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PBT chain mobility from the ESR saturation spectra studies

RAPID COMMUNICATION

Summary — Temperature and microwave power dependence of ESR spectra of the spin probes in PBT has been studied. The observed changes of ESR signal allowed to determine the long correlation times ($\tau \approx 10^{-4}$ — 10^{-5} s) as well as other parameters characterizing the saturation processes and involved relaxation processes. It was established that at low temperature range (≈ 120 — 200 K) the rotational mobility of used nitroxide radicals was related to local relaxation processes of the methylene sequences (3—4 CH₂ groups) in an amorphous region of PBT. The obtained results show the possibility of that type of investigation also for other polymers. Determination of polymer properties *via* analysis of parameters obtained in saturation experiments is also raised.

Keywords: poly(butylene terephthalate), electron spin resonance (ESR), spin probes, relaxation processes, ESR saturation effects.

In our previous paper the results of relaxation processes investigations in an amorphous part of poly(butylene terephthalate) (PBT) have been presented [1]. ESR spin probe method [2—4] has been used at 4—380 K temperature range and 10^7 — 10^9 Hz frequency range. The possibility of extension of that work by studies of saturation effects has been also noted. The obtained results indicated that the rotational mobility of small spin probes in PBT was related to γ relaxation [1]. This relaxation observed at low temperature is not sufficiently studied so far and usually attributed to the methylene groups [3, 5]. However, the limitations of the spin probe method considered, as not a direct method of relaxation process investigations should be taken into consideration. Taking into account the dimensions of the used probe (≈ 3.5 Å) [4] and the kinetic fragments of the PBT chain $-(\text{CH}_2)_4$ or $-(\text{CH}_2)_4\text{-O-CO-}$ the discussed relaxation is probably the last one that could be studied by the conventional ESR, *i.e.* to the frequencies $\approx 10^4$ Hz in a mode of continuous saturation [2—4, 6, 7]. This possibility could be verified by extrapolation of data from [1] on the relaxation diagram into the range of low temperature and the comparison with the saturation study results. In this paper an attempt to confirm this proposition is described as well as the use of other parameters obtained in the saturation investigations in the process

of clarification of the polymer dynamics. Similar studies, although for a narrower temperature range, were carried out for the biological systems [8—10]. Polymers have been rarely studied and some earlier results were presented in [2—4].

EXPERIMENTAL

PBT showing the molecular weight $M \approx 35\,000$ was synthesized according to [11] in the Department of Chemical Fibers and Physical Chemistry of Polymers, Technical University of Szczecin. Densities of amorphous and crystalline phases were: $\rho_a = 1.26$ g/cm³ and $\rho_c = 1.33$ g/cm³ respectively, while crystallinity degree = 55—75%.

2,2,6,6-Tetramethylpiperidine-1-oxyl (C₉H₁₈NO; TEMPO) nitroxide radical (molecular weight $M = 156$) was used as a spin probe in a concentration < 0.01 wt. %.

ESR measurements were carried out in a standard "X-band Bruker E500" spectrometer with variable microwave power in 0—100 mW range. Conventional ESR registration mode, that is, the first derivative of absorption signal was obtained in conditions of continuous saturation (CW) [2, 6].

Oxford helium flow cryostat was used to study temperature dependence of ESR spectra at the 4—263 K

range. From the obtained three-line ESR spectrum the intensity of the central line ($m = 0$) was chosen and analyzed [1].

RESULTS AND DISCUSSION

Saturation characteristics

Saturation characteristics presented previously (Fig. 5 in [1]) are redrawn in Fig. 1 by changing the axes. On x-axis instead microwave power attenuation (in dB) now the square root of microwave power $P^{1/2}$ is given.

These curves were simulated using the following equation:

$$I(m=0) = A \cdot P^{1/2} [1 + (2^{1/\epsilon} - 1)P/P_{1/2}]^{-\epsilon} \quad (1)$$

where: I — intensity, A — the scaling factor, $P_{1/2}$ and ϵ — adjustable parameters.

$P_{1/2}$ is the power at which the first derivative amplitude is reduced to half of its unsaturated value, ϵ is a measure of the homogeneity of saturation of the resonance line. For the homogenous and inhomogenous saturation limits, $\epsilon = 1.5$ and $\epsilon = 0.5$, respectively. Fig. 1. suggests that our results correspond to an intermediate case between the homogenous and inhomogenous broadening. Satisfactory agreement between the experimental and simulated curves could be seen.

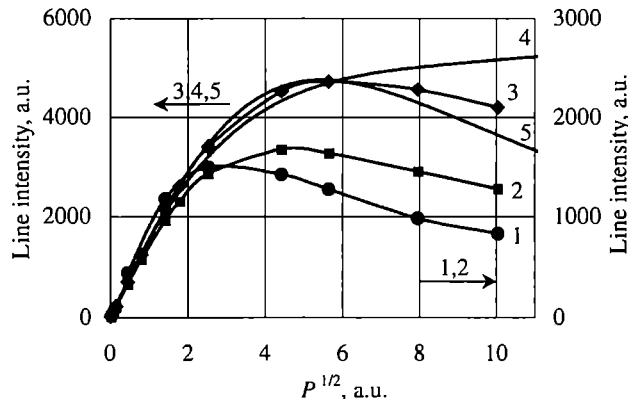


Fig. 1. Example of fitting of experimental curves to the eq. (1): 1, 2, 3 — experimental and calculated curves for 130, 190 and 263 K, respectively; 4, 5 — calculated curves in the case of inhomogenous ($\epsilon = 1.5$) and homogenous ($\epsilon = 0.5$) saturation, respectively; the other parameters in eq. (1) are assumed to be the same as obtained for $T = 263$ K

In order to elucidate the role of these results in understanding polymer dynamics the $\epsilon(T)$ and $P_{1/2}(T)$ dependences have been analyzed (Fig. 2). The parameter $P_{1/2}(T)$ decreases linearly with the temperature decrease what makes the ESR signal easier to saturate. Extrapolating the straight line describing $P_{1/2}(T)$ to zero, the temperature around 98 K could be calculated what explains the lack of signal below this temperature even at low micro-

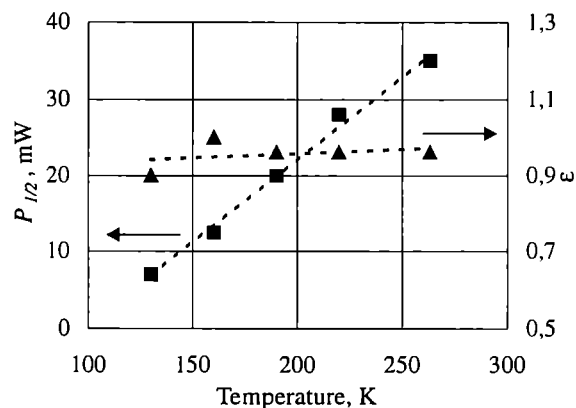


Fig. 2. Temperature dependencies of $P_{1/2}$ and ϵ

wave powers. This transition was also observed in NMR investigation [12]. As could be seen in Fig. 2, the value of ϵ is around 1.0 what is an intermediate value between limiting values (0.5 and 1.5) and seems to be temperature independent. Whether this is an universal behavior is difficult to decide now due to the lack of such data for other polymers.

Calculations and analysis of the correlation times

For a very slow rotation regime the saturation effects are used by studying the dependence of the line intensity and line width on the magnetic field of a microwave. The knowledge of $Z^{(m)}$ parameter, and particularly $Z^{(0)}$ enables the determination of long relaxation times in the range of typical (CW) saturation measurements ($\sim 10^5$ — 10^6 Hz) using the ESR method [2, 4, 7]. $Z^{(0)}$ is expressed by the following formula:

$$Z^{(0)} = I^{(0)}(\text{sat}) / I^{(0)}(\text{nonsat}) \cdot B(\text{nonsat}) / B(\text{sat}) \quad (2)$$

where: $I^{(0)}(\text{sat})$, $I^{(0)}(\text{nonsat})$ — intensities of the central line ($m = 0$); $B(\text{sat})$, and $B(\text{nonsat})$ — magnetic field in conditions of saturation (large power of microwave) and without saturation (low power of microwave), respectively.

Our calculations involved the central line ($m = 0$) of the spectrum described in [1] and the value of correlation time (t) was determined from $Z^{(0)}$ values calculated from eq. (2) and $Z^{(0)}(\tau)$ dependence [7].

As it was done previously, change of variables, according to $f = 1/(2\pi\tau)$ (f — frequency), was made. Because of the relation $B \sim P^{1/2}$, the parameters of the experimental spectrum are usually presented as a function of $P^{1/2}$ (Fig. 1.) and difficult to determine absolute values of magnetic field B are not necessary to calculate the τ or other parameters. The ESR signal allowed to determine long correlation times ($\tau \equiv 10^{-4}$ — 10^{-5} s). The location of such determined values at the relaxation diagram (Fig. 3) is consistent with the previous ESR results [1] and confirms that the observed spin probe mobility could be related to the relaxation of methylene sequences (groups) in PBT, designated usually as γ relaxa-

tion. Other examples of relaxation of this type could be found in [1, 3, 4, 12].

The physical meaning of $P_{1/2}$ parameter could be deduced from comparison of the relaxation curves and the $P_{1/2}$ parameter (see Fig. 3). The non-zero value of $P_{1/2}$ seems to vanish at temperature close to the temperature of the appearance of γ relaxation at frequency of 10^4 Hz. Based on this study, the decrease in $P_{1/2}$, and the decrease or vanishing of the ESR signal (or sometimes transformation to the powder spectrum) could be related to the appearance (or disappearance) of γ relaxation.

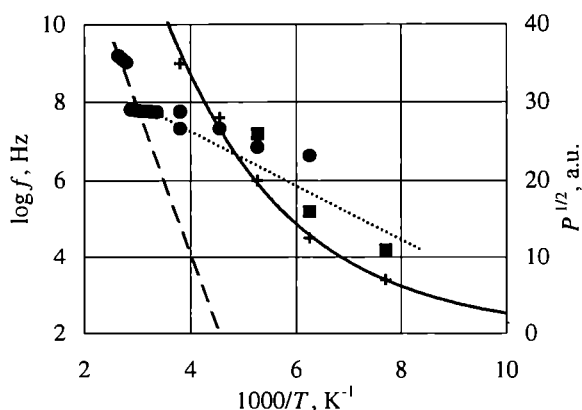


Fig. 3. Relaxation diagram for PBT and some results of the saturation investigations: dashed line — relaxation run based on [1], ● — the results of earlier ESR investigations [1], ■ — the saturation ESR results (this work), dotted line — common regression line (● and ■), + — the temperature dependence of $P_{1/2}$ parameter

However, it should be added that the spin probe method is not a direct method of investigation of the relaxation processes in the polymers. After attributing the probe mobility to a polymer relaxation — for example using the relaxation diagram — often a question arises about the mechanism of the spin probe interaction with the polymer chain. The question could be formulated in another way: what mobile fragments of the polymer chain activate the probe rotations?

The review papers [3, 4] deal with this question. The answer is usually expected in finding relation between the geometrical size of the spin probe and the kinetic fragment of the chain. Another way is to find a similar relation between masses of the spin probe and the polymer fragments. If the interaction of similar masses was a deciding factor, then for PBT it would mean that the interaction of the spin probe ($M = 156$) and methylene-ester fragments ($M = 170$) should be taken into consideration.

On the other hand, from NMR investigations of conformation structure of olefines chains, for example [3, 4, 12, 13], as well as from the similar analysis for poly(tetra-

methylenoxide) (PTMO) [14] or for natural rubber (NR) [3, 4] it results that the sizes of a 3—4 methylene sequences ($M \approx 60$) are comparable with the dimensions of spin probe used. Based on NMR investigations it is assumed that the relaxation of methylene groups was realized by the two jumps mechanism [13]. The most likely motions are three-bond motions involving either the relocation of a *gauche* (*g*) bond from the sequence ttg^{\pm} to $g^{\pm}tt$ or creation of the sequence $g^{\pm}tg^{\pm}$ containing two *gauche* bonds from all-*trans* (*t*) sequence ttt [13].

Moreover, the agreement between the activation energy of methylene groups in the systems not containing the ester fragments and the energy obtained by us from ESR method is noted. Törmälä [3] reported the value ~ 10 kJ/mol for the small probes and 9.5 kJ/mol from NMR measurements for poly(isobutylene) and similar values (9—12 kJ/mol) for other polymers. Bower [13] gives a value of 9.7 kJ/mol for methylene groups (no segmental motions) in isotactic polypropylene from NMR investigations, while according to Bojanowski [12] this value is 11.2 kJ/mol. We have obtained the value 11.6 kJ/mol.

Similarity of these results suggests that the interaction of the spin probe with $(CH_2)_{3-4}$ groups plays a decisive role in the spin probe mobility and enables the observation of this relaxation transition by the ESR method at low temperature.

CONCLUSIONS

— The described saturation effects indicate the usefulness of the saturation technique to study the relaxation processes in the polymers.

— In the semicrystalline polymers the spin probe penetrates the amorphous regions and saturation investigations provide information about the low-temperature relaxation processes — in case of PBT it is γ relaxation, which is usually related to the movements of methylene sequences.

— Deeper understanding of the meaning of certain parameters determined in such measurements requires investigation of a greater number of other polymers. We hope that such a study might establish a more precise relation between the parameters and the polymer structure. Such study has already been undertaken.

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KALENDARZ IMPREZ

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4—9 lipca 2004 r. Paryż, Francja. Międzynarodowe sympozjum pod egidą IUPAC w ramach Światowego Kongresu MACRO 2004: „40th International Symposium on Macromolecules”.

Organizatorzy: Centre National de la Recherche Scientifique (CNRS) + Université P. & M. Curie, Paris.

Tematyka: chemia polimerów — reakcje i procesy, architektura makrocząsteczek, techniki charakteryzacji polimerów, polimerowe układy kompleksowe, polimery do nowoczesnych zastosowań, przetwórstwo tworzyw sztucznych, nowe polimery komercyjne (artykuły tworzywowe, tworzywa inżynieryjne, elastomery).

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18—23 lipca 2004 r. Praga, Czechy. 11th International Conference on Polymers and Organic Chemistry 2004 (POC'04).

Organizator: Academy of Sciences of the Czech Republic, Institut of Chemical Process Fundamentals.

Tematyka: podstawowe nośniki polimerowe, katalizatory polimeryzacji, polimery w medycynie i bioche-

mii, elektro- i światłoczułe polimery funkcyjne, polimery w ochronie środowiska, przetwórstwo polimerów funkcyjnych, nowe polimery funkcyjne.

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22—27 sierpnia 2004 r. Seul, Korea. „XIV International Congress on Rheology — ICR 2004”.

Tematyka: Referaty plenarne uzupełnione nw. programem mikrosympozjów: 1. Reologia obliczeniowa 2. Niestabilność cieczy 3. Pianki, emulsje i środki powierzchniowo czynne 4. Żywność i biomateriały 5. Przetwórstwo materiałów 6. Modelowanie mikrostrukturalne 7. Nanoreologia i mikrostrumienika 8. Mechanika cieczy nienewtonowskich 9. Stopy polimerowe 10. Roztwory polimerów 11. Reometria i metody eksperymentalne 12. Kompozyty 13. Zawiesiny i koloidy.

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