

Pulse n.m.r. study of the dynamics of fluctuations of local anisotropy in the solutions of liquid crystalline R–F polymers

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Temperature dependencies of proton magnetic relaxation times and forms of transversal magnetisation decay in chloroform-d solutions of three liquid crystalline polyesters with fumaroil-bis-oxybenzoate mesogenic units connected by different flexible spacers (CH₂)₅, (CH₂)₆ and CH₂(CH₂CH₂O)₂CH₂ (poly(R-M5), poly(R-M6) and poly(R-EO2), respectively) are studied in the concentration range 9–20 w/w%. Chemical exchange is shown to influence the form of transversal magnetisation decay and the dependencies of spin–spin relaxation time on the time interval in Carr–Purcell sequence. The rate of exchange is shown to depend on spacer flexibility and evenness, and on molecular mass and concentration. The exchange parameters (life time, chemical shift difference, populations) for poly(R-M6) solutions are estimated, and their dependencies on temperature and concentration are discussed in terms of heterophase fluctuations of local order. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

It is well known that in low molecular liquid crystal (LC), only the long-range ordering vanishes during the l.c.–i transition, although fluctuations of the local order still exist in the pretransitional area in the isotropic phase^{1,2}. Strong correlations of orientation act at the scale of coherence length, i.e. within the cluster. Local order in the isotropic phase of l.c. manifests itself in anomalies of light scattering, birefringence, spin–lattice relaxation, etc.

In liquid crystalline polymers (LCP) the pretransitional phenomena also take place. It is important to study them, because in the pretransitional range the LCP structure starts to form. However, it is difficult to attain the equilibrium structure in LCP because of their high viscosity and the necessity of annealing^{3–5}. In our opinion, a study of LCP solutions can give better insight into this problem, since the fluctuations in the solutions are not restricted by the high viscosity as in the melts. In addition, concentration and solvent quality can be convenient variables to control the kinetics of fluctuations and structure of the solution. The majority of studies on structure formation in the solutions of LCP consisting of mesogenic units attached to the main chain have dealt with comb-like LCP, since LCP, the main chain of which contains rigid (R) mesogenic fragments, connected by flexible (F) spacers (we shall call them R–F LCP) are insoluble as a general rule. It was shown^{6,7} that even in very dilute solutions of comb-like LCP the local ordering of mesogenic units still exists, giving rise to the anomalously high values of optical anisotropy per segment. Very little attention has been paid to the dynamics of fluctuations, although cluster formation was shown to manifest itself also in the dynamic properties of solutions. For example, the dielectric relaxation data showed that in

addition to the normal local relaxation process, the extra relaxation range with a high activation energy characteristic of cooperative motion appeared⁸. The corresponding solutions are known to form gels at very low concentrations (ca. 0.3 w/w%). Since these gels are not typical temperature-reversible gels of the kind observed in solutions of readily crystallisable flexible chain polymers (the main difference is in the nature of ‘normal’ and intermacro-molecular LC nucleus⁹) we shall call them ‘para’-gels. Early para-gel formation in the solutions of comb LCP prevents lyotropic ordering and makes it impossible to study the concentration dependence of dynamics and structure of clusters. From this point of view, a more favourable situation is supposed to exist in some rare representatives of soluble R–F LCP. It is obvious (*Figure 1*) that in the R–F LCP the local concentration of mesogenic fragments is not so high as in comb LCP and can be controlled by the spacer length and rigidity. In fact, the para-gel threshold concentration in the solution of R–F LCP¹⁰ is higher than in the solutions of comb-like LCP. Therefore, the investigation of the fluctuation dynamics in the former solutions seems to be promising. It is interesting to study the influence not only of concentration and temperature but also that of the spacer (its rigidity, length and evenness) on the fluctuation dynamics. In fact, the spacer is known to play an active role in the mesophase structure of R–F LCP, even larger than in the comb-like LCP^{11–14}. Unfortunately, a full description of the spacer role in R–F LCP, taking into account the combined action of anisotropic attractive forces and steric interactions, is absent¹⁵, though the attempts of calculation of phase diagrams of LCP with alternating rigidity on the base of lattice theories^{16,17}, or molecular dynamics approach¹⁸ gave a general outlook on the problem. (An example of the inconsistency of experimental data and theory for the thermotropic/lyotropic R–F LCP can be found in Ref. 19). Therefore, experimental investigations of

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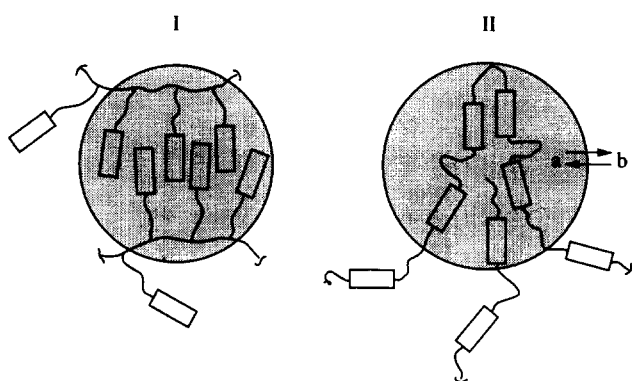


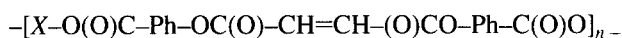
Figure 1 Schematic representation of cluster formation in the solutions of comb-like LCP (1) and R-F LCP (2): a, cluster; b, isotropic phase

properties of solutions of R-F LCP should play an essential role. However, the number of soluble R-F LCP is very limited, and thus their solutions almost have not been studied. The dynamics of fluctuations have not been studied at all as far as we are concerned. In the previous work dealing with the dielectric relaxation in semi-dilute solutions of R-F LCP²⁰, the relaxation of the dipole polarisation of mesogenic fragments with activation energy $E = 100 \text{ kJ mol}^{-1}$ has been observed in addition to the ordinary local relaxation process. High activation energy of this process indicated the cooperative character of motion of mesogenic units. This behaviour, of course, is similar to the dynamic behaviour observed in the solutions of comb-like LCP, and therefore some kind of structure formation could be supposed in the studied solutions. However, in the solutions of R-F LCP the proposal of local ordering is not supported by the large amount of structural data, as in the more thoroughly studied comb-like LCP. To prove the idea of cluster formation in semi-dilute and concentrated solutions of these LCP on the base of dynamic experiments we have to estimate the life time of fluctuations and/or the dynamics of the exchange of the molecular units between the ordered and disordered states. In the current work we used pulsed n.m.r. to study the exchange dynamics in the solutions of R-F LCP.

EXPERIMENTAL

Polymers

In the current work we studied the chloroform-d solutions of three R-F LCP (poly(R-M5), poly(R-M6) and poly(R-EO2)):



where $X = (\text{CH}_2)_5$, $(\text{CH}_2)_6$ and $\text{CH}_2(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2$, respectively. The intrinsic viscosities $[\eta]$ in chloroform at 23°C are 0.74 dl g^{-1} and 0.47 dl g^{-1} for the two samples of poly(R-M6), 0.60 dl g^{-1} for poly(R-M5) and 0.40 dl g^{-1} for poly(R-EO2).

The basic principles of synthesis of polyesters studied are described in Ref. ²¹. These polymers are known to exhibit mesomorphic properties in the bulk state²². The solubility of R-F LCPs with fumaroil-bis-oxybenzoate mesogenic units increases with spacer length. Among the investigated polymers the solubility of poly(R-M6) is the worst (fumaroil-bis-oxybenzoates with shorter spacers are insoluble). Therefore, poly(R-M6) was dissolved at 40°C, the other polymers were dissolved at room temperature. At the polymer concentration $C > 20 \text{ w/w\%}$ the gel is slowly

formed in poly(R-M6) solutions at room temperature. Upon heating the gel is destroyed at 35–40°C in some minutes. The study of polymer and solvent dynamics in the vicinity of this transition is underway. In the current work, solutions with $C < 20\%$ at $T < 35^\circ\text{C}$ were studied. Since the solutions of poly(R-M6) at $C = 20\%$ are unstable, they were preheated at 40°C before measurement.

Pulsed n.m.r.

In its simplest non-selective version, n.m.r. was used for the investigation of molecular dynamics and the dynamics of exchange. Proton magnetic relaxation of the chloroform-d solutions of poly(R-M5), poly(R-M6), and poly(R-EO2) was studied at 16 MHz on RRP-1 apparatus equipped with a variable temperature unit.

Spin-spin relaxation times (T_2) were measured with the help of a two-pulse $90^\circ-t-180^\circ$ and multiple-pulse Curr-Purcell $90^\circ-t-180^\circ-2t-180^\circ-2t-180^\circ\dots$ sequences. Spin-lattice relaxation times (T_1) were measured using a $90^\circ-t-90^\circ$ pulse sequence. The accuracy of t_2 and T_1 values depends on the concentration of the polymer in the solution (it increases from 5% for $C = 20\%$ to 15% for $C = 5\%$).

High resolution PMR spectrum was recorded on a spectrometer Bruker AC-200 (200 MHz).

It is well known²³ that the form of the transverse magnetisation decay (TMD) as measured in the two-pulse experiment and the dependence of T_2 on $t_{cp} = 2t$ in the Curr-Purcell sequence can be sensitive to the exchange of spin magnetisation between environments differing in mobility and/or in the local magnetic field (the last case is called in n.m.r. the chemical exchange). Spin-lattice relaxation is insensitive to chemical exchange, it characterises only the exchange between states differing in mobility.

It should be mentioned that in the presence of exchange the analyses of dynamic experiments are very complicated, since the results depend on the relationship between the life time (t_1) and the observation time (t_{obs}). If $t_1 \gg t_{obs}$ then two relaxation processes in the free and associated states would be observed. In the opposite limit ($t_1 < t_{obs}$), only one middle relaxation process should be observed. Observation times in n.m.r. relaxation are of the order of relaxation times T_1 or T_2 . If the multiple-pulse sequence is used to measure the spin-spin relaxation then the observation time becomes t_{cp} , i.e. it can be changed independently. Therefore, pulsed n.m.r. experiments are powerful tools with which to study exchange phenomena.

Exchange can be observed only in favourable experimental conditions, depending on the correspondence of the rate of the exchange to the line width, or to the chemical shift difference, or to the relaxation rate. Variations of temperature, concentration, polymer flexibility, and t_{cp} made it possible to find the experimental conditions at which the exchange kinetics were reliably determined.

RESULTS

Study of TMD forms

The common property of all solutions studied in the present work was the change of the form of TMD from exponential ($A = A_0 \exp(-t/T_2)$, A and A_0 being the amplitudes of magnetisation decay at the current and initial moments) to non-exponential with increasing temperature. The dome-shaped form of the TMD (Figure 2) indicates that in addition to the rotational mobility of macromolecular units, another mechanism of relaxation due to the local magnetic field inhomogeneity exists. In general, two types

of motion can be responsible for such effects: self-diffusion in the external magnetic field gradient, and chemical exchange. For the TMD form to be influenced, much higher values of external magnetic field gradients are required for polymer self-diffusion than were used in our relaxometer (0.4 Gs cm^{-1}); thus, chemical exchange caused the change of TMD form. We considered the influence of chemical exchange on TMD according to Woessner²⁴. Woessner has shown that the maximum damping of TMD is observed when $1/t_1$ is ca. $\delta\omega/\pi$, $\delta\omega = \omega_a - \omega_b$ being the chemical shift difference between the exchanging states. Woessner formulae contain too many parameters of exchange, creating a serious problem when attempts are made to fit them to the experimental TMD curve. However, we shall use them later after some of the parameters are obtained from the analyses of the Curr-Purcell experiment.

Investigation of exchange kinetics on the basis of combined analyses of TMD and the results of the Curr-Purcell experiment

The Curr-Purcell sequence is usually applied in n.m.r. to diminish the additional damping of TMD caused by variations of the local magnetic field due to self-diffusion or chemical exchange²³. In fact, as can be seen in Figure 2, TMD as measured by Curr-Purcell sequence becomes exponential, i.e. the influence of exchange is really damped. Still the exchange phenomena manifest themselves in the Curr-Purcell experiment by the dependence of T_2 on t_{cp} plotted in Figure 3 for the solutions of poly(R-M6) ($[\eta] = 0.74 \text{ dl g}^{-1}$) $C = 9, 12, 20\%$, $[\eta] = 0.47 \text{ dl g}^{-1}$ $C = 17\%$, for the solutions of poly(R-M5) and poly(R-EO2) $C = 9\%$ in chloroform-d at 30°C. We used the Luz-Meiboom formula²⁵ derived for the exchange between two states differing in chemical shift in the wide range of t_{cp}/t_1 to describe the dependencies of T_2 on t_{cp} :

$$1/T_2 = 1/T_{20} + Bt_1 F(t_1) \quad (1)$$

where $B = p_a p_b (\delta\omega)^2$, $F(t_1) = 1 - (2t_1/t_{cp}) \text{th}(t_{cp}/2t_1)$, p_a and $p_b = 1 - p_a$ are the populations of states, and t_{20} characterises the spin-spin relaxation time at $t_{cp} < t_1$, i.e. in the absence of exchange.

Experimental dependencies of T_2 on t_{cp} were fitted by equation (1) using the procedure described in Ref. ²⁶.

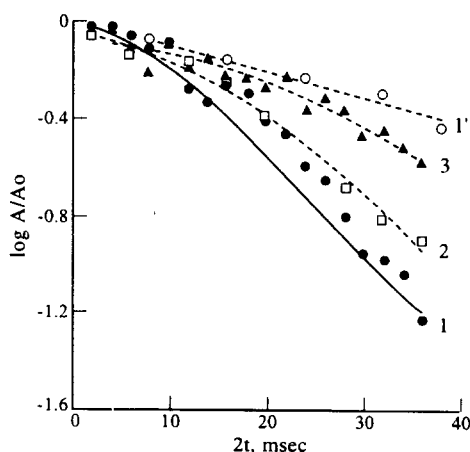


Figure 2 Transversal magnetisation decays of R-F LCP in chloroform-d solutions at concentration 9 w/w% measured at 30°C. Curves 1–3 represent the result of two-pulse $90^\circ-t-180^\circ$ experiment, curve 1' is measured by a multiple-pulse sequence $90^\circ-t-180^\circ-2t-180^\circ-2t$. TMD of the solutions of poly(R-M6) (curves 1, 1'), poly(R-M5) (curve 2), poly(R-EO2) (curve 3) are shown. The solid curve represents the results of TMD fitting of curve 1 according to refs.^{24–26}, the dotted lines are just a guide for eye

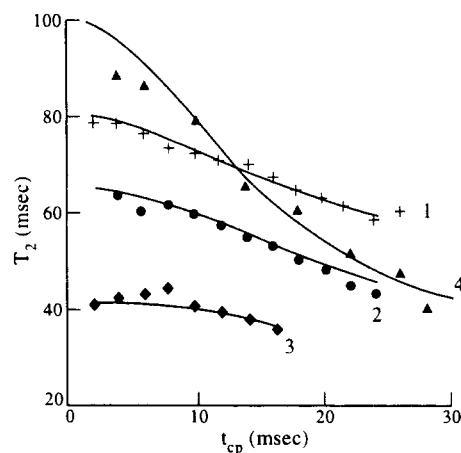


Figure 3 Spin-spin relaxation time vs. t_{cp} at 30°C in chloroform-d solutions of poly(R-M6) $[\eta] = 0.74 \text{ dl g}^{-1}$ $C = 9, 12$ and 20 w/w% (curves 1–3, respectively), poly(R-M6) $[\eta] = 0.47 \text{ dl g}^{-1}$ $C = 17$ w/w% (curve 4). For the solutions of the other polymers T_2 is independent of t_{cp} and is not shown for clarity. The lines are the results of data fitting using the Luz-Meiboom formula (equation (1)). The corresponding parameters are given in Table 1

According to ²⁶, the dependence of $1/T_2$ on $F(t_1)$ must be linear with the slope equal to Bt_1 and the intercept of $1/T_{20}$ at $t_1 = 0$ if the values of t_1 and B are chosen correctly. The criterion of the correct choice of t_1 and B corresponds to the minimum dispersion of experimental points.

The results of data fitting (parameters t_1 , B , and T_{20}) are listed in Table 1, and the Luz-Meiboom curves obtained are shown in Figure 3.

The observed increase of t_1 with concentration (Table 1) indicates the influence of intermolecular contacts on the exchange kinetics. The molecular weight dependence of exchange kinetics, of course, should be studied more thoroughly. The dependence of B on concentration can be influenced by the changes in $\delta\omega$ and/or in p_a and p_b . We obtained these parameters by the combined analyses of multiple-pulse data and the TMD form in the two-pulse experiment: the parameters obtained from equation (1) were inserted into Woessner's formulae. Therefore, only one fitting parameter in the latter approach remained— p_a . The calculated TMD curves are represented in Figure 2, and the corresponding exchange parameters are represented in Table 1. It follows from Table 1 that p_a significantly increases in the vicinity of the gel threshold concentration. Thus, the most obvious mechanism of gel formulation is the percolation of clusters (Figure 4).

For poly(R-M6) ($[\eta] = 0.47 \text{ dl g}^{-1}$) the temperature dependence of the lifetime (τ) was obtained. It is plotted in Figure 5. From Figure 5 it follows that this dependence can be described by the Arrhenius equation: $\tau = \tau_0 \exp(-E/RT)$, E and τ_0 being the activation energy and the frequency factor, respectively. The least-square fit of this dependence gives $E = 20 \text{ kJ mol}^{-1}$ and $\tau_0 = 10^{-6} \text{ sec}$. The low value of E is characteristic of the local motion; however, for the isotropic local motion much lower values of $\tau_0 = 10^{-14} \text{ sec}$ are usually observed²⁷. The frequency factor characterises the entropy changes during the exchange, and its extremely high value in our case indicates that the exchange between ordered and disordered local states is very pronounced. Therefore, we propose that the exchange is taking place between clusters (a) and the isotropic state (b), as indicated in Figure 1.

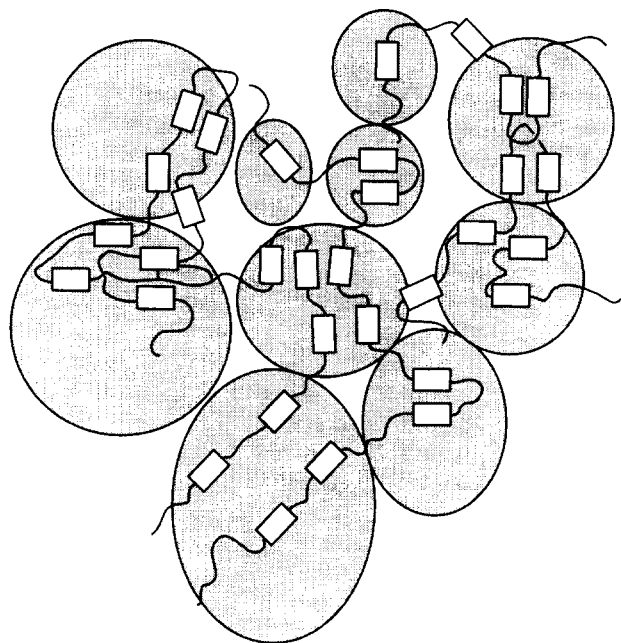
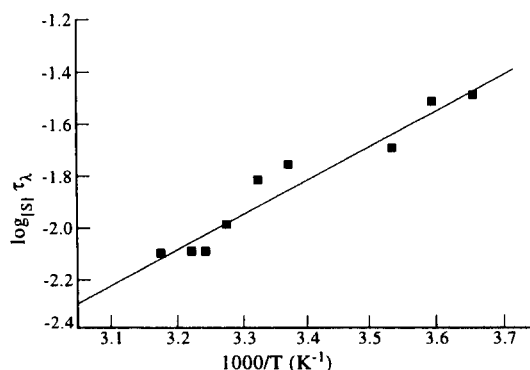
It can be seen from Figure 3 and Table 1 that T_{20} depends on concentration and molecular weight. In general, this

Table 1 Parameters of the kinetics of local order fluctuations for the solutions of poly(R-M6) at 30°C as determined by pulsed n.m.r.

$[\eta]$ (dl g ⁻¹)	C (w/w%)	T_{20} (ms)	t_1 (ms)	p_a	$1/t_1$ (sec ⁻¹)	$\delta\omega/2\pi$ (Hz)
0.74	9	80	7	0.08	170	60
0.74	13	64	14	0.15	70	80
0.74	20	42	25	0.90	50	120
0.47	17	100	15	0.16	67	25

value depends on the mobility of the polymer in the solution without the complications caused by exchange. The T_{20} decrease with concentration indicates the influence of intermolecular contacts on mobility.

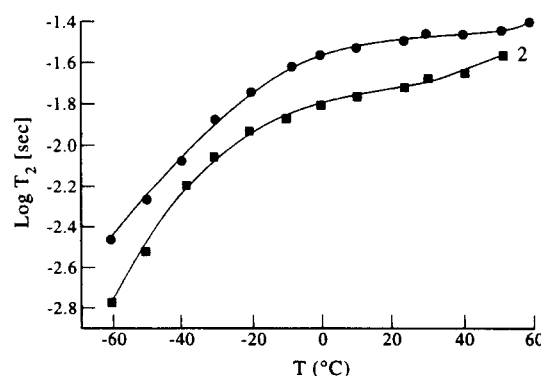
The temperature dependencies of T_2 are presented in Figure 6. At low temperatures where TMD is exponential, values of T_2 were determined from the two-pulse experiment. At higher temperatures, where the non-exponential form of TMD is observed, the values of T_2 at minimal t_{cp} are plotted. Figure 6 shows the unusual T_2 -temperature behaviour of the solutions: the lowering of the slope of T_2 curves with temperature, nearly causing T_2 to be independent of temperature in the high-temperature region. The origin of

**Figure 4** Schematic representation of the gel formation mechanism as a cluster percolation based on the results of n.m.r. analyses**Figure 5** Arrhenius plot of the mean life time of molecular units for chloroform-d solution of poly(R-M6) $[\eta] = 0.47$ dl g⁻¹, $C = 17$ w/w%

independence of T_2 on temperature lies in the two-fold nature of spin-spin magnetic relaxation, which can be controlled by two types of dipole-dipole interactions: secular and non-secular^{28,29}. Secular interactions prevail in the low-temperature region. If mobility is completely frozen, then the low-temperature plateau of the relaxation rate is observed. At high temperatures the anisotropy of motion can also lead to non-averaging of magnetic dipole-dipole interactions, and hence to the plateau region. In fact, the high-temperature plateau of T_2 is characteristic of the viscoelastic region of polymer networks or swollen gels where the anisotropy of the segment motion is due to the constraints imposed on the chain by the cross-links²⁹. In the present situation the independence of T_2 on temperature in the solutions indicates the non-averaging character of motion of polymer units due to their local ordering. Therefore, exchange can take place between ordered and disordered states characterised by different values of local magnetic fields.

From this point of view let us consider the values of $\delta\omega$ listed in Table 1. They increase with concentration. Since the origin of exchange is intermacromolecular, as was shown by the concentration dependence of the other exchange parameters, the concentration dependence of chemical shifts can originate from the growth of the local field inhomogeneity with the growth of cluster size.

How can it be that the n.m.r. spectra of these solutions did not give any evidence of chemical exchange³⁰? As an example, the n.m.r. spectrum of 5% chloroform-d solution of poly(R-M6), $[\eta] = 0.74$ dl g⁻¹ is shown in Figure 7. It presents no evidence of exchange (nor broadening of the adsorption maxima, nor their doubling). However, there is no inconsistency with the pulse n.m.r. data. It is well known that the latter method is sensitive to the faster exchange than the former one³¹. In fact, the condition of fast exchange for n.m.r. spectroscopy ($1/t_1 > \delta\omega/2\pi$) is fulfilled for the solutions of poly(R-M6) of $C < 13\%$ (see data in Table 1).

**Figure 6** Semilogarithmic dependence of the spin-spin relaxation time on temperature for chloroform-d solutions of poly(R-M6) $[\eta] = 0.74$ dl g⁻¹, $C = 13$ and 20 w/w% (curves 1 and 2, respectively). The other data are omitted for clarity

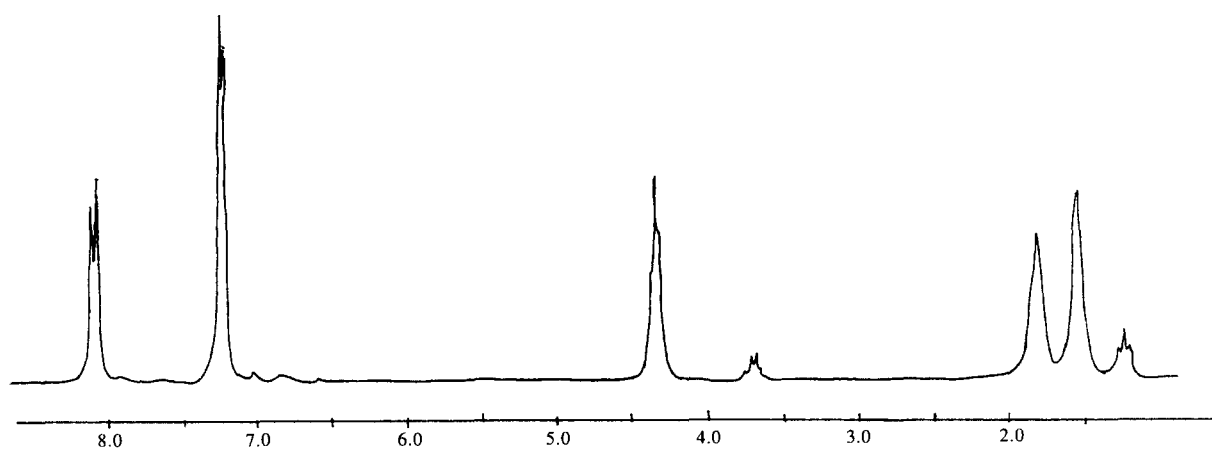


Figure 7 The n.m.r. spectrum of poly(R-M6) $[\eta] = 0.74 \text{ dl g}^{-1}$ in chloroform-d solution. Polymer concentration is 5 w/w%

For the solutions of two other polymers, the situation is less favourable than for the solutions of poly(R-M6) for the determination of exchange parameters. Since no dependence of T_2 on t_{cp} is observed, the TMD data can be analysed only qualitatively. Of course, the dome-shaped TMD (Figure 2) shows that chemical exchange is present. However, the independence of T_2 on t_{cp} can take place in two limiting cases: $t_1 \gg t_{cp}$ or $t_1 < t_{cp}$. The choice between these two extremes will be made on the basis of the analyses of temperature dependencies of T_1 .

Temperature dependencies of spin-lattice relaxation times

The temperature dependencies of T_1 are plotted in Figure 8 for the chloroform-d solutions of three polymers: poly(R-M6), poly(R-M5) and poly(R-EO2) at polymer concentrations of 9 w/w%. For the solution of poly(R-EO2), the dependencies of longitudinal magnetisation recovery are exponential in the whole temperature range, for the other two polymers only at temperatures higher than -30°C . The change of magnetisation recovery curve roughly indicates that the transition from the fast ($t_1 < T_1$) to the slow exchange limit ($t_1 > T_1$) takes place with the temperature decrease. In the solution of poly(R-EO2) the fast exchange limit is valid in the whole temperature range studied. In the case of non-exponential magnetisation recovery, relaxation time T_1 values were determined from the initial slope of the magnetisation recovery curve.

Further supporting evidence of the exchange phenomenon comes from the temperature dependencies of T_1 in

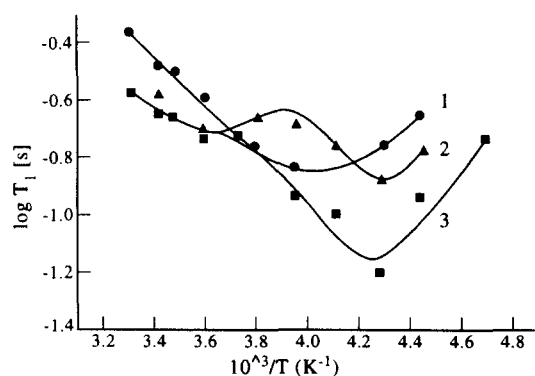


Figure 8 Semilogarithmic dependence of spin-lattice relaxation time on the reciprocal temperature for chloroform-d solutions of poly(R-EO2), poly(R-M5), poly(R-M6) $[\eta] = 0.74 \text{ dl g}^{-1}$, curves 1–3, respectively. Polymer concentration is 9 w/w%

Figure 8. Two minima of T_1 at -40 and 5°C are observed for the solutions of LCP with methylene spacers, and only one minimum at -20°C is observed in the solution of poly(R-EO2). The extrapolation of dielectric data of these solutions²⁰ measured at 10^2 – 10^5 Hz at the n.m.r. frequency of 16 MHz shows that two relaxation areas corresponding to the motion of the mesogenic unit should appear in temperature dependencies of T_1 at 72 and 8°C . Therefore, the low temperature T_1 process at -40°C in the solution of poly(R-M6) and poly(R-M5) at concentration 9% can be attributed unambiguously to the spacer motion. The high-temperature process at 5°C in these solutions can be attributed to the motion of spacers in associated states or of mesogenic units in the free state. Since the interproton distance is larger in the mesogenic fragments than in CH_2 groups of the spacer, the main part of relaxation reflects the spacer mobility. T_1 relaxation area in the solution of poly(R-EO2) is in the middle between these two processes, indicating the fast exchange of spacers between the associated and free states in contrast to the solutions of polymers with methylene spacers.

Turning back to the results of the Curr–Purcell experiment, we can say that the independence of T_2 on t_{cp} in the solutions of poly(R-M5) and poly(R-EO2) can be attributed to the different exchange limits: the fast one for poly(R-EO2) solution and the slow one for the poly(R-M5) solution. It should be noted that the analyses of exchange kinetics made on the basis of T_1 and T_2 relaxation data correspond. In fact, the comparison of t_1 , as derived from its temperature dependence with T_1 values, shows that at lower temperatures t_1 should exceed T_1 . Thus, the transition from the fast to slow exchange limit can take place, and in fact this is the case observed from the analyses of the form of magnetisation recovery curves.

CONCLUSIONS

The existence of a local order in the solutions of main-chain LCP is shown. Areas of local ordering (clusters) have a nature of heterophase fluctuations³². The exchange kinetics of molecular units between ordered and disordered states is determined. Spacer rigidity and evenness are the most important factors to influence the exchange kinetics. Fast exchange takes place in the solutions of poly(R-EO2). Of the three polymers studied, solutions of poly(R-M5) exhibit slow exchange. The temperature dependence of the life time is obtained and is shown to be of the Arrhenius type. The life

time changes with temperature rather slowly, because of the low activation energy characteristic of the local type of motion (20 kJ mol^{-1}). However, high values of life times are observed owing to the large entropy difference between the exchanging states, the frequency factor in the Arrhenius equation being extremely high (10^{-6} sec). This is evidence of the change in the order parameter during the exchange between the local ordered states in clusters and isotropic in the main phase. The local ordering in clusters manifests itself also in the high-temperature plateau value of T_2 . Therefore, the data presented show the importance of heterophase fluctuations of anisotropy which can also be treated as virtual 'glimpses' of the LC phase in solutions of thermotropic LCP which, as a rule, do not form any kind of lyotropic mesophase. The estimation of life times provides a quantitative basis for describing not only the different n.m.r. data but also the other experiments. In fact, the fast exchange limit is predicted and takes place in the n.m.r. spectra of poly(R-M6) solutions. In contrast, the dielectric relaxation data²⁰ must fall in the slow exchange limit, because the observation time in dielectric relaxation is of the order of correlation time, i.e. it is lower than t_1 in the frequency range studied (10^2 – 10^5 Hz).

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