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polymer

Polymer 40 (1999) 3891–3894

Polymer Communication

Molecular mobility in liquid-crystalline phase of oriented wholly aromatic copolyester as revealed by proton magnetic resonance

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Received 20 April 1998; revised 15 September 1998; accepted 15 September 1998

Abstract

Broad line proton magnetic resonance (PMR) has been used for the study of molecular motion in wholly aromatic thermotropic liquid-crystalline (LC) copolyester at high temperatures up to 340°C. Specimens were thin highly oriented fibers produced from a copolymer of hydroxybenzoic acid and hydroxynaphthoic acid (HBA/HNA). In the vicinity of the thermotropic transition temperature a fine structure of PMR spectra was revealed for as-spun fibers. Annealing leads to smoothing of this structure. Theoretical spectra were calculated and compared with the experimental ones. This made it possible to obtain information on large-scale segmental motion of macromolecules in the LC phase. Heat treatment leads to retardation of the chain cooperative mobility. Dynamic inhomogeneity of the fibers at high temperatures is discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular mobility; Liquid-crystalline copolyester; Proton magnetic resonance

Macromolecules of wholly aromatic liquid-crystalline (LC) polymers are so rigid that a real segmental (micro-Brownian) motion is impossible in these materials. High molecular orientation in LC polymer fibers and films can be achieved already in the spinning process [1,2], however the significant structure transformations, which lead to the strengthening, result from the special heat treatment. There is a great body of information about increase of crystallinity, modifications of crystalline lattices and change of elastic modulus as a consequence of annealing [3–6]. For such large-scale rearrangements a specific molecular mobility has to occur. The molecular mobility, especially in the LC phase, is the subject of this work. The broad line proton magnetic resonance (PMR) was used for this purpose. The samples were highly oriented thin (diameter about 12 μm) fibers of copolymer Vectra A950, prepared from 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), with monomer ratio HBA : NBA = 70 : 30 [7]. The fibers were spun from material of the Celanese Research Company. A PMR spectrometer, built in the Physical-Technical Institute, was used to record the spectra in form of the first derivative up to 340°C and in addition, in form of the original absorption spectra directly, by modulation of the magnetic field with high-amplitude rectangular pulses. The latter method of recording, described previously [8], was used only for matching our results to literature data. Experimental spectra (the first derivative) are shown in Fig. 1 for parallel and perpendicular fiber orientations to the magnetic field at different temperatures. The amplitude of modulation varied from 0.5 to 0.06 G depending on the spectrum structure. Specimens were heated in a nitrogen atmosphere. The spectra (a)–(e) and (g)–(i) (Fig.1) correspond to fibers in the initial (as-spun) state, the fibers undergoing high temperature for not more than 10 min so that annealing effect did not take place. The spectra (f) and (j) are for annealed states: (f) – with annealing directly in the spectrometer coil during 3 h, and (j) – with annealing by the special program outside the spectrometer.

As one can see, below the thermotropic transition temperature (T_m) spectra are triplets, as in Ref. [9], but above T_m ($T_m = 285$°C by DTA data) the fine structure of the spectra of as-spun fibers at the both orientations was revealed. This structure is similar to that observed previously only for thermotropic low molecular liquid crystals [10]. It indicates that high molecular weight nature does not interfere with cooperative molecular motion in the LC phase. Annealing of the sample leads to smoothening of the spectrum structure. To obtain further information about molecular motion above T_m, analysis of the spectrum fine structure was performed for the case of fiber orientation along the magnetic field. In doing so, data on proton–proton

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PII: S0032-3861(98)00661-2

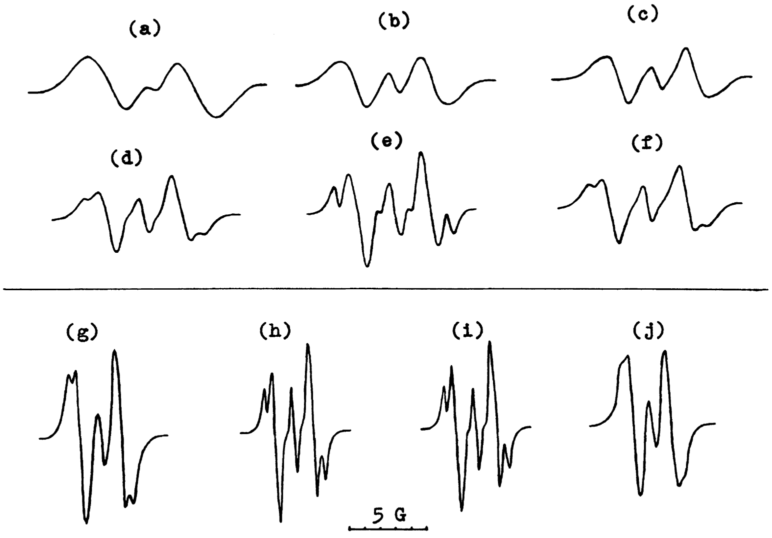

Fig. 1. Experimental PMR spectra of the oriented (HBA/HNA) copolyester at different temperatures: (a) 20°C, (b) 150°C, (c) 200°C, (d) 270°C, (e) and (f) 300°C, (g) 255°C, (h) 290°C, (i) and (j) 300°C; (a)–(e) and (g)–(i) – as-spun fibers, (f) and (j) – after heat treatment; fibers orientation to the spectrometer magnetic field: (a)–(f) – parallel, (g)–(j) – perpendicular.

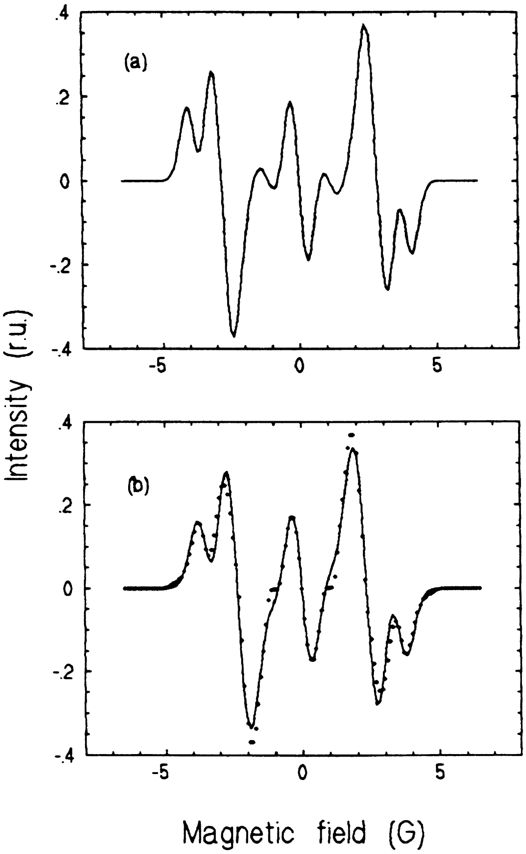

Fig. 2. Theoretical PMR spectra, calculated for fiber orientation parallel to the magnetic field: (a) – completely oriented chains; (b) – with consideration for ‘‘quasi-segmental’’ motion (solid line), points denote the experimental spectrum (e) from Fig. 1 (areas of absorption spectra are normalized to unity).

distances and angular parameters for naphthalene and phenylene rings were taken from literature [11–13]. The dipole–dipole magnetic interactions between the nearest protons in the rings are responsible for the spectrum fine structure. Isolated proton pairs of the phenylene rings and triads of the naphthalene rings give two and seven lines, respectively [14,15]. Each of these lines was believed to be Gaussian broadened with dispersions β_p^2 and β_n^2 for phenylene and naphthalene rings. These parameters are the second moment contributions from protons outside the groups.

As the first approximation, the theoretical spectrum was calculated for the simplest case i.e. perfect chain orientation (Fig. 2(a)). Parameters $\beta_p^2 = 0.18\ \mathrm{G}^2$ and $\beta_n^2 = 0.09\ \mathrm{G}^2$ were determined by the trial-and-error method. It is seen that this spectrum coincides in shape with the experimental one rather well (matches visually to spectrum (e), Fig. 1), but the spectrum width proved to be larger than experiment. So, in this theoretical spectrum the separation between the doublet components of the phenylenes was larger by 23% and the separation between the outer components of naphthalene rings was larger by 10% than in the spectrum (e). This difference cannot be ascribed to a static (invariable in time) angular segments disorientation in the fibers. Let us introduce vector **D**, which coincides with direction of each segment of the macromolecules. Making allowance for a static angular **D**-distribution resulted only in broadening the structure of the calculated spectrum. Obviously, a new type of motion, a cooperative one, has to be taken into account [16]: on entering the LC state the angular distribution of vectors **D** should be considered not as static, but as dynamic. Cooperative molecular motion causes the vectors **D** to change their orientation continually within certain limits. Oscillations of **D**-vectors have to be rapid enough to average the local magnetic fields. In this case all segments should be in an identical state. The angular amplitude (ϕ) of vector **D** oscillation can be used as a measure of cooperative motion in mesophase. Here ϕ is counted from the fiber orientation axis (and the magnetic field direction in this instance). The aforementioned model of chain cooperative mobility made it possible to describe the contribution of the naphthalene rings to the theoretical spectrum with reasonable exactness, but the doublet separation from the phenylene protons still remained larger than that in the experimental spectrum (e). In our opinion, the chief cause of this discrepancy is the fact that in the real as-spun fibers above T_m the phenylene rings (their rotational axes) are deflected through a sizable angle ψ_0 from the fiber orientation axis. This angle should also be considered as time-averaged, because the cooperative macromolecular motion has to set the rings into additional oscillation.

Fig. 2(b) (solid line) gives the spectrum, calculated using the aforementioned model of cooperative motion with parameters $\phi = 23°$, $\psi_0 = 17°$, $\beta_p^2 = 0.26\ G^2$, $\beta_n^2 = 0.14\ G^2$, found by the trial-and-error method. The rectangular probability distribution was taken for description of the vector **D** oscillation. Such a distribution seems to be reasonable in the case of relaxation motion of the chains, yet the results of calculation turned out to be only slightly dependent on the distribution form. In Fig. 2(b) the experimental spectrum (e) is denoted by points. As can be seen, there is a rather good agreement between theory and experiment, especially if one takes into account that the spectra are in form of the first derivative. This result provides sufficient reason to consider the above parameters as a realistic characterization of the chain motion in the mesophase. The value of ψ_0 turns out to be higher for LC state than in the solid crystal (about 10°, according to data [11]), hence it follows that the ''sinuous nature'' [4] of the chains shows itself more clearly in the mesophase.

Some supplementary information on molecular motion in LC phase may be derived from the spectra recorded for fibers orientated perpendicular to the spectrometer magnetic field ((h) and (i), Fig. 1). Under this condition the good resolution of the spectrum satellites implies that the macromolecular segments are in addition able to take part in rotation (or oscillation with large amplitude, but not only 180° jumps) around axes parallel to the fiber orientation axis because otherwise the inter-proton vectors should make a temporally constant angular (azimuth) distribution in the same plane where the vector of the spectrometer magnetic field lies. This should lead to broadening of the spectral structure.

Thus, macromolecules of this wholly aromatic oriented copolyester have the capability to execute a large-scale conformational motion in the mesophase. The motion of this type may be considered as ''quasi-segmental'' and de Gennes's reptation-in-tube model [17] seems to be useful for visualizing it in more detail: the movement of the ''defect'' (stored length) along the chain leads to ever changing orientation of segments. Of course, the ''tubes'' in this case have to be straighter than for the gel. Moreover, the concept of reptation may be drawn on for discussion of structure rearrangement and strengthening during the heat treatment [18]. There is a good reason to note the qualitative similarity between the quasi-segmental motion and really segmental (micro-Brownian) one in flexible-chain crystalline polymers particularly from the standpoint of mobility influence on structure rearrangement, strengthening process and, perhaps, on glass transition [19].

Heat treatment results in retardation of quasi-segmental motion above T_m as evidenced by deterioration of component resolution in the spectra (f) and (j). It is reasonable to assume that the annealed specimen becomes dynamically inhomogeneous: it contains both remaining LC microregions and newly formed ''rigid'' ones. Let the fraction of the former be denoted as α and assume that the shape of their spectrum is similar to (e) if the specimen is oriented along the magnetic field. Conformational motion does not proceed in the ''rigid'' microregions and only local rotation of rings is possible. This situation is the same as at 150°C because spectrum identical to (b) may be attributed to ''rigid'' microregions. Now it is possible to estimate the dynamic inhomogeneity by the same way as ''mobile fraction'' or ''dynamic crystallinity'' of flexible-chain crystalline polymers [20]. Let us consider the spectrum (f) as a sum of spectra (b) and (e). The best correspondence between the real and that obtained by summing spectra was achieved at $\alpha = 0.4$. Thus, under annealing, about 60% of specimen volume passes into the phase which is solid above T_m, and, evidently, these microregions include not only three-dimensional crystallites [3]. The magnitude of α turns out to be dependent on the annealing method and it may be used as a characteristic of the process.

Fine structure manifests itself in the PMR spectra beginning at 200°C. So, at 230°C α may be estimated as a few percent and at 270°C this value rises to 40%. As one can see, the spectrum (d) is in fact identical to (f). It seems reasonable to say that with respect to molecular mobility the transition of the as-spun copolyester into LC state takes an extended temperature interval similar to the rise of ''mobile fraction'' in the flexible-chain polymers.

It should be remarked that LC polymers can be oriented along a magnetic field [16,21,22] but for the highly oriented fibers being perpendicular to the magnetic field above T_m no chain reorientation was observed in this work.

Acknowledgements

The authors are grateful to the Russian Foundation for Fundamental Investigations (RFFI) for supporting this work (Grant No.97-03-32624).

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