Polymer Bulletin 34, 235–242 (1995)

Polymer Bulletin

Slow molecular motion in uniaxially stretched poly(ethyl methacrylate) as observed by double modulation electron spin resonance

Srećko Valić[1], Boris Rakvin[1], Zorica Veksli[1], Zlatka Grubišić-Gallot[2]

[1] Ruđer Bošković Institute, POB 1016, 41001 Zagreb, Croatia
[2] Institut Charles Sadron (CRM-EAHP), F-67083 Strasbourg, France

Received: 19 September 1994/Revised version: 21 November 1994/Accepted: 22 November 1994

Summary

The double modulation ESR (DMESR) technique has been applied to investigate the change of very slow molecular dynamics ($\tau_R > 10^{-7}$ s) of nitroxide spin probe in amorphous poly(ethyl methacrylate) (PEMA) at low drawing ratios. The polymer has been characterized by means of size exclusion chromatography (SEC) apparatus fitted with three detectors in series with continuous viscometer, low angle light scattering photometer and differential refractometer. The side chain group motion and segmental motion well below the glass transition temperature are discussed in terms of local density changes induced by orientational anisotropy of the chain segments.

Introduction

The study of local molecular arrangements within amorphous polymers has drawn considerable attention in polymer research in recent years. The change of the structure, i.e., molecular arrangement of the amorphous material imposed by the thermomechanical treatment is essential for understanding mechanical and transport properties such as elastic modulus, toughness, sorption and diffusion of foreign molecules in the polymer (1-3).

Drawing of the amorphous polymer is a typical case which demonstrates how the molecular arrangement can be changed. Molecular segments tend to orient locally upon drawing: fractional free volume and segmental mobility is reduced.

There are several molecular probe techniques such as fluorescence depolarization or phosphorescence depolarization (4,5) and electron spin resonance (ESR) spin probe method (6-8) sensitive to the anisotropy of free volume and reduced molecular dynamics in oriented polymers. The double modulation ESR (DMESR) technique has emerged as a powerful tool for probing local dynamics in the slow motion region (9-12).

In this work DMESR method was used to investigate the change of molecular dynamics generated in amorphous poly(ethyl methacrylate) (PEMA) at low drawing ratios, L/L_0, up to 2,5. The change of molecular motion of a spin probe is discussed in terms of local orientation of polymer segments.

Experimental

Preparation and characterization of the samples: Poly(ethyl methacrylate) (PEMA) sample was synthesized via anionic polymerization technique at the Institute Charles Sadron (ICS). Its molecular characteristics (Table 1) were determined with a Waters 150C chromatograph coupled on line with a home-made continuous viscometer and a low angle laser light scattering (LALLS) photometer Chromatix CMX-100. The mobile phase was tetrahydrofuran with a flow rate of 1 ml/min.

Table 1 : Molecular weight, molecular weight distribution and intrinsic viscosity of nonstretched and stretched PEMA

	L/L_0	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	$[\eta]_{(ml/g)}$
PEMA-1		62 000	61 000	1,02	31,8
PEMA-NS[a]	1,0	61 000	59 000	1,03	31,0
PEMA-S-1	1,5	60 000	59 000	1,02	32,0
PEMA-S-2	2,5	61 000	60 000	1,02	31,4

[a] The specimen had the same thermal treatment as the stretched specimens

Oriented samples have been obtained by stretching uniaxially parallelepipedic specimens at a temperature of 366 K (~T_g+15 K). The experiments were carried out with an extensional rheometer designed at ICS (13). During the stretching, the specimens were immersed in a silicone oil bath in which the temperature is constant to within 0,2 K. The stretching was carried out at constant elongational strain rate (0,2 s^{-1} for all samples), which means an exponentially increasing velocity of the clamps. Two specimens (PEMA-S-1 and PEMA-S-2) of the sample have been stretched with different values of the final extension ratio L/L_0 (1,5 and 2,5). The chain orientation induced by the extensional flow is then frozen-in by rapid quenching (at room temperature) of the stretched specimens. The rheometer has been specially designed for efficient quenching: it only takes a few seconds for the temperature of elongated specimens to decrease below T_g.

The perdeuterated spin probe, 4-oxo-2,2,6,6-tetramethyl-1-piperidinyl-oxy was incorporated into the PEMA matrix prior to stretching at low concentrations not exceeding 0,02 mass %.

DMESR measurements: The DMESR spectra were recorded on a Varian E-109 X-band spectrometer equipped with an additional coil and a Wavetek radiofrequency source (9). The spectra were accumulated in a standard PC computer. The linewidth at half height of the DMESR line, Δ_{obs} (in frequency units), is related to spin-lattice relaxation time, T_1, under the condition that $T_1 >> T_2$ (11,14,15) where T_2 is spin-spin relaxation time.

$$(\pi\Delta_{obs})^{-1} \sim \mathrm{T}_1 \qquad (1)$$

Results and discussion

The temperature dependence of the DMESR linewidths for a spin probe embedded in the unoriented and oriented PEMA samples, respectively, is shown in Fig. 1. The spectra were recorded with the magnetic field centered on the central ESR line (I=0) at a maximal signal intensity. The signal corresponds to the change in the intensity of the ESR signal when a second modulation frequency was swept in the range from 250 to 350 kHz. The linewidth $(\pi\Delta_{obs})^{-1}$ is related to the rotational correlation time, τ_R,

$$(\pi\Delta_{obs})^{-1} \sim \tau_R/4{,}5 \qquad (2)$$

This relation is derived (11) by calibrating DMESR linewidths in the slow motion region to τ_R values extrapolated from the τ_R values of Hwang et al. (16). The linewidth, Δ_{obs}, was determined by fitting the experimental spectra to the Lorentzian line shape by using a least-square criteria (17).

The standard deviation error was less than 5%. All PEMA samples $(L/L_0 = 1,\ L/L_0 = 1{,}5$ and $L/L_0 = 2{,}5)$ reveal three relaxation processes of the spin probe over the temperature interval investigated (Fig. 1). The

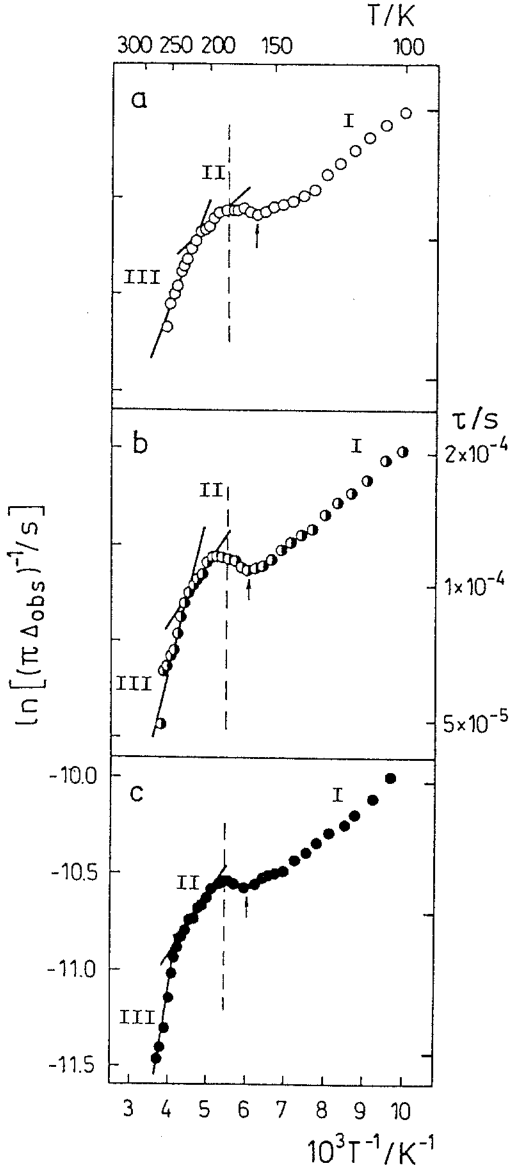

Figure 1. Temperature dependence of the DMESR linewidths of spin probe dispersed in PEMA at various draw ratios (a) $L/L_0 = 1$, (b) $L/L_0 = 1{,}5$ and (c) $L/L_0 = 2{,}5$. On the right hand vertical scale τ_R denotes calculated values according to equation (2). The dashed line marks the temperature of the intrinsic spin probe transition.

behaviour of a spin probe dispersed in the PEMA matrix shows a similarity with the PMMA matrix (10). However, the position of a small minimum which appears in region I (below the intrinsic transition of the spin probe) is shifted to higher temperatures as compared with PMMA minimum. This minimum has been ascribed to the coupling of low-temperature ester side chain group motion with the nitroxide molecule (10). It has been shown by NMR T_1 measurements that the more bulky ethyl group terminating the side chain, shifts the corresponding minimum to a higher temperature (18). Above the internal spin probe transition (≈ 190 K) two discrete relaxation processes are present. The low activation energy of the relaxation in region II and region III, is characteristic for the high-frequency motion of side chain groups and is consistent with all the results obtained so far (10,18,19). Accordingly, molecular motion of a spin probe defined as region II is assigned to the ester side chain $-C_2H_5$ motion, whereas at higher temperatures, region III, the spin probe motion may be affected by the main chain $-CH_3$ relaxation.

It can be seen that the stretching induces differences in the DMESR linewidth broadening corresponding to both relaxation processes (Fig. 1b and 1c). As the extension ratio is increasing the linewidth becomes broader. The activation energies obtained from the slopes of the Arrhenius plot at two temperature intervals (region II and region III) are listed in Table 2.

Table 2 : Activation energies of spin probe motions in PEMA

		E_a(kJ mol^{-1})	
	L/L_0	Region II	Region III
PEMA-NS	1,0	1,6	4,5
PEMA-S-1	1,5	2,7	7,3
PEMA-S-2	2,5	2,7	9,8

The conventional ESR spin probe method has shown that at low temperatures the effects of different L/L_0 values, even up to $L/L_0 = 18$, on spin probe motion in the amorphous phase in various polymers are rather small (8). However, the substantial reduction of molecular mobility was observed at higher temperatures, which was explained with the dimensional scale of the motion. The effects of low L/L_0 values on the rotational correlation time, τ_R, in the slow motion region are attenuated due to the inhomogeneously broadened conventional ESR spectra. In order to deduce very small changes in the slow motion region, a homogeneous contribution within an ordinary inhomogeneously broadened ESR line has to be detected. As demonstrated earlier the DMESR method can be very successfully employed as an alternative method to detect a slow motion (10). It is important to point out that even at small L/L_0 values not exceeding 2,5, the differences in DMESR linewidth broadening or in E_a values, are evident in these measurements (Figure 1, Table 2).

Upon drawing the amorphous chain segments orient locally parallel to the draw direction and the structure can be characterized by medium-range order and orientational anisotropy. The interchain interactions which determine the structure in the densely packed oriented phase are similar to those found in corresponding crystal structures as shown by recent x-ray diffraction measurements in some polymers (20). Local density of the oriented chains or reduced fractional free volume will impose a certain constraint on the segmental mobility of the oriented polymer chains. At low temperatures, where the correlated segmental backbone motions become frozen in, the spin probe embedded in the locally denser matrix will be in a closer contact with the side chain groups motionally active at these temperatures. This would cause an increased molecular interaction between the side groups and the spin probe molecule. Indeed, a faster linewidth broadening is observed in PEMA-S-1 and PEMA-S-2, respectively, (Fig. 1b, 1c) due to the prevailing influence of the high-frequency motion of side chain groups above 190 K. The corresponding activation energies found in region II and III show an increase for the higher values of L/L_0.

The effect of drawing can be compared with the influence of molecular weights. An increase of molecular mass affects the local density distribution and decreases the free volume (21). Thus a stronger coupling of a spin probe with the polymer side chain groups is expected. Even if a certain hindrance of side group motion can be expected, due to the reduction of free volume upon drawing, the spin probe molecules are in closer proximity to side chain groups so that their rotational reorientation will be predominantly affected by the high-frequency motion as shown in our experiments.

We conclude that the DMESR method is sensitive to small changes of the local dynamic in the slow motion region.

Acknowledgement - The authors extend their gratitude to Prof. René Muller from ISC-EAHP for the stretching of PEMA samples. This work was supported by the Ministry of Science and Technology of the Republic Croatia.

References

1. DeCandia F, Perullo A, Vittoria V, Peterlin A (1984) Interaction between Processing Structure and Properties of Polymeric Materials. Elsevier, Amsterdam, p. 713
2. DeCandia F, Vittoria V, Peterlin A (1970) J Polym Sci Polym Phys Edn 23: 1217
3. Vittoria V, de Candia F, Capodanno F, Peterlin A (1986) J Polym Sci Polym Phys Edn 24: 1009
4. Guillet J (1985) Polymer Photophysics and Photochemistry. University Press, Cambridge, England
5. Tran-Cong Q, Tanaka H, Soen T (1992) Macromolecules 25: 7389
6. Kumler PL (1980). In: Fava RA (ed) Molecular Structure and Dynamics. Academic, New York (Methods of Experimental Physics, vol 16, part A, pp 442-479)
7. Choy CL, Leung WP, Ma TL (1985) J Polym Sci Polym Phys Edn 23: 557
8. De Candia F, Russo R, Vittoria V, Krisyuk BE, Popov AA, Zaikov GE (1986) Polymer 27: 1743
9. Rakvin B (1984) Chem Phys Letters 109: 280
10. Valić S, Rakvin B, Veksli B, Grubišić-Gallot Z (1990) Macromolecules 23: 5182
11. Rakvin B, Valić S, Veksli Z (1991) Chem Phys Letters 182: 171
12. Valić S, Rakvin B, Ranogajec F, Veksli Z, Grubišić-Gallot Z (1993) Polymer 34: 2929
13. Muller R, Froelich D (1985) Polymer 26: 1477
14. Below PG, Milov AD (1988) Chem Phys Letters 151: 79
15. Alekseev BF, Tikhonov AB, Bogachev YuV, Gasimov OG, Yanchurov VA (1990) Fiz Tverd Tela 32: 1305 (Soviet Phys Solid State 32: 764)
16. Hwang JS, Mason RP, Hwang LP, Freed JH (1975) J Phys Chem 70: 489
17. Rakvin B (1994) J Magn Res A106: 245
18. Powles JG, Hunt BI, Sandiford DJH (1964) Polymer 5: 505

19. Tsay FD, Gupta A (1987) J Polym Sci Polym Phys Edn 25: 855
20. Murthy NS, Minor H, Bednarczyk C, Krimm S (1993) Macromolecules 26: 1712
21. McCrum NG, Read BA, Williams G (1967) Anelastic and Dielectric Effects in Polymer Solids. John Wiley, New York