Dynamics of soft segments phase in copoly(etherester) elastomers—a spin probe study

Franciszek Lembicz*
Institute of Physics, Technical University of Szczecin, Al. Piastów 17, 70-310 Szczecin, Poland

and Jerzy Słonecki
Institute of the Chemical Technology, Technical University of Szczecin, Al. Piastów 17, 70-310 Szczecin, Poland

Two oligodiols, poly(ethylene oxide)glycol and poly(propylene oxide)glycol, and synthesized copoly (etherester) elastomers having these oligodiols as soft segments were investigated by the spin probe method. It was found that the rotational mobility of the probes is connected with the local mode $\alpha + \beta$ and β-relaxations in these materials. Comparison of the results obtained with analogous data for poly(oxytetramethylene) and related elastomers have shown that the relaxation runs for all oligodiols are almost the same and no difference was found for elastomers.

(Keywords: spin probes; poly(ethylene oxide)glycol; poly(propylene oxide)glycol; copoly(etherester elastomers); electron spin resonance)

INTRODUCTION

Thermoplastic copoly(etherester) elastomers exhibit microphase separation. In the so-called soft segment phase the hard polyether blocks aggregate into crystalline domains which act as physical crosslinks. This amorphous rubbery phase is a mixture of flexible polyether segments and uncrystallized polyester hard blocks. In recent years many papers have been published (see for example ref. 1 and the references therein) on the subject of these copolyetheresters. Previously, we have shown the usefulness of the spin probe method for the investigation of the soft segment dynamics in these elastomers. The studies of poly(oxytetramethylene) (PMTO)[2] and elastomers based on it allowed us to draw a conclusion that the spin probe method gives valuable pieces of information concerning a local mode relaxation in the high frequencies region[3].

In the present paper we report the results of the investigations, using the above method, on two other ether oligodiols and on elastomers built from them in order to study, in a more systematic way, relaxational properties of elastomers as a function of a chemical structure of the soft segment.

EXPERIMENTAL

The oligodiols investigated here were: poly(ethylene oxide)glycol (PEO), molecular weight about 1000, (Hoechst, FRG) and poly(propylene oxide)glycol (PPO), molecular weight about 1000 (Zakłady Chemiczne Rokita, Poland). Both copoly(etherester) elastomers (CPEE) were synthesized as described in ref. 4 using the following components: PEO: 1,4-butanediol (4G): dimethyl terephthalate (T) = PEO CPEE and PPO:4G: T = PPO CPEE. The elastomers contained 50 wt% of tetramethylene terephthalate segments (4GT).

2.2.6.6-tetramethylpiperidin-1-oxyl-4-yl benzoate was used as a spin probe. Samples of the oligodiols were prepared for e.s.r. investigations by dissolving the crystallized radicals in molten oligodiols at about 340 K. The incorporation of free radicals into the copolymers was achieved through solution of the crystallized free radicals in benzene and swelling of the elastomer in this solution. Then the elastomerss was dried for a few hours at about 340 K and 1 kPa.

The free radical concentration and the measurement procedure were similar to that used previously[2,3].

RESULTS AND DISCUSSION

Temperature induced changes in the e.s.r. spectra of free radicals were investigated in the range of fast and slow rotations.

In the range of fast rotations the spectra recorded for all samples were typical three-line spectra characteristic of nitroxide radical in viscous liquids and polymers. Due to the aspherical structure of the probe two models of rotational reorientation for free radicals in polymer matrix have been considered: (i) rotations of spherical radicals in an isotropic medium as a first approximation; and (ii) rotations of aspherical radicals in an isotropic medium.

The calculations for rapid rotations region assuming model (i) were carried out using the following relation[5]:

$$\tau_{RR} = K_{m_1 m_2} \Delta B(m_2) [\{I(m_2)/I(m_1)\}^{1/2} - 1] \qquad (1)$$

where I is the line intensity, $\Delta B(m)$ is the line width, and $m = -1, 0, +1$ is the nuclear magnetic quantum number. We inserted the values $m_1 = -1$; $m_2 = +1$; $K_{-1,+1} = 6.65 \times 10^{-14}$ $\bar{m}(s/T)$ into equation (1).

The approach according to model (ii) enables the correction of the effective values of τ, derived from model (i), by taking into account the relative position of the paramagnetic fragment with respect to the main axis of the radical molecule. This correction was carried out by including the anisotropy parameter ε assuming that the free radical molecule is an ellipsoid:

$$\varepsilon = \left[\frac{I(0)}{I(+1)}\right]^{1/2} - 1 \Bigg/ \left[\frac{I(0)}{I(-1)}\right]^{1/2} - 1 \qquad (2)$$

In the range of slow rotations the calculations were performed using the equation given in refs. 5 and 6:

$$\tau_{SR} = a(1 - S)^b \qquad (3)$$

where a and b are constants depending on the postulated model for diffusion and S is the ratio of the separation between the external extremes of the spectrum for a given temperature to its maximum value. Prior to the application of equation (3) one has to decide about the model of the tumbling leading to a proper choice of the a and b values in equation (4). This can be solved by the analysis of the change in the R parameter defined below[5]:

$$R(\Delta B_{+1}) = \frac{\Delta B_{-1}}{\Delta B_{+1}}$$

where ΔB_{-1} and ΔB_{+1} are the shifts in the position of the high and low field extremes.

Comparison of the theoretical and experimental data presented in *Figure 1* indicates that the motion of the probe in elastomers and oligodiols, except PTMO, is close to that described by the model for Brownian diffusion. A better agreement between the theoretical and experimental data cannot be expected because of substantial experimental errors and because the theoretical curve was obtained assuming isotropic rotations of the probe. As shown below this latter assumption is not fully justified. Therefore also taking into account that the 'final' line width is about 0.2 mT, the following previously
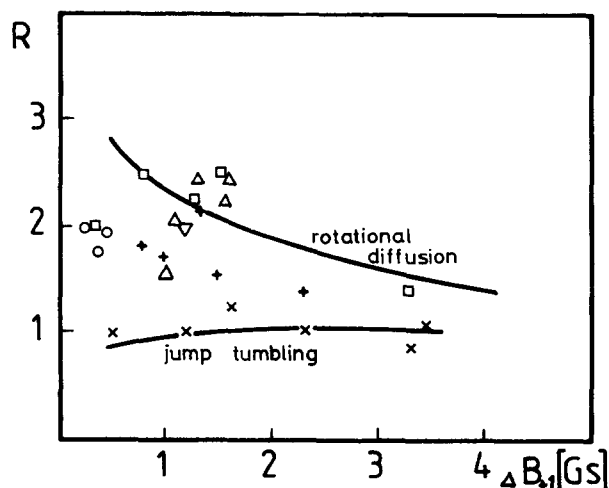

Figure 1 Theoretical and experimental dependence of the parameter R on ΔB_{+1} for: (O), PEO CPEE; ($\triangle$), PPO CPEE; ($\square$), PTMO CPEE; (+), PEO; (∇), PPO; ($\times$), PTMO
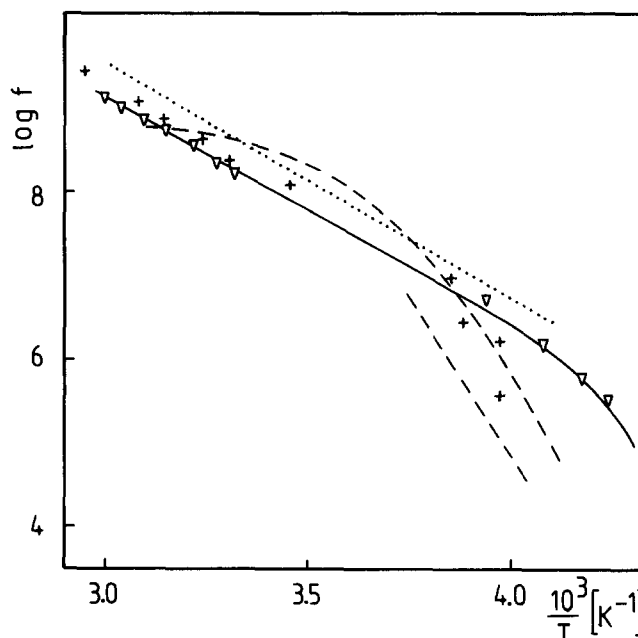

Figure 2 Relaxation diagram and e.s.r. data for oligodiols: PEO (— — — — dielectric data[7]; +, e.s.r., this work); PPO (— — — dielectric data[7]; ∇ e.s.r., this work); PTMO (· · · · · · from ref. 2)

recommended values of a and b (ref. 5) were used in our calculations: $a = 4.17 \times 10^{-10}s$; $b = -1.5$.

Assuming the isotropy of the probe motion we calculated the rotational frequencies using the relation $f = (2\pi\tau)^{-1}$ in the range of fast rotations. The results together with the data obtained for the range of slow rotations allowed us to construct the relaxation diagram which is presented in *Figure 2*. It was found by us previously that the probe in PTMO follows the $\alpha + \beta$-relaxation[2]. A similar conclusion applies to PEO and PPO as can be seen from *Figure 2*.

Although some inconsistencies between e.s.r. and dielectric data for PEO can be noted, they are most probably caused by the fact that the relaxation depends on molecular weight, different thermal treatment, and so on. The presence of both components – amorphous and crystalline – influences the measured relaxation times depicted in the relaxation diagram obtained from dielectric data.

It is well known that the spin probes having a tendency to be localized in the amorphous regions of semicrystalline polymers naturally yield only information about their surroundings. It is worth noting that the relaxational processes in oligodiols are almost identical and only slight differences are observed, particularly, in the high frequency region. *Figure 3* illustrates the e.s.r. results for elastomers.

By comparison of the plots presented in *Figures 2* and *3* and discussion in ref. 3 it is implied that the rotations of the probe are connected with the $\alpha + \beta$-relaxation in the rapid rotations region and with the β-relaxation in the slow rotation region.

The relaxation spectra for oligodiols differ in themselves only slightly whereas the relaxation runs for elastomers are the same, within experimental error.

Further information about the character of the probe motion and the relationship between its motion and the dynamics of soft segments in elastomers can be achieved taking into account the validity of the assumption
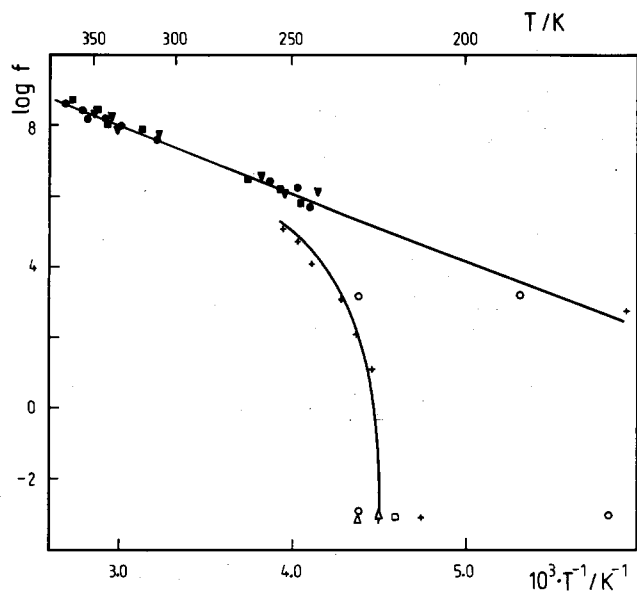
Figure 3 Relaxation diagram and e.s.r. data for elastomers PEO CPEE (○, dielectric data[9]; ■, e.s.r.); PPO CPEE (△, dielectric data[9]; ▼, e.s.r.); PTMO CPEE (+, dielectric data[10]; ●, e.s.r.)
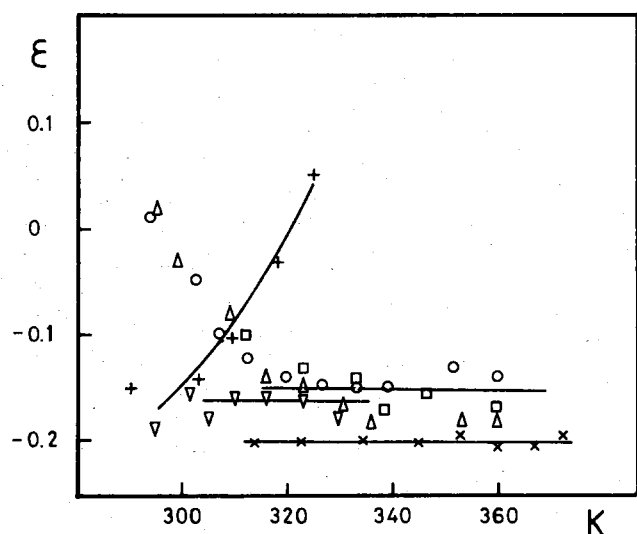

Figure 4 Degree of anisotropy *versus* T for (○), PEO CPEE ; (△), PPO CPEE; (□), PTMO CPEE; (×), PTMO; (▽), PPO; (+), PEO

underlying model (ii). In this case the shape of an aspherical probe is approximated by an ellipsoid the motion of which is usually characterized by the anisotropy coefficient ε (see *Figure 4*) and correlation times $\tau_{\perp}$, $\tau_{\parallel}$.

As implied in *Figure 4* the anisotropy coefficient for PTMO and PPO is independent of the temperature which means that the mobility of the radical is mainly determined by its shape. However, strong temperature dependence on the anisotropy coefficient is detected for PEO.

If for the purposes of our qualitative analysis the spin probe can be treated as an ellipsoid with long axis along the N–O bound then the observed change of the ε during the temperature increase may be related with a natural tendency that the relaxation times $\tau_{\perp}$ and $\tau_{\parallel}$ become less distinguishable. Within the terms of the above interpretation the data on PEO are exceptional and the reasons underlying such a behaviour are not yet explicitly known.

Let us note that in order to explain the temperature dependence of ε for the elastomers, the determination of $\tau_{\perp}$ and $\tau_{\parallel}$ is only possible when both $\tau_{\perp}$ and $\tau_{\parallel}$ are in the range of rapid rotations $(5 \times 10^{-11} < \tau < 10^{-9} \text{ s})$.

If the above condition is fulfilled only by the longer correlation time then the pattern of the spectrum depends mainly on the value of this correlation time[5]. It implies that the calculated 'isotropic' values of τ in model (i) (see *Figures 2* and *3*) are closer to the longer relaxation time which characterizes the tumbling of the ellipsoidal probe about its shorter axis (i.e. $\tau_{\perp}$). The spectra of the elastomers observed above 320 K fulfilled the condition for rapid rotations. The ratio $\tau_{\perp}:\tau_{\parallel} \approx 5$ can be obtained from these spectra.

A question arises concerning whether the independence of relaxation on the soft segment type is a result of the method used (because, for example, the probe may be insensitive to the chemical structure of chains due to their large size) or the relaxation times are identical in all elastomers investigated.

We prefer the second explanation because:

1. The differences in relaxation runs are insignificant in oligodiols;
2. Some modification of oligodiol properties caused by their incorporation as soft segments takes place (for example, the entanglements of chains hinder the crystallization which causes the soft segments phase to be more amorphous than the initial oligodiols);
3. The presence of uncrystallized hard segments and of chemically non-bonded oligodiols result in the disappearance of the differences between individual properties of oligodiols;
4. The measurements using the small probe gave the same results for all investigated elastomers[8].

Furthermore, the position of the results on the relaxation diagram derived from methods other than e.s.r. (*Figure 3*) strongly supports the fact that the above explanation is correct.

Finally, we would like to note that the results presented in this paper, and especially the independence of relaxation on the oligodiol type, can be of practical use and can give some indication about the choice of the components during decision making in manufacturing of elastomers.

ACKNOWLEDGEMENTS

REFERENCES

1 Castels, J. L., Vallance, M. A., McKenna, J. M. and Cooper S. L. *J. Polym. Sci. Polym. Phys. Edn.* 1985, **23**, 2119
2 Lembicz, F. *Makromol. Chem.* 1985, **186**, 665
3 Lembicz, F. and Ukielski, R. *Makromol. Chem.* 1985, **186**, 1679
4 Hoeschele, K. and Witsiepe, W. K. *Angew. Makromol. Chem.* 1973, **29/30**, 267
5 Kuznietsov, A. N. 'Spin Probe Method', Nauka, Moscow, (1976) (in Russian)
6 Boyer, R. F. and Keinath, S. E. 'Molecular Motion in Polymers by ESR', Harwood Academic Publishers, New York, (1980)
7 McCrum, N. B., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York (1967)
8 Lembicz, F. unpublished data
9 Ouszczejkin, G. A., Medvedeva, F. M., Wojteszonok, O. I., Polewaja, M. K. and Pin, O. D. *Plast. Massy* 1985, **10**, 16
10 Lembicz, F. and Ukielski, R. *Polimery* 1985, **30** (3), 105