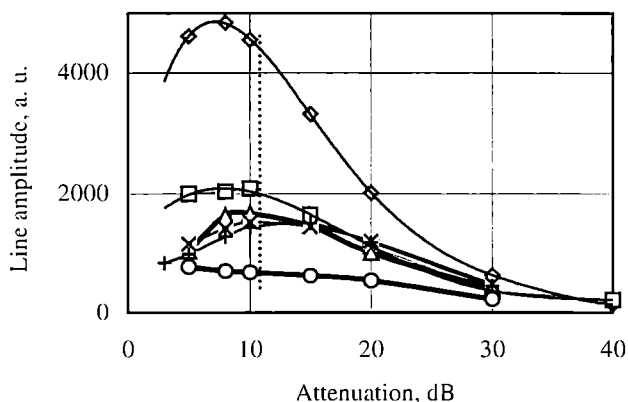


Fig. 5. The dependence of the amplitude of the central line ($m = 0$) on the microwave attenuation various temperatures; the dotted line crosses the experimental curves in the following order (from above): $T = 263; 220; 190; 160; 130; 70$ K

A comparison of the temperature mentioned above with the position of γ relaxation on the extended relaxation diagram suggests that this effect might be the result of hitting on that relaxation and a subsequent saturation of the ESR signal.

Both the findings give a possibility of obtaining an information on long correlation times (VS -region) and the extension of relaxation diagram to lower temperatures (Fig. 4). These effects will be the subject of further analysis and studies also for other polymers.

CONCLUSIONS

Application of the spin probe method leads to an increase of knowledge on the relaxation processes in the polymers. In case of PBT these processes are: merged glass and segmental motion relaxations at higher tem-

peratures (above T_g) and the local relaxation processes connected most probably with the movements of methylene groups at low temperatures (below T_g). Spin probe experiments described above indicate the usefulness of modern ESR spectrometers in the study of relaxation processes in the polymers, by saturation effects, particularly for study of the low-temperature relaxations, usually connected with the motions of small molecular entities.

Information about these processes is obtained from ESR studies at high microwave powers. The above presented study points out on the need of caution in the interpretation of the spin probe spectra, particularly at low (\approx tens K) temperatures and for limited EPR frequencies ($\approx 10^4$ Hz).

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