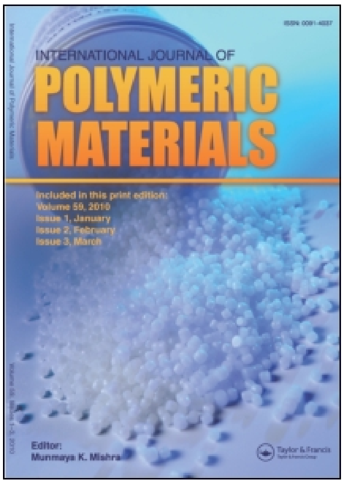

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Fridrikh, S. V. , Medvedev, G. A. and Gotlib, Y. Y.(1993) 'Continuous and Discrete Dynamics of Heterogeneous Mesogenic Polymer Chain', International Journal of Polymeric Materials, 22: 1, 65 — 73
To link to this Article: DOI: 10.1080/00914039308012059
URL: http://dx.doi.org/10.1080/00914039308012059

Intern. J. Polymeric Mater., 1993, Vol. 22, pp. 65–73
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Printed in Malaysia

Continuous and Discrete Dynamics of Heterogeneous Mesogenic Polymer Chain

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Two types of dynamic models—continuous and lattice—are considered describing a heterogeneous liquid-crystalline polymer chain built from mesogenes and spacers. The chain heterogeneity leads to enriching a set of possible motions of the chain. Each branch of the chain relaxation spectrum consisting of the isotropic phase of one acoustic and some optical branches is shown to be split into a longitudinal and transverse components. The magnitude of the splitting is found to depend on the scale of motions and the mechanism of the chain mobility. The dependence of the relaxation times on the degree of order is shown to be different for the chains with rigid and flexible spacers.

KEY WORDS Main-chain liquid crystalline polymers, mean field approximation, polymer dynamics, lattice model, relaxation spectrum.

INTRODUCTION

In the recent years dynamic properties of polymers with mesogenic groups in the main polymer chain have been investigated both experimentally[1–6] and theoretically.[7–11] In the majority of main-chain mesogenic polymers macromolecules consist of alternating mesogenic groups and flexible spacers. As is known from the experimental results, statistical properties of these polymers with a given mesogenic group, such as temperature of phase transition from the isotropic to the liquid crystalline (LC) state, depend on the spacer length.[5,6]

In our previous papers[7–11] devoted to the relaxational properties of the homogeneous main-chain mesogenic polymers we used the simplest dynamic models in which the spacers were supposed to be short and played the role of junctions between the mesogenes. This approach allows to take into account the spacer properties only via thermodynamic rigidity of the model chain.

The aim of this paper is to describe the influence of the chain heterogeneity and the spacer properties on the relaxational properties of the heterogeneous main-chain mesogenic polymer.

Of special interest are the local motions which are manifested in the dielectric relaxation spectra and NMR. The choice of the model describing dynamic properties of the polymer depends on the scale of the motions to be investigated. The least small-scale motions such as conformational changes in the aliphatic, siloxane or oxyethylenic spacer can be realistically described by the discrete mobility rotameric model considered below. We

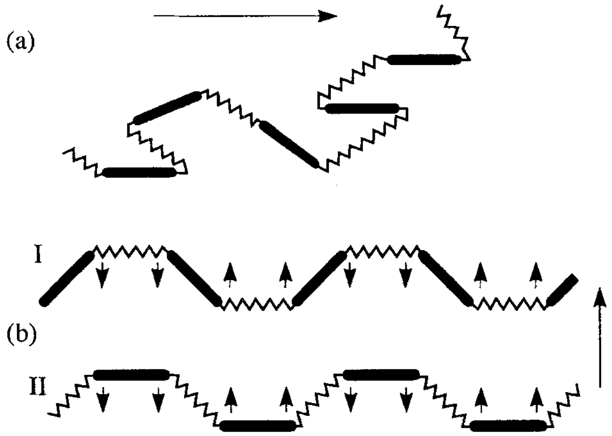

FIGURE 1 (a) Heterogeneous macromolecule in the orienting field. (b) Motions of heterogeneous chain for acoustical (I) and optical (II) branches ($p = 1$). Mesogenes are colored black, the arrows show the direction of motion of chain junctions.

will first analyze more simple continuous dynamic models which can be applied to the description of segmental mobility, i.e. motions of the kinetically independent polymer chain segments.

CONTINUOUS DYNAMIC MODEL

It is assumed that kinetic segments can contain either a mesogenic group and several bonds of the spacer or only several bonds of a spacer. The model polymer chain is represented by a sequence of alternating freely joint "mesogenes" and "spacers" (Figure 1a), with the orienting field influencing only the mesogenes. Each spacer consists of p freely joint kinetic segments ($p = 0$ corresponds to the homogeneous polymer chain). The viscous friction centers are located at the chain junctions, the neighboring mesogene and spacer forming a repeating unit of the polymer chain.

The liquid crystalline ordering is described within the frames of the mean field approximation (the Maier–Saupe approach).[12,13]

In our previous works the dynamic viscoelastic model of the homogeneous chain oriented by the quadrupole ordering field was considered.[7,8] The model can be generalized for the case of the heterogeneous chain.[9–11] In this approximation the chain motions are described by a set of linear equations for the average projections of the chain segments. The solution of these equations can be represented as a combination of normal modes, each normal mode being characterized by a phase shift between the neighboring repeating units of the polymer chain ψ and its own relaxation time.

In the absence of the orienting field the relaxational spectrum of the heterogeneous chain, unlike that of the homogeneous chain, consists of $(p + 1)$ branches: p "optical" and one "acoustical". The phase transition into the ordered phase causes splitting of each branch of the relaxational spectrum into longitudinal and transversal components. The components correspond to the relaxation of the chain segment projections on the order and the perpendicular axes (Figure 2).

The main factor causing the retardation of the parallel projection relaxation is the

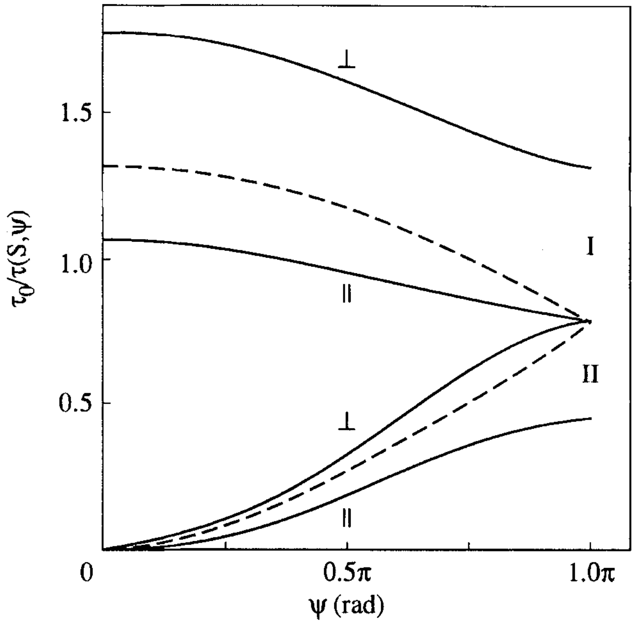

FIGURE 2 The relaxational times spectrum of the heterogeneous polymer chain for optical (I) and acoustical (II) branches in presence (solid curves) and absence (dashed curves) of the fields. Symbols || and ⊥ denote the longitudinal and transversal branch components, respectively. Each spacer of the chain consists of a single kinetic unit ($p = 1$). τ_0 is a characteristic time of chain element rotation diffusion.

necessity for mesogenes to overcome the potential barrier of the ordering field. For a single mesogene placed in the quadrupole ordering field, which corresponds to the low molecular weight nematic, there must be exponential dependence of the longitudinal relaxational time $\tau^{\|}$ on the magnitude of the ordering field potential barrier U_{orient}:[13]

$$\tau^{\|}(U_{\text{orient}}) = \tau^{\|}(0)\exp\left(\frac{U_{\text{orient}}}{k_{\text{B}}T}\right).$$

Taking into account the dependence of U_{orient} on the order parameter S one can write:[9]

$$\tau^{\|}(S) = \tau^{\|}(0)\exp\left(\frac{3S}{(1-S)(1+2S)}\right).$$

By contrast, the transversal projection relaxation is accelerated with the growth of S due to the increasing of steepness of the potential well slopes.[14]

The behavior of the polymer chain segments is determined by orienting field action as well as by the fact that they are connected in the united chain. Thus the relaxational processes in the chain are characterized by the whole set of the relaxation times—relaxation spectrum.

If the spacer can be represented as a single kinetic segment ($p = 1$), the relaxation spectrum of the polymer chain in the isotropic state will consist of two branches: the acoustical and the optical one. The repeat unit of such a chain consisting of a mesogene and a spacer contains two chain junctions. The acoustical branch corresponds mostly to cophasal motions of the chain elements within a given repeat unit; for the optical branch the opposite is true.

The dependence of the relaxation time of a given mode on the order parameter is determined by the type of the motion of mesogenes. The molecular LC field affects mainly rotational motions of the mesogenes. If mesogenes take part only in translational motions, the relaxation time of the corresponding normal mode in our model will not depend on the order parameter.

It is interesting to compare the relaxation times of normal modes with phase shift $\psi = \pi$ belonging to the longitudinal components of acoustical and optical branches (Figure 1b). One of the modes is characterized by the translational motions of the spacers and rotations of the mesogenes (the optical branch); the other— by rotations of the mesogenes and translational motions of the mesogenes (the acoustical branch). In the isotropic state both modes have the same relaxation times. The phase transition into the ordered phase increases drastically the relaxation time of the acoustic branch mode $\psi = \pi$ without changing the optic branch mode $\psi = \pi$.

We can conclude that in the relaxation spectrum of the heterogeneous chain, in contrast to that of the homogeneous chain, there occur local motions uninfluenced by the orienting field, which are mostly related to the translational mobility of mesogenes.

LATTICE DYNAMIC MODEL

For the adequate description of the short-range motions account should be taken of the details of the chain structure, namely: the links are not deformable and the bond angles are fixed. Here the model chain on the tetrahedral lattice is considered. The proposed treatment is a generalization of the method used in References 9,15 for the homogeneous model of LC polymer chain. The back step on the lattice, i.e. overlapping of adjacent bonds, is forbidden as compared to the continuous model studied above. The excluded volume effect is not taken into account.

As mentioned above, the mean field Maier–Saupe approach is used to describe the LC ordering. In this way the chain heterogeneity is determined by the orienting field acting immediately only upon the bonds of the model which mimic mesogenes. In contrast to the freely-jointed chain the ordering of the spacer is also due to the statistical correlation between mesogenes and spacers in the chain. For the simplest model with equivalent rotational isomers this correlation is determined only by the fixation of the tetrahedral bond angle and the Kuhn segment consisting correspondingly of two bonds.

The repeat unit of the chain includes a mesogene and p equal spacer bonds. It should be noted that the lattice orientation with respect to director corresponds to the condition of the free energy minimum.[15] The homogeneous chain consisting of the mesogenes only was investigated earlier[9,10] and can be used for comparison.

As the temperature decreases the system undergoes a phase transition to the ordered LC state. The chain conformation becomes anisotropic. In the homogeneous lattice model ($p = 0$) the LC state is accompanied by the increase of the stretched isomer fraction and extinction of the coiled isomers. Longitudinal persistent length increases infinitely with ordering as well as for the persistence model.[16] There is an increase in the chain rigidity.

The situation changes essentially for the heterogeneous chain ($p > 0$). An increase of the order degree results in the orientation of the mesogenes along the director. For

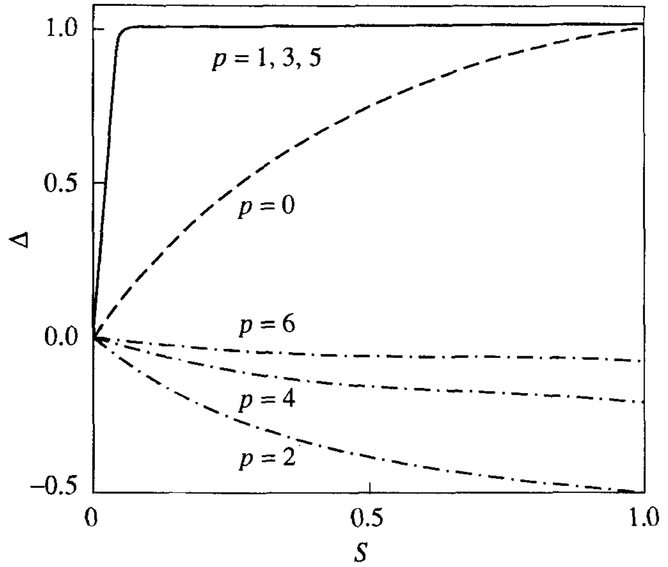

FIGURE 3 Conformation change of the model chain on the tetrahedral lattice in the ordered state. $\Delta = (\langle h_{\parallel}^2 \rangle - \langle h_{\perp}^2 \rangle)/(\langle h_{\parallel}^2 \rangle + 2\langle h_{\perp}^2 \rangle)$ is the chain anisotropy, where $\boldsymbol{h}$ is the end-to-end vector of the chain. S is the degree of LC order. p is the number of spacer bonds.

odd spacers ($p = 1, 3, \ldots$) this orientation causes a strong alignment of the whole chain. As for even spacers ($p = 2, 4, \ldots$), the chain conformation remains coiled (Figure 3). However, if the spacer is sufficiently flexible (i.e. its length exceeds the Kuhn segment) each repeat unit of the chain proves to be coiled and disordered (Figure 4). Thus the persistent length does not increase. One can say that the very increase of the chain rigidity is "heterogeneous" for the heterogeneous model. It means that the orienting field strictly fixes the position of the mesogene and the nearest spacer bonds, the orientation of distant bonds, however, is sufficiently free in long spacers. The force which restores mesogene to its equilibrium orientation increases drastically with ordering. This leads to the relaxation acceleration of normal modes which involve the motions of the mesogenes. On the other hand, the normal modes connected mostly with the motions of the spacer bonds are hardly influenced by the ordering.

In such a model the chain motion occurs by jumping of three-bond and four-bond kinetic units.[17] This mechanism of motion can be described in linear approximation in terms of the mobility tensor for the average projections of the bonds. The mobility tensor sets the relationship between the rates of the projection change and thermodynamic forces. The relaxation process caused by the application of perturbation electrical field of dipole symmetry will be considered here. In this case the thermodynamic forces are proportional to the components of bond dipole moment towards the chain contour. These conditions correspond to the experiment on the dielectric relaxation in the main-chain LC polymers. The excitation of the longitudinal or transversal relaxation process is provided by applying the dipole field towards or perpendicular to the LC director, respectively.

In the case of the heterogeneous chain ($p > 0$) the jump rates may be different (even in the isotropic state) depending on whether the considered kinetic unit includes the mesogene.

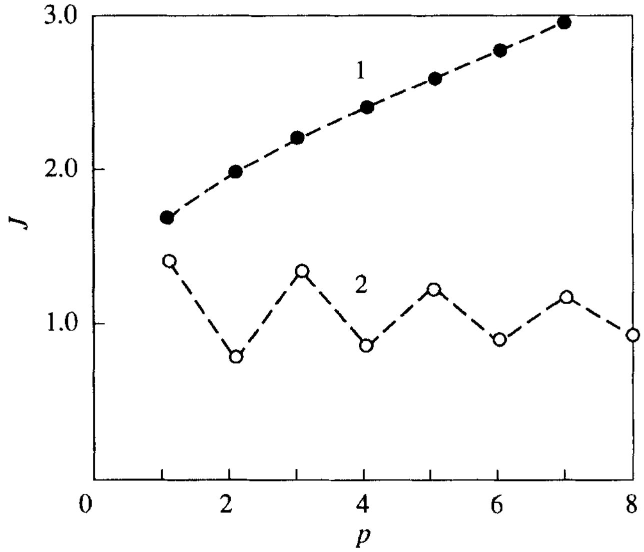

FIGURE 4 Conformation of the chain repeat unit consisting of $p+1$ bonds in the completely ordered state. J is the dimensionless ratio of values r for ordered ($S = 1$) and isotropic ($S = 0$) state, where $r \equiv (\langle L_{\parallel}^{2}\rangle S)^{1/2}$ is the longitudinal (towards the director) mean square projection of the end-to-end vector of the repeat unit L. Segment of the homogeneous chain of the same length (curve 1), heterogeneous chain (curve 2).

In fact, the friction coefficient of the bulky mesogene differs from that of the spacer bond. As a consequence, the mobility tensor is heterogeneous. The relaxation time spectrum consists of $(p+1)$ branches: one acoustic and p optical. In the anisotropic state ($S > 0$) each branch splits into the longitudinal and transversal sub-branches.

The dependence of the mobility tensors on the order parameter is determined by at least two factors.

(i) The hindrance effect arising due to the action of the molecular field barrier slowing down the reorientation of the mesogene with respect to director. However, for the discrete model and given lattice orientation this effect is sufficiently weak. In fact, by jumping on the lattice the mesogene overcomes the field barrier, if at all, as is shown in Figure 5. In this case the transition kinetics is controlled in the final analysis by the smaller barrier U_2 which is about one-ninth of the field magnitude. The difference in energy of the initial and final position of the bond U_1 contributes to the statistical factor determining the probability of the given conformation.

(ii) The extinction effect. The relaxation times in the case of the discrete mobility mechanism are determined by the probability of the appearance of the conformation suitable for jump. However, when the chain adopts ordered conformation the number of the kinetic units capable of a jump decreases. This effect is essentially manifested for the chains with short spacers ($p < 3$). It can be visualized, as shown in Figure 6a, for the three-bond kinetic unit at $p = 1$. The change of longitudinal projection of spacer can take place only if three adjacent mesogenes are non-parallel to director. The probability of this conformation is proportional to $(1-S)^3$ at $S \to 1$. The corresponding term in the mobility tensor proves to be very small. By contrast, the change of transversal projection of spacer is possible in the most advantageous conformation when the mesogenes are parallel to director

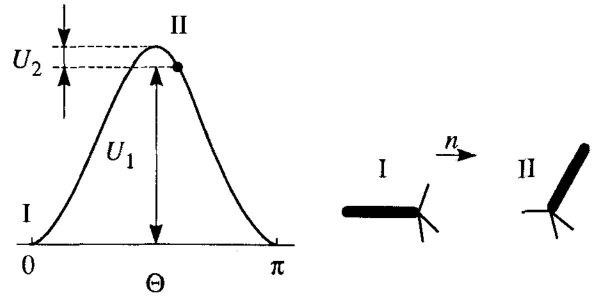

FIGURE 5 The potential barrier of LC field overcome by the mesogene during the jump on the tetrahedral lattice. θ is the angle between mesogene long axis and director $\boldsymbol{n}$.

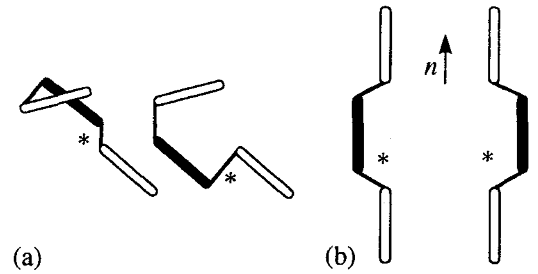

FIGURE 6 Explanation of the extinction effect for the three-bond kinetic unit. (a) Change of the longitudinal projection of marked (*) spacer bond. (b) Change of the transversal projection of the same bond.

(Figure 6b). For the chains with long spacers ($p > 2$) the orientation of the mesogenes does not influence the distribution of the isomers in the chain and therefore the extinction effect is negligible.

As a result the dependence of the relaxation times on S for the lattice model is determined by the competition of induced rise in the chain rigidity, extinction effect ($p < 3$) and to a smaller degree the influence of the molecular field barrier. As was shown in Reference 9, there exist two different types of relaxation time behavior with the ordering for the homogeneous lattice model ($p = 0$). For the short-range motions the effect of the rigidity increase and extinction effect are in equilibrium. Thus the splitting of the relaxation spectrum was shown to be rather small (Figure 7a). For the long-range motions both effects lead to an increase of the longitudinal relaxation times, but remain in equilibrium balance for the transversal ones, which results into drastic splitting. However, provided the chain is heterogeneous, ($p > 0$) leads to the change of the possible types of the relaxation time behavior.

Long-range motions. Such type of motions includes the normal modes with the small phase shift between the state of adjacent repeat units belonging to the acoustic branch. It should be emphasized, however, that the proposed interpretation concerns the scales smaller than the chain contour length. The dependence of the longitudinal relaxation time $\tau^{\parallel}$ on the degree of order S at $\psi \to 0$ is feeble (Figure 7a) due to the weakness of the correlation of the longitudinal bond projections mentioned above. From this viewpoint the heterogeneous lattice model is close to the continuous one. The dependence of the transversal relaxation time $\tau^{\perp}$ on S at $\psi \to 0$ is also weak in contrast to the continuous

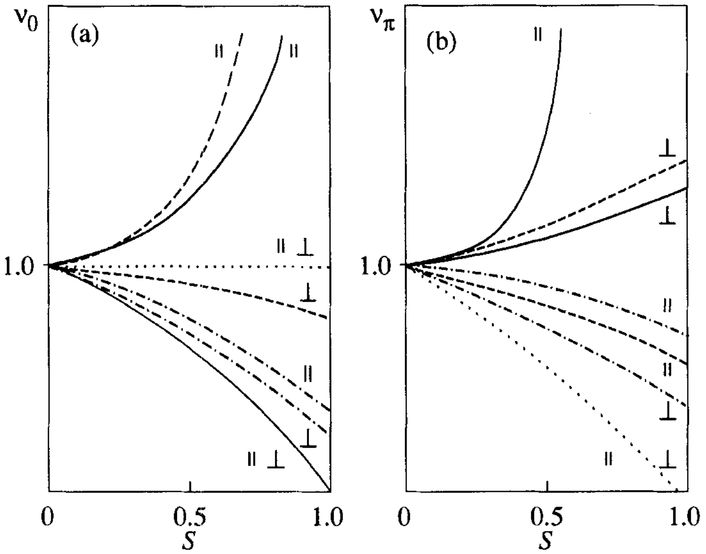

FIGURE 7 Dependence of the relaxation times on the order parameter S for the different models of the chain. (a) Long-range motions $\nu_0 = \tau(\psi, S)/\tau(\psi, 0)$ at $\psi \to 0$. (b) Short-range motions $\nu_\pi = \tau(\psi, S)/\tau(\psi, 0)$ at $\psi = \pi$. Symbols || and ⊥ denote the longitudinal and transversal projections. Continuous model (——), lattice homogeneous model at $p = 0$ (- - - -), lattice heterogeneous model at $p = 1$ (— · —), and lattice heterogeneous model at $p > 2$ (· · · · · ·).

model. This discrepancy is explained by the fact that for the lattice model the transversal projection of the bond cannot be as arbitrarily small as for the continuous one. Thus, the splitting of the relaxation times is insignificant.

Short-range motions. They include the normal modes belonging to p optical branches and the normal modes with the phase shift $\psi = \pi$ belonging to the acoustic branch. Two cases of rigid ($p < 2$) and flexible ($p > 2$) spacer appear to be essentially different.

For $p = 1$ the splitting of the relaxation times which is controlled by the extinction effect and the effect of rigidity increasing is the same as for the homogeneous model (Figure 7b). The time $\tau^{||}$ at the strong ordering limit $S \to 1$ and $\psi = \pi$ does not increase since the influence of the field barrier is weak.

For the flexible spacers the extinction effect is negligible. Thus there exists a normal mode for both longitudinal and transversal projections which is characterized by the strong dependence on the order parameter. The relaxation time of this peculiar mode diminishes to zero at $S \to 1$ due to the local increase of the chain rigidity (Figure 7b). This normal mode is excited in the case of macromolecules in which the mesogenes possess their own dipole moment. The other p branches exhibit weak dependence on the order parameter. Note that for the above considered continuous model with the freely jointed spacers the longitudinal relaxation time $\tau^{||}$ at $\psi = \pi$ does not decrease but dramatically increases as in the case of the low-molecular nematics.[18] For the lattice model we face a purely polymeric phenomenon—an effective weakening of the action of the field potential barrier as a result of the correlated character of the bond motion in the chain.

References

1. K. Müller, P. Meier, and G. Kothe, *Progr. in NMR Spectroscopy*, **17,** 187 (1985).
2. K. Müller and G. Kothe, *Polymer Preprints*, **29,** 42 (1988).
3. J. S. Moor and S. I. Stupp, *Macromolecules*, **20,** 282 (1987).
4. V. V. Zuev, G. S. Smirnova, N. A. Nikonorova, T. I. Borisova, and S. Skorokhodov, *Makromol. Chem.*, **191,** 2865 (1990).
5. R. Blumstein and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **165,** 361 (1988).
6. P. W. Wojtkowski, *Macromolecules*, **20,** 740 (1987).
7. Y. Y. Gotlib, G. A. Medvedev, and E. A. Karpov, *Vysokomol. Soedinen.*, **A31,** 1136 (1989).
8. Y. Y. Gotlib, *Colloid Polym. Sci.*, **80,** 245 (1989).
9. Y. Y. Gotlib, G. A. Medvedev, and S. V. Fridrikh, *Makromol. Chem. Macromol. Symp.*, **52,** 209 (1991).
10. Y. Y. Gotlib, G. A. Medvedev, and S. V. Fridrikh, *Polymer Preprints*, **33,** 549 (1992).
11. Y. Y. Gotlib, G. A. Medvedev, and S. V. Fridrikh, *Polym. Sci., USSR*, **34,** 531 (1992).
12. W. Maier and A. Saupe, *Z. Naturforsch.*, **A13,** 564 (1958).
13. W. Maier and A. Saupe, *Z. Naturforsch.*, **A13,** 882 (1958).
14. I. Dozov and N. J. Kirov, *J. Chem. Phys.*, **69,** 1527 (1987).
15. Y. Y. Gotlib and G. A. Medvedev, *Vysokomol. Soedinen.*, **A32,** 2426 (1990).
16. M. Warner, G. Gunn, and A. Baumgartner, *J. Phys.*, **A18,** 3007 (1985).
17. L. Monnerie, B. Valeur, J.-P. Jarry, and F. Geny, *J. Polym. Sci.*, **13,** 667 (1975).
18. W. Maier and G. Meier, *Z. Naturforsch.*, **A16,** 1961 (1961).