The Orientation Order of Liquid-Crystalline Polymer, Measured by ESR and Optical Dichroism Techniques

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ABSTRACT: Molecular orientation order and rotation mobility of comb-shaped liquid crystalline polymer forming nematic and smectic mesophases are characterized by spin probe and dichroism technique in the temperature range 100–420 K. The models describing the mechanism of molecular rotations in different temperature ranges were determined by quantitative numerical simulations of ESR spectra. In the vicinity of the glass transition point of the polymer, where the fast amplitude-restricted molecular reorientations take place, the quasi-libration model was found to be adequate for the description of ESR spectra, while the often used Brownian rotational diffusion is appropriate at higher temperatures only. Orientation distribution function of probe molecules was characterized quantitatively by order parameters up to sixth rank for a wide temperature range. The orientation order parameters measured *via* the spin probe technique are shown to correlate with orientation order parameters measured by optical techniques. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. **2019**, *57*, 819–825

KEYWORDS: liquid-crystalline polymers; molecular mobility; order parameters; orientation order; spin probe

INTRODUCTION In the previous years, large scientific and technological interest has been drawn to the class of substances collectively referred to as soft matter [1], which includes thermotropic and lyotropic liquid crystals, polymers, colloids, and others. In such systems, the long-range orientation order leads to anisotropy of macroscopic properties of the material, which can be effectively controlled with relatively weak forces, such as magnetic fields,[2] command surfaces,[3,4] action of light.[5–7] Among these substances, particular interest is drawn to liquid crystalline (LC) polymers,[8] which combine advantageous optical properties of liquid crystals with mechanical durability of polymer materials.

The important problem is obtaining characteristics of structural and molecular organization of such materials, including orientation order parameters, amplitudes, and frequencies of rotational motions of molecules in these media, characteristics of translation order.

One of the powerful techniques, employed for measuring these characteristics, is ESR. The advantages of this technique for studying soft matter are the following:

- High sensitivity towards orientation order and the opportunity to determine the orientation order parameters of higher (>2) ranks;[9]
- The possibility to determine the characteristics of molecular motions in the range of times 10^{-6}-10^{-9} s;[10] the possibility to clarify complex mechanisms of rotation movements, not limited to Brownian rotation diffusion.[11–14]

Whereas ESR spectra of spin probes in polymers[15–22] and liquid crystals [23–29] have been extensively investigated, only a few works have been devoted to the spin probe studies of LC polymers.[30–34] The spin probe studies of soft materials show convincingly that for well-founded characterization of rotation mobility[35–40] and orientation order[23,26,36,41–43] of these systems, the quantitative numerical simulation of ESR spectra is necessary.[9,44] It has been shown that for obtaining unbiased and reliable results, the joint simulation of series of ESR spectra recorded at different temperatures,[45] and (for anisotropic samples) at different sample orientations with respect to the spectrometer magnetic field,[25,46] should be performed. Furthermore, recent studies of spin probes in polymer matrices showed that a hierarchy of rotational motions of different frequencies and amplitudes is present in polymer materials,[45,47] and the models of complex rotational motions should be implemented to account for ESR spectra.[12]

The aim of the present work is to characterize the mobility and orientation order of spin probes in LC polymer forming nematic and smectic mesophases and to test the applicability of models developed for simulation of ESR spectra of spin

Additional Supporting Information may be found in the online version of this article.

probes in polymers and liquid crystals. The characteristics of orientation alignment obtained with the spin probe technique are compared with those obtained with polarized optical absorbance spectroscopy, which can be regarded as complementary for the former technique.

EXPERIMENTAL

The structure of the polymer used in this work is presented in Figure 1(a). This is a comb-shaped liquid crystalline polyacrilate, synthesized according to the technique described in Ref. 48. This polymer demonstrates the following LC phases:[48]

SmC~ 343 $\mathbf{N_{Re}}$ 384 **SmA** 411 **N** 421 **I** (temperature in °K). The polymer demonstrates glass transition point at 317 K.[48]

For polarized optical absorbance study, the co-polymer containing 0.5 mol % perylene groups was synthesized [Fig. 1(b)]. The phase transition behavior of this material was determined using polarization optical microscopy and is as follows: **SmC**$^{\sim}$ 338-340 K $\mathbf{N_{re}}$ 385–387 K **SmA** 403–404 K **N** 410–411 K **I**. The optical absorbance spectrum and microscopic textures in crossed polarizers corresponding to different mesophases are shown in Supporting Information (Figs. S1, S2).

Two spin probe molecules were used. The first one was mesogenic probe I, synthesized in the group of Prof. R. Tamura[49] [Fig. 1(c)]. This molecule has a rod-like geometric shape and includes mesogenic phenyl benzoate moiety. Due to that, the probe effectively embeds in the structure of LC materials and reliably characterizes their orientation order. This probe had been previously used to study orientation in liquid crystals.[50,51] The second spin probe used [Fig. 1(d)] was synthesized in the group of Prof. S. Nakatsuji.[52] This probe contains azobenzene group covalently linked to the nitroxide moiety. This feature allows using it as a single-molecule probe both for ESR and for optical absorbance anisotropy measurements.

For the study of order of the polymer with ESR technique, the mixtures of the polymer [Fig. 1(a)] and spin probes were prepared. For this, the chloroform solutions of the polymer and the spin probe were mixed, and then the solvent was removed firstly by evaporation, and then by evacuation to 10^{-6} bar at 70 °C for 5 days.

For the preparation of the ordered sample of LC polymer, the material was placed between two quartz plates, covered with polyimide film, and rubbed by clean cotton cloth. As it is well known, rubbing causes the appearance of microscopic relief (grooves) on the surface of polyimide that leads to the orientation of liquid crystal parallel to rubbing direction.[2,53,54] The polymer between the rubbed quartz plates was aligned upon slow cooling (0.1 °C/min) from the isotropic phase to room temperature.

ESR spectra were recorded using X-band spectrometer Bruker EMX plus. The magnetic field sweep was controlled using the 3rd and the 4th components of ESR spectrum of internal standard consisting of Mn(II) traces in polycrystalline MgO. The distance between these lines is equal to the hfc constant on ^{55}Mn nucleus (86.76 G). The temperature of the samples was set in the range 100–420 K using the flow of nitrogen gas. To compensate for systematic errors produced by the temperature control unit of the ESR spectrometer, the temperature of the gas flow was calibrated using an external thermocouple. Thus, the accuracy of temperature setting was about ±0.5 K. For recording of angular dependencies, the sample was rotated in the cavity of ESR spectrometer using goniometer setup. The accuracy of angle setting was ±0.2°.

To record the temperature dependence of dichroism of the perylene and azobenzene groups in the matrix of LC polymer, the ordered sample was placed in a thermostated hot stage and slowly (1 °C/min) heated from 293 K to 420 K. The spectra of optical absorbance in the polarization parallel and perpendicular to the sample director were recorded in the course of heating. The dichroism was calculated according to equation

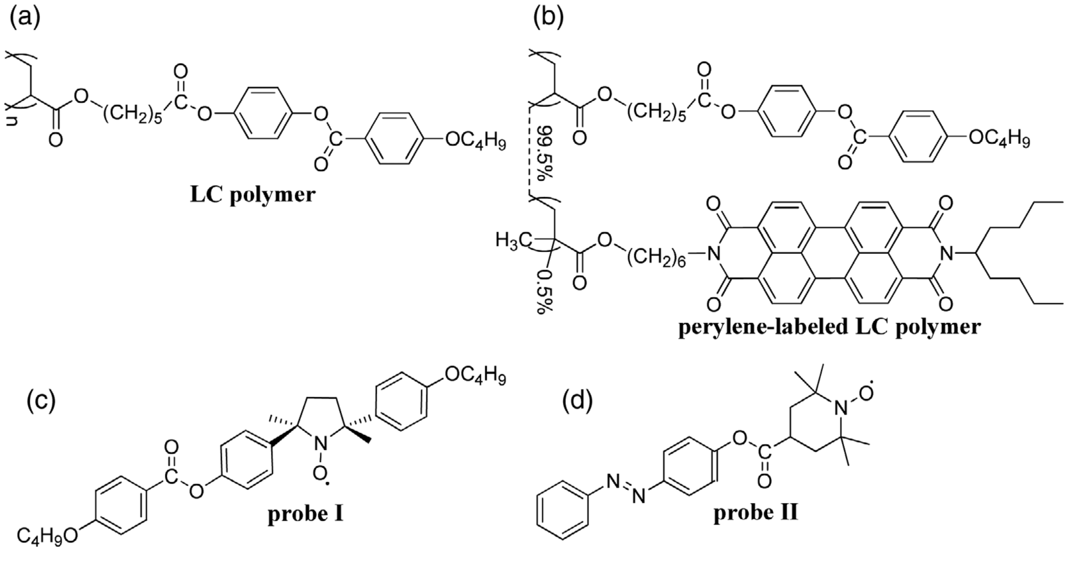

FIGURE 1 Chemical structures of materials used in the present work.

$d = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ are absorbances at parallel and perpendicular polarizations, respectively. The dichroism was measured at wavelength 534 nm for perylene groups and 340 nm for azobenzene groups. The example optical absorbance spectrum of the polymer containing the probe II at 293 K is presented in the Supporting Information (Supporting Information Fig. S3).

DETERMINATION OF ORIENTATION ORDER PARAMETERS FROM ESR SPECTRA

The orientation order of molecules is characterized with the orientation distribution function $\rho(\Omega)$, which is the number density of molecules oriented at each direction:

$$\rho(\Omega) = \frac{dN(\Omega)}{d\Omega}, \tag{1}$$

where $\Omega = (\varphi, \theta, \psi)$ is a set of Euler angles, which transform the molecular reference frame into the sample frame. For axial orientation distributions, the function $\rho(\Omega)$ is conventionally represented as a series of Legendre polynomials:[55,56]

$$\rho(\Omega) = \sum_{j=0}^{\infty} \frac{2j+1}{2\pi} \langle P_j \rangle P_j(\cos\theta) \tag{2}$$

where the values $\langle P_j \rangle$ compose the set of orientation order parameters. To determine order parameters from experimental spectra, the numerical simulation of ESR spectra was used. Numerical simulation of ESR spectra was performed by minimization of sum of squared deviations of calculated spectra from the experimental ones. The procedure of spectra simulation in the absence of spin probe rotation (rigid limit) and corresponding software is described in detail elsewhere.[9] For the simulation of spectra in the slow-motional regime homemade software based on the original program by Schneider and Freed [10] was used.

The orientation and rotation parameters were determined from ESR spectra by a two-step procedure. In first step, ESR spectrum of an isotropic sample in the rigid limit was simulated. The principal values of Zeeman and hyperfine interaction tensors were determined in the course of this procedure. For the probe I, the magnetic parameters were determined from the isotropic spectrum at 293 K, which is 24 K below glass transition temperature. In the probe II, due to the internal motions of the nitroxide groups, the spectrum at 293 K cannot be described in the framework of rigid limit, and therefore it cannot be used to determine magnetic parameters. For this probe, the spectra recorded at 100 K were used for magnetic parameter determination. The parameters obtained in the result of simulation are presented in Table 1. The agreement between the experimental spectrum and the simulated one is illustrated in Figure 2. In the second step of spectra simulation, the obtained values of magnetic parameters were used then to simulate angular dependence of ESR spectrum of aligned sample. For this, 8–10 ESR spectra recorded at different orientations of the sample relative to the magnetic field of ESR spectrometer were simulated jointly. For the lowest temperature spectra, where no rotational motions of radicals take place, ESR spectra were calculated within the rigid limit framework. The spectrum comprises the superposition of spectra for individual orientations, weighed over the orientation distribution.[9] For the simulation of spectra in the rigid limit, the model-free approach to the determination of orientation distribution was used. Orientation order parameters were explicitly varied during spectra simulations, and thus, they were independently determined from the angular dependence of the spectra.

In the slow-motional regime, the spectra were simulated in the framework of the model of Brownian diffusion in the orientation potential.[28] In this model, the molecules are assumed to undergo Brownian rotation in the anisotropic mean-field potential $U(\Omega)$. The shape of the potential $U(\Omega)$ was varied during the spectra simulation, and the orientation order parameters were determined therefrom:

$$\rho(\Omega) = \frac{1}{Q}\exp[-U(\Omega)/k_B T]d\Omega \tag{3}$$

where k_B is Boltzmann constant and $Q = \int \exp[-U(\Omega)/k_B T]\, d\Omega$ is normalization factor.

The quality of spectra simulation is illustrated in Figure 3. The spectra simulated in the model of rigid limit are presented in Figure 3(a), whereas Figure 3(b) illustrates the slow-motional spectra. Representative values of dynamical and orientational parameters obtained from the spectra of probes I and II in the slow-motional regime are listed in Supporting Information (Supporting Information Table S1).

RESULTS AND DISCUSSION

Temperature dependences of principal values of magnetic tensors of the probe I, obtained as a result of simulation, are presented in Supporting Information (Supporting Information Fig. S4). In the vicinity of the glass transition point of the host polymer, the partial averaging of magnetic tensors is observed.

TABLE 1 Magnetic resonance parameters of spin probes I and II, determined from ESR spectra of isotropic samples of the LC polymer doped with the probes

Probe I, 293 K				Probe II, 100 K			
g_{xx}	2.0089 ± 0.0002	A_{xx}	(5.5 ± 0.5) G	g_{xx}	2.0096 ± 0.0002	A_{xx}	(7.62 ± 0.5) G
g_{yy}	2.0063 ± 0.0002	A_{yy}	(4.2 ± 0.6) G	g_{yy}	2.0066 ± 0.0002	A_{yy}	(5.92 ± 0.6) G
g_{zz}	2.0023 ± 0.0002	A_{zz}	(31.5 ± 0.05) G	g_{zz}	2.0019 ± 0.0002	A_{zz}	(34.16 ± 0.05) G

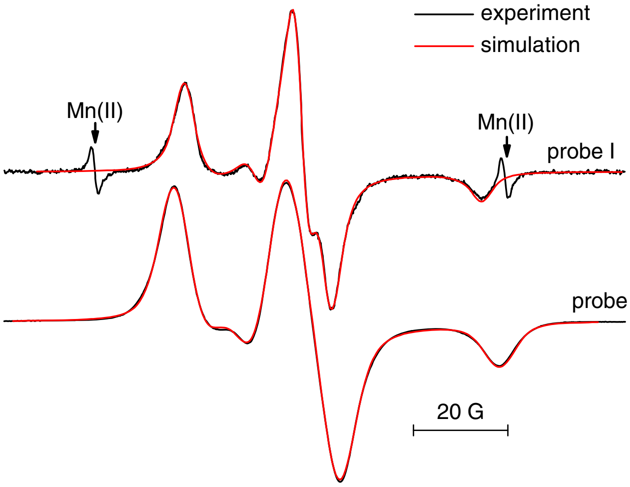

FIGURE 2 The experimental (black) and simulated (red) ESR spectrum of the spin probes I and II in the isotropic samples of LC polymer at 293 K (probe I) and 100 K (probe II). Narrow lines at the sides of the spectrum of the probe I correspond to internal standard consisting of Mn(II) impurities in polycrystalline MgO. [Color figure can be viewed at wileyonlinelibrary.com]

Such behavior is known to be brought about by high-frequency stochastic rotational motions of molecules with limited amplitudes, known as quasi-librations.[45] The amplitudes of these motions can be estimated on the basis of the obtained effective values of magnetic parameters:

$$\mathbf{g}_L = \frac{1}{Q}\int_0^{2\pi} d\varphi \int_0^{L_\perp} \sin\theta d\theta \int_{-L_\parallel}^{+L_\parallel} d\psi \mathbf{R}(\Omega)\mathbf{g}_0\mathbf{R}^T(\Omega) \qquad (4)$$

where $\mathbf{g}_L$ is the apparent g-tensor in the presence of libration motions, $\mathbf{g}_0$ is the initial g-tensor in the absence of rotation motions, $L_\parallel$ and $L_\perp$ are quasi-libration half-amplitudes around the axis of orientation of the molecule and around the perpendicular axes, correspondingly, $\mathbf{R}(\Omega)$ is the rotation matrix for set of Euler angles $\Omega = (\varphi, \theta, -\varphi + \psi)$, $Q = \int_0^{2\pi} d\varphi \int_0^{L_\perp} \sin\theta d\theta \int_{-L_\parallel}^{+L_\parallel} d\psi$ is normalization factor.

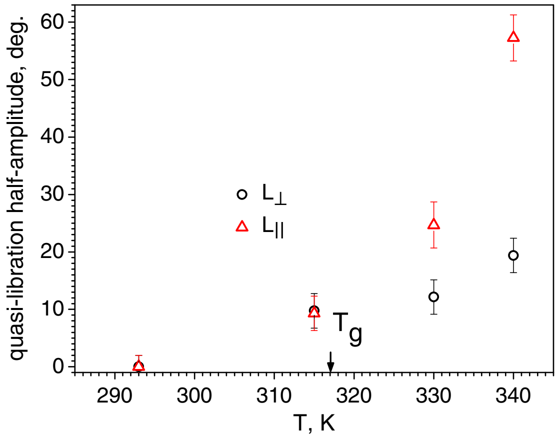

FIGURE 4 Quasi-libration amplitudes for the probe I depending on the temperature. [Color figure can be viewed at wileyonlinelibrary.com]

The analogous expression holds for hyperfine splitting tensor **A**:

$$\mathbf{A}_L = \frac{1}{Q}\int_0^{2\pi} d\varphi \int_0^{L_\perp} \sin\theta d\theta \int_{-L_\parallel}^{+L_\parallel} d\psi \mathbf{R}(\Omega)\mathbf{A}_0\mathbf{R}^T(\Omega)$$

The temperature dependence of quasi-libration amplitudes for the probe I, obtained with the use of the expression (4), is presented in Figure 4. It is seen that near the glass transition temperatures, the substantial increase in quasi-libration amplitudes is observed, which is consistent with the results known in the

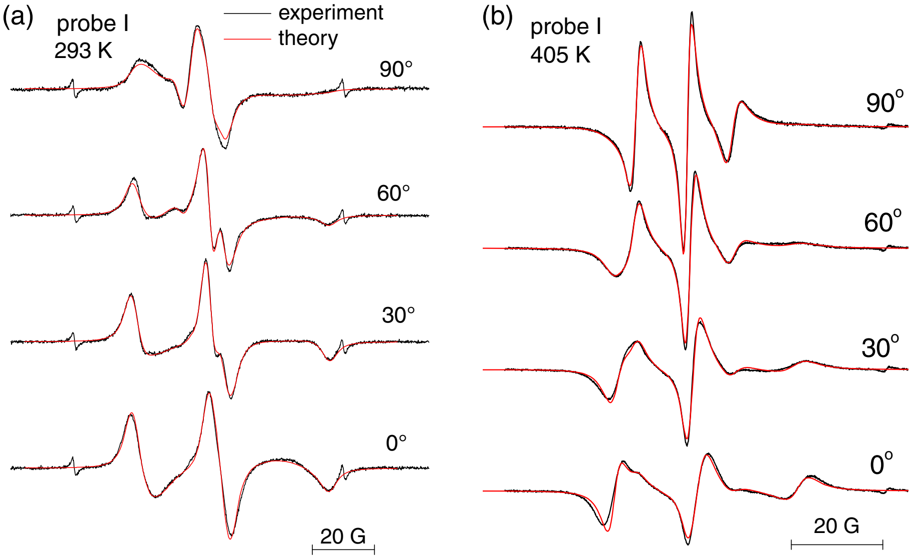

FIGURE 3 Experimental (black lines) and simulated (red lines) spectra of the spin probe I in the aligned samples of LC polymer at 293 K (a) and 405 K (b). [Color figure can be viewed at wileyonlinelibrary.com]

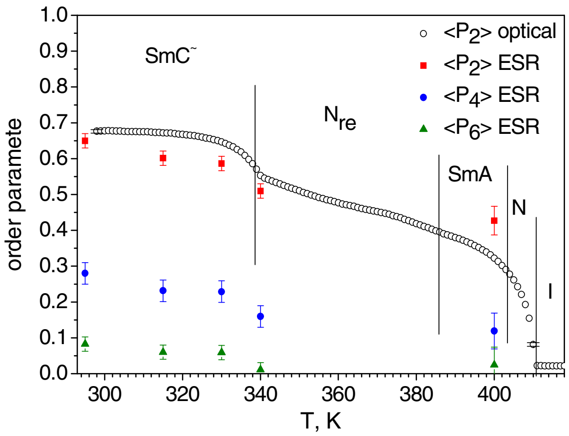

FIGURE 5 The order parameters of the LC polymer obtained by ESR technique (probe I, filled points) and from measurements of optical dichroism of perylene groups of the copolymer (open circles). [Color figure can be viewed at wileyonlinelibrary.com]

literature.[45,57] It should be noted that in the ordered LC polymer quasi-libration motions around the axis perpendicular to the main orientation axis lead to partial disordering of the molecular fragments. The order parameters measured with ESR technique relate to the averaged values of g- and hfc-tensors, and do not take into account such disordering. For this reasons, the order parameters obtained from ESR spectra in the presence of quasi-librations, should be corrected according to the formula:[50]

$$\langle P_n \rangle = \langle P_n \rangle_L \cdot P_n(\cos L_\perp),$$

where $\langle P_n \rangle_L$ are order parameters obtained from the spectra with the use of averaged tensors $\mathbf{g}_L$ and $\mathbf{A}_L$, $P_n(\cos L_\perp)$ is Legendre polynomial of rank *n*.

Orientation order parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$, $\langle P_6 \rangle$ determined in the course of simulation of ESR spectra of the probe I are presented in Figure 5 (filled points). Unlike the optical techniques, which are only capable of measurement of the second rank order parameter $\langle P_2 \rangle$, the spin probe technique yields order parameters of higher ranks, that characterize the detailed shape of orientation distribution function. The values of order parameter $\langle P_2 \rangle$ obtained from ESR spectra can be compared with those obtained from optical measurements with copolymer containing perylene groups (Fig. 5, open points). It is seen that the two techniques give consistent results.

Simulation of ESR spectra of the probe II at temperatures 298–340 K gives much higher discrepancies between simulated and experimental spectra than those for the probe I. The ESR spectra of the probe II could not be described well within the rigid limit approximation. Obviously the reason of these deviations lies in the structure of the probe II, which allow for internal rotation of probe moieties around the ester bond. These rotations at glass transition temperature lead to the change of the ESR spectrum shape and cause deviations from the rigid limit shape.

To illustrate this, in Figure 6, two simulations of the same ESR spectrum are presented: within the framework of rigid limit model [Fig. 6(a)] and in the model of slow-motions [stochastic Liouville equation approach, Fig. 6(b)]. The spectra were recorded at 320 K, that is, in the glassy state of the host polymer. It is seen that the simulation with the slow-motional model gives better results. However, the quantitative agreement between the simulated spectra and the experimental ones cannot be reached. The reason of the nonideal description of spectra lies in the complexity of the rotational motions of the probe II in the glassy matrix. The nitroxide group takes part in a number of rotational moves on different timescales that includes: conformational changes of the probe, quasi-librations of the probe as a whole in

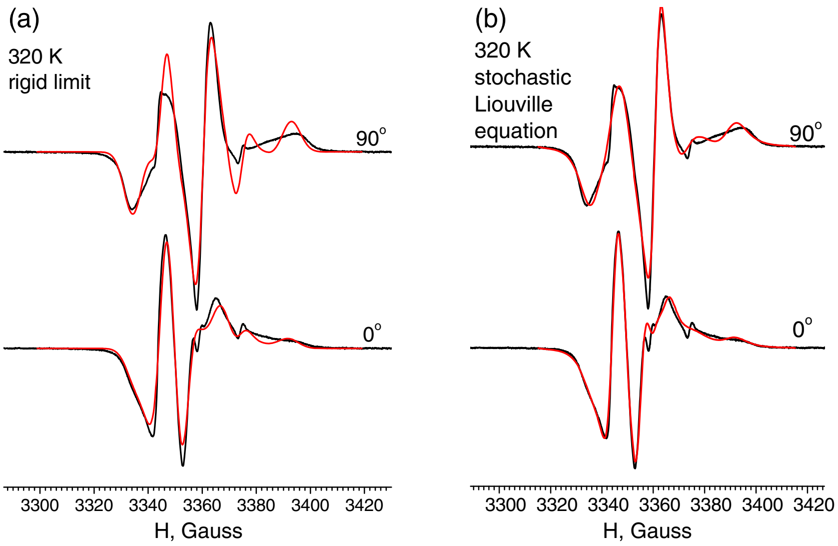

FIGURE 6 Simulation of ESR spectrum angular dependency of the probe II at 320 K in the rigid limit approximation (a) and in the slow-motional model (b). Only two spectra of the angular dependence are shown for clarity (black lines – experiment, red lines – simulation). [Color figure can be viewed at wileyonlinelibrary.com]

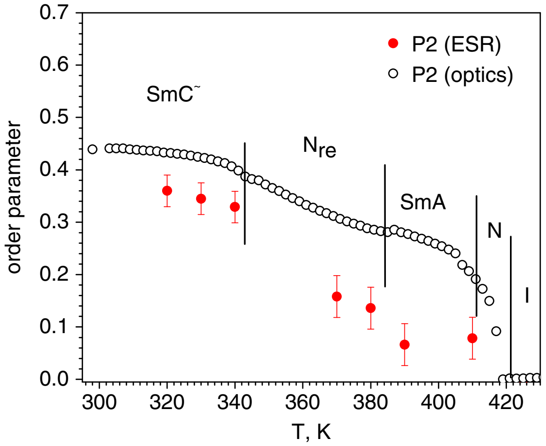

FIGURE 7 The order parameters of the LC polymer obtained by ESR technique (probe II, filled points) and from measurements of optical dichroism of azobenzene groups of the probe II (open points). [Color figure can be viewed at wileyonlinelibrary.com]

a cage of the glassy matrix, probe rotations. The set of these motions is not well described by simple rotation diffusion model. The additional contribution in the complex shape of ESR spectra can be introduced by the heterogeneity of polymer medium.[12,57]

Due to the nonquantitative description of ESR spectra of the probe II, one can expect that the orientation order parameters obtained from the simulation in this case are determined with larger uncertainties. For this reason, in this work we present only the estimates of the order parameter of rank 2 obtained as a result of the simulations of ESR spectra of the probe II. These values are presented in Figure 7 as filled points. In this figure, the order parameters $\langle P_2 \rangle$ obtained from ESR spectra of nitroxide fragment of the probe II are compared with the values of optical dichroism of azobenzene fragment of the same probe. Comparison of these values with order parameters $\langle P_2 \rangle$ for the probe I (Fig. 5, filled squares) shows that both optical dichroism and order parameter of the nitroxide group of the probe II are smaller than that of the probe I. It should be noted that all three values show similar character of temperature dependence. These observations indicate that all these values reflect the orientational ordering of the matrix, but the probe II is weaker aligned in the medium of the LC polymer. Figure 7 shows that the order parameters of nitroxide fragment are smaller than the values of optical dichroism of azobenzene group of the same probe, which may be caused by conformational mobility of the nitroxide fragment relatively to azobenzene fragment.

CONCLUSIONS

In this work, the spin-probe technique was applied to measure orientation order and rotation mobility of a LC polymer. The results obtained with ESR spectroscopy were compared with the optical measurements. It was shown that the orientation order parameters differ for different spin-probe molecules. The most reliable results are obtained for the rigid-core spin-probes. Such probes are effectively aligned in the LC medium, and the interpretation of ESR spectra is less complicated by the conformational mobility of the probe molecules. For the rigid probe in the vicinity of the glass transition point, fast amplitude-restricted angular reorientations (quasi-librations) of the probe should be taken into account to quantitatively simulate spectra.

The obtained order parameters for the studied ESR and optical probes are consistent with the known fact that different structural units of the LC polymer possess different degree of orientation order.[58,59] Using multiple probes of different molecular structure allows enhancing the informativity of the obtained data, and reveal molecular orientation distributions of different regions of the polymer matrix.

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REFERENCES

1 M. Kleman, O. Lavrentovich, *Soft Matter Physics: An Introduction*; Springer: New York, **2003**.

2 L. M. Blinov, *Electro-Optical and Magneto-Optical Properties of Liquid Crystals*; Wiley: New York, **1983**.

3 J. A. Castellano, *Molecular Crystals and Liquid Crystals*, **2007**; Vol. *94*, p. 33.

4 B. Jerome, *Rep. Prog. Phys.* **1991**, *54*, 391.

5 F. Simoni, O. Francescangeli, *J. Phys. Condens. Matter* **1999**, *11*, R439.

6 A. Natansohn, P. Rochon, In *Photoreactive Organic Thin Films*; Z. Sekkat, W. Knoll, Eds.; Elsevier Science: San Diego (USA), **2002**, p. 399.

7 A. Bobrovsky, A. Ryabchun, A. Medvedev, V. Shibaev, *J. Photochem. Photobiol. A Chem.* **2009**, *206*, 46.

8 V. P. Shibaev, A. Y. Bobrovsky, *Russ. Chem. Rev.* **2017**, *86*, 1024.

9 A. K. Vorobiev, N. A. Chumakova, In *Nitroxides - Theory, Experiment and Applications*; A. I. Kokorin, Ed.; InTech: Rijeka, Croatia, **2012**, p. 57.

10 D. J. Schneider, J. H. Freed, In *Biological Magnetic Resonance, v. 8, Spin Labeling. Theory and Applications*; L. J. Berliner, Ed., New York, **1989**, p. 1.

11 A. Polimeno, J. H. Freed, *J. Phys. Chem.* **1995**, *99*, 10995.

12 D. A. Chernova, A. K. Vorobiev, *J. Appl. Polym. Sci.* **2011**, *121*, 102.

13 D. Braun, P. Törmälä, *Colloid Polym. Sci.* **1977**, *255*, 496.

14 D. Leporini, G. Jeschke, *Philosop. Mag.* **2004**, *84*, 1567.

15 P. Törmälä, *J. Macromol. Sci., Part C: Polym. Rev.* **1979**, *17*, 297.

16 D. Hinderberger, EPR Spectroscopy in Polymer Science. In *EPR Spectroscopy. Topics in Current Chemistry*; M. Drescher, J. G, Eds.; Springer: Berlin, Heidelberg, **2011**; Vol. *321*, p. 67.

17 M. Brustolon, A. Barbon, In *EPR of Free Radicals in Solids I. Progress in Theoretical Chemistry and Physics*; A. Lund, M. Shiotani, Eds.; Springer: Dordrecht, Netherlands, **2013**; Vol. *24*.

18 G. Jeschke, H.-W. Spiess, In *Novel NMR and EPR techniques. Lecture Notes in Physics*; J. Dolinšek, M. Vilfan, S. Žumer, Eds.; Springer: Berlin, Heidelberg, **2006**; Vol. *684*.

19 J. Bartoš, L. Andreozzi, M. Faetti, O. Šauša, D. Račko, J. Krištiak, *J. Non Cryst. Solids* **2006**, *352*, 4785.

20 K. C. Khulbe, F. Hamad, C. Feng, T. Matsuura, T. Gumi, C. Palet, *Polymer* **2003**, *44*, 695.

21 J. Zhang, Z. Luz, H. Zimmermann, D. Goldfarb, *J. Phys. Chem. B* **2000**, *104*, 279.

22 Y. Xia, Y. Li, A. O. Burts, M. F. Ottaviani, D. A. Tirrell, J. A. Johnson, N. J. Turro, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 19953.

23 W.-J. Lin, J. H. Freed, *J. Chem. Phys.* **1979**, *83*, 379.

24 E. Meirovitch, Z. Luz, S. Alexander, *Molecul. Phys.* **1979**, *37*, 1489.

25 E. Meirovitch, J. H. Freed, *J. Phys. Chem.* **1984**, *88*, 4995.

26 C. F. Polnaszek, G. V. Bruno, J. H. Freed, *J. Chem. Phys.* **1973**, *58*, 3185.

27 C. F. Polnaszek, J. H. Freed, *J. Phys. Chem.* **1975**, *79*, 2283.

28 E. Meirovitch, D. Inger, E. Inger, G. Moro, J. H. Freed, *J. Chem. Phys.* **1982**, *77*, 3915.

29 A. V. Bogdanov, A. K. Vorobiev, *Phys. Chem. Chem. Phys.* **2016**, *18*, 31144.

30 K.-H. Wassmer, E. Ohmes, G. Kothe, *Makromol. Chem., Rapid. Commun.* **1982**, *3*, 281.

31 K.-H. Wassmer, E. Ohmes, M. Portugall, H. Ringsdorf, G. Kothe, *J. Am. Chem. Soc.* **1985**, *107*, 1511.

32 D. Xu, D. E. Budil, C. K. Ober, J. H. Freed, *J. Phys. Chem.* **1996**, *100*, 15867.

33 D. Xu, R. H. Crepau, C. K. Ober, J. H. Freed, *J. Phys. Chem.* **1996**, *100*, 15873.

34 A. Bogdanov, A. Vorobiev, *J. Phys. Chem. B* **2013**, *117*, 12328.

35 S. A. Zager, J. H. Freed, *J. Chem. Phys.* **1982**, *77*, 3344.

36 J. H. Freed, Theory of Slow Tumbling ESR Spectra for Nitroxides. In *Spin Labeling. Theory and Applications*; L. J. Berliner, Ed.; Academic Press: London, **1976**, p. 53.

37 B. Y. Mladenova, D. R. Kattnig, G. Grampp, *J. Phys. Chem. B* **2011**, *115*, 8183.

38 L. Alessi, L. Andreozzi, M. Faetti, D. Leporini, *J. Chem. Phys.* **2001**, *114*, 3631.

39 V. Bercu, M. Martinelli, C. A. Massa, L. A. Pardi, D. Leporini, *J. Chem. Phys.* **2005**, *123*, 174906.

40 G. G. Maresh, M. Weber, A. A. Dubinskii, H. W. Spiess, *Chem. Phys. Lett.* **1992**, *193*, 134.

41 C. Barcchiocchi, I. Miglioli, A. Arcioni, I. Vecchi, K. Rai, A. Fontecchio, C. Zannoni, *J. Phys. Chem. B* **2009**, *113*, 5391.

42 S. A. Brooks, G. R. Luckhurst, G. F. Pedulli, J. Roberts, *J. Chem. Soc. Faraday Trans.* **1976**, *2*, 72 651.

43 G. R. Luckhurst, *Thin Solid Films* **2006**, *509*, 36.

44 D. E. Budil, S. Lee, S. Saxena, J. H. Freed, *J. Magn. Reson. A* **1996**, *120*, 155.

45 D. A. Chernova, A. K. H. Vorobiev, *J Polym Sci B* **2009**, *47*, 107.

46 T. S. Yankova, N. A. Chumakova, D. A. Pomogailo, A. K. Vorobiev, *Liq. Cryst.* **2013**, *40*, 1.

47 S. A. Dzuba, E. P. Kirilina, E. S. Salnikov, L. V. Kulik, *J. Chem. Phys.* **2005**, *122*, 094702.

48 N. I. Boiko, V. P. Shibaev, B. Ostrovskii, S. Sulyanov, D. Wolff, J. Springer, *Macromol. Chem. Phys.* **2001**, *202*, 297.

49 N. Ikuma, R. Tamura, S. Shimono, N. Kawame, O. Tamada, N. Sakai, J. Yamauchi, Y. Yamamoto, *Angew. Chem. Intl. Ed. Eng.* **2004**, *43*, 3677.

50 T. S. Yankova, A. Y. Bobrovsky, A. K. Vorobiev, *J. Phys. Chem. B* **2012**, *116*, 6010.

51 N. A. Chumakova, A. K. Vorobiev, N. Ikuma, Y. Uchida, R. Tamura, *Mendeleev Commun.* **2008**, *18*, 21.

52 S. Nakatsuji, M. Fusino, S. Hasegawa, H. Akutsu, J. Yamada, V. S. Gurman, A. K. Vorobiev, *J. Org. Chem.* **2007**, *72*, 2021.

53 L. T. Creagh, A. R. Kmetz, *Molecul. Cryst. Liquid Cryst.* **2007**, *24*, 59.

54 Y. Sato, K. Sato, T. Uchida, *Jpn. J. Appl. Phys. Part* **1992**, *2* (31), L579.

55 C. Zannoni, In *The Molecular Physics of Liquid Crystals*; G. R. Luckhurst, G. W. Gray, Eds.; Academic Press: London, New York, **1979**, p. 51.

56 M. v. Gurp, *Colloid Polym. Sci.* **1995**, *273*, 607.

57 A. V. Bogdanov, A. K. Vorobiev, *Chem. Phys. Lett.* **2011**, *506*, 46.

58 U. Wiesner, N. Reynolds, C. Boeffel, H. W. Spiess, *Liq. Cryst.* **1992**, *11*, 251.

59 C. Kulinna, S. Hvilsted, C. Hendann, H. W. Siesler, P. S. Ramanujam, *Macromolecules* **1998**, *31*, 2141.