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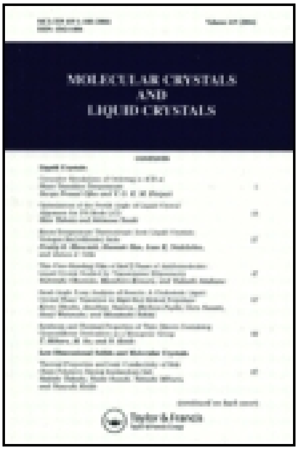

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Mechanical Dynamic Properties of a Main Chain Liquid-Crystalline Copolyether. II. Influence of the Molecular Weight

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Mechanical Dynamic Properties of a Main Chain Liquid-Crystalline Copolyether. II. Influence of the Molecular Weight

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The study of the molecular weight dependence of the mechanical dynamic properties of the LC copolyether—poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene)—has evidenced that the times of adaption for the realization of rheological stationary states increases substantially with the molecular weight of the copolymer: from 2 days for the copolymer with $M_n = 5{,}800$ to 7 days for the copolymer with $M_n = 16{,}400$. The rheological stationary states are characterized by constant and reproducible values of the moduli. The stationary states realized after prolonged annealing show that $G' > G''$, whereas the stationary states attained after shear show $G'' > G'$. The time-temperature superposition procedure applies only for the latter data.

Keywords: nematic main chain copolyether, rheology, stationary states, time-temperature superposition.

INTRODUCTION

In a foregoing study it has been shown that different rheological stationary states can be obtained in the nematic phase by annealing or by shear of a LC-copolyether poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene).[1] These states are characterized by constant and reproducible moduli measured after prolonged times of adaption. The moduli of the stationary nematic state realized after time controlled annealing (at least for 4 days) and subsequent shear (for 2 days) obey the time-temperature superposition, but the belonging shift factors are unusually small. Nevertheless, the time-temperature superposition is not valid for the moduli of the solely annealed sample. The transition from the nematic into the isotropic phase is characterized by jumps of the respective moduli, and mainly of the dynamic viscosity.

The realization of different stationary nematic states by annealing or by annealing and subsequent shear has been explained by changes in orientation, the reduction in orientation being higher the longer the relaxation time during annealing. This affirmation is based on the observation that for the annealed and sheared sample the loss modulus exceeds the storage modulus, i.e. $G'' > G'$, whereas for the solely annealed sample $G' > G''$.

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Taking into account that orientation in mesophases of LC-polymers may depend on the molecular weight, it seemed interesting to analyse in a subsequent study the influence of the molecular weight on the mechanical dynamic properties of the stationary nematic phases. Beside the polymer studied in the precedent paper (polymer II) two further LC-copolyethers were investigated, one with the lower (polymer I) and the second with the higher molecular weight (polymer III).

EXPERIMENTAL

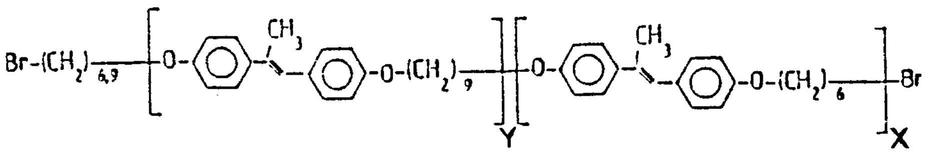
The synthesis and purification of the 6/9 LC-copolyether—poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene)-HMSt(*h*/*n*)—with a ratio of 20:80 of the hexamethylene/nonamethylene alkylspacer units has been carried out according to the prescriptions of Percec *et al.*[2-6] To prevent degradation during the prolonged mechanical dynamic measurements 0.1% of the stabilizer Irganox 1076 (Ciba Geigy), an octadecyl-3-(3,5-ditert.-butyl-4-hydroxyphenyl)propionate, were added to the polymer samples. It was proved that the addition of the stabilizer has no influence on the measured mechanical dynamic data.

DSC measurements were carried out on a PERKIN ELMER DSC 7 using heating and cooling rates of 10 K/min. Molecular weights were determined by both vapor-pressure osmosis and GPC. The mechanical dynamic measurements in the oscillatory mode were executed on an INSTRON RHEOMETER 3250, using the cone and plate geometry. The diameter of the plate was 40 mm, the cone angle 21 mrad. The measurements were performed in the frequency range of 0.05–15 Hz using a strain amplitude of 2.1 mrad. The chosen temperature ranges for the measurements were 120–150°C for the LC-copolymer I, 120–205°C for II and 120–200°C for III (see Table I).

TABLE I

Molecular weights and phase transition temperatures of the LC-copolyethers

Copolyether poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene) HMSt(*h*/*n*)−*A*, random $x{:}y = 20{:}80$



	Molecular Weight		Phase Transition Temps., °C				
Polymer	M_n (osmosis)	M_w GPC	T_g	T_m	T_i Onset	T_i Max	ΔH_i kJ/mol
I	5,300	14,000	20.0	112.5	142.7	173.0	7.1
II	9,500	15,900	20.5	105.7	161.3	184.0	11.4
III	13,400	16,400	27.7	112.3	171.5	194.1	12.3

RESULTS AND DISCUSSION

The characteristics of the studied LC-copolyethers are shown in Table I. The included transition temperatures correspond to the reproducible values measured during the second heating scan, recorded at the rate of 10 K/min (see Figure 1). The glass temperature, T_g, refers to the mid-point temperature, whereas the melting temperature, T_m, represents the peak maximum temperature. Both the clearing temperature, T_i, and the heat of isotropization, ΔH_i, increase with the increasing molecular weight of the LC-copolyether.[5-10] The width of the nematic phase in-

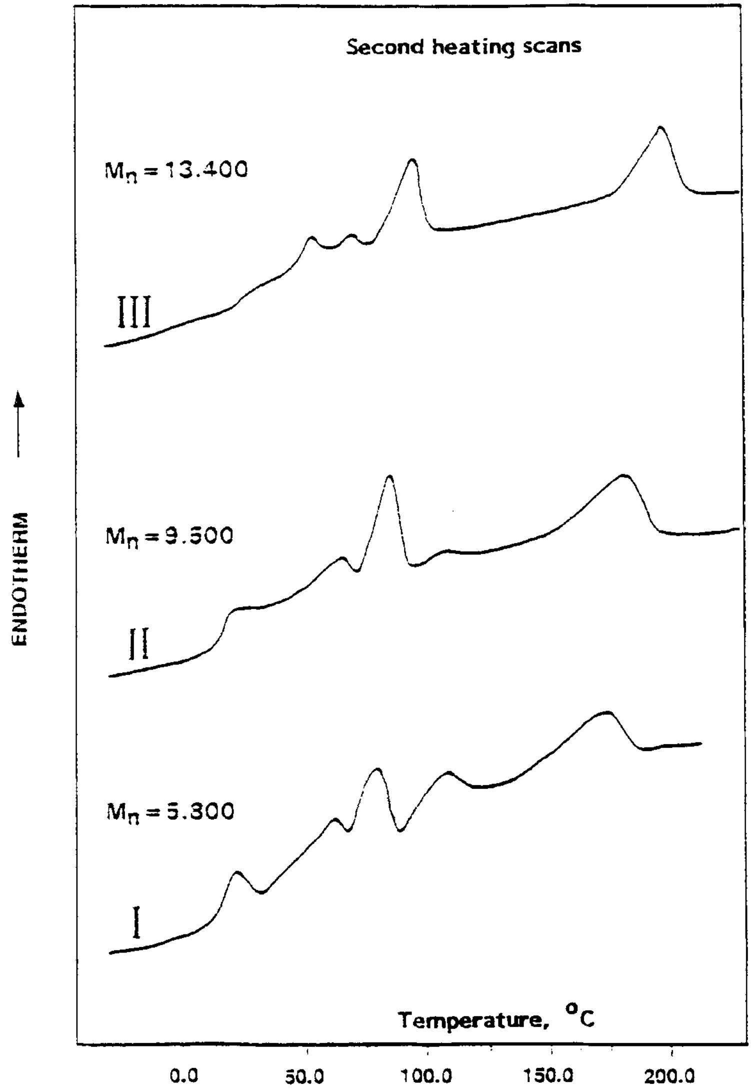


FIGURE 1 DSC curves of the studied LC-copolyethers. Second heating scans at the heating rate of 10°C/min.

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creases simultaneously because T_m is less affected by the molecular weight than T_i.

For the first set of rheological measurements the polymer samples were annealed in the rheometer all three at the same temperature of 140°C for 24 h to assure complete melting of the crystallites. Then isotherm frequency sweeps were carried out in the range of 0.05–15 Hz. The used strain amplitude was of 2.1 mrad to assure linear vicoelastic response (proved by the perfect sinusoidal response observed on an oscilloscope connected to the output of the rheometer).

The mechanical dynamic measurements in the nematic phase were carried out beginning with the temperature of 120°C. At each new higher temperature the measurements were started after a waiting time of 10 min as soon as the respective temperature was reached. The isotherms were recorded in steps of 5°C for polymer I and of 10°C for polymers II and III.

The influence of the temperature on the storage modulus, G′, and the dynamic viscosity, η', in the nematic phase is illustrated in Figure 2. The curves of the loss modulus look similar. Polymer III with the highest molecular weight exhibits surprisingly both the lowest viscosity and the lowest storage modulus. Polymer I and II show, however, the usual behaviour, i.e. polymer II with the higher molecular weight is the more viscous of the two.

The temperature dependence of the moduli of the three studied copolymers at the lowest and highest used frequency in the temperature range of the respective nematic phase is illustrated in Figure 3a. It is evident that for all three polymers $G' < G''$ in the entire LC-range, suggesting an increased flow tendency. The attempt to construct mastercurves for the storage modulus of the nematic phase is shown in Figure 3b. The reference temperatures were 120°C.

The results show that for both the polymers I and II, time-temperature superposition is not working. The moduli increase, in spite of the increasing temperature, for polymer I starting with 130°C and for II beginning with 145°C. The effect is especially accentuated at the lower frequencies.

The failure of the time-temperature superposition suggests the presence of nonstationary states in the nematic phase, which relax at the higher temperatures. Taking into account that the relaxation is accompanied by an increase of both the moduli and the dynamic viscosity, a diminuation of the initial order of the nematic phase is assumed.

For polymer III, the time-temperature superposition is valid, but only for the lower temperatures of 120–160°C. The corresponding shift factors are, however, unusually small, the calculated values of the WLF constants being of $c_1 = 1.9$ and $c_2 = 72.7$, i.e. $c_1c_2 = 138.1$. At the higher temperatures of 165–170°C the moduli of polymer III start also to increase, suggesting the supposed beginning of relaxation.

The initially higher orientation of polymer III with respect to polymers I and II is suggested by the corresponding lower values of the moduli and the dynamic viscosity, although the molecular weight of polymer III is the higher.

These results were unexpected taking into account that the order in main chain LC-polymers increases with the molecular weight due to the decreasing flexibility and the reduction of the free volume fraction.[7-9] A possible explanation could be

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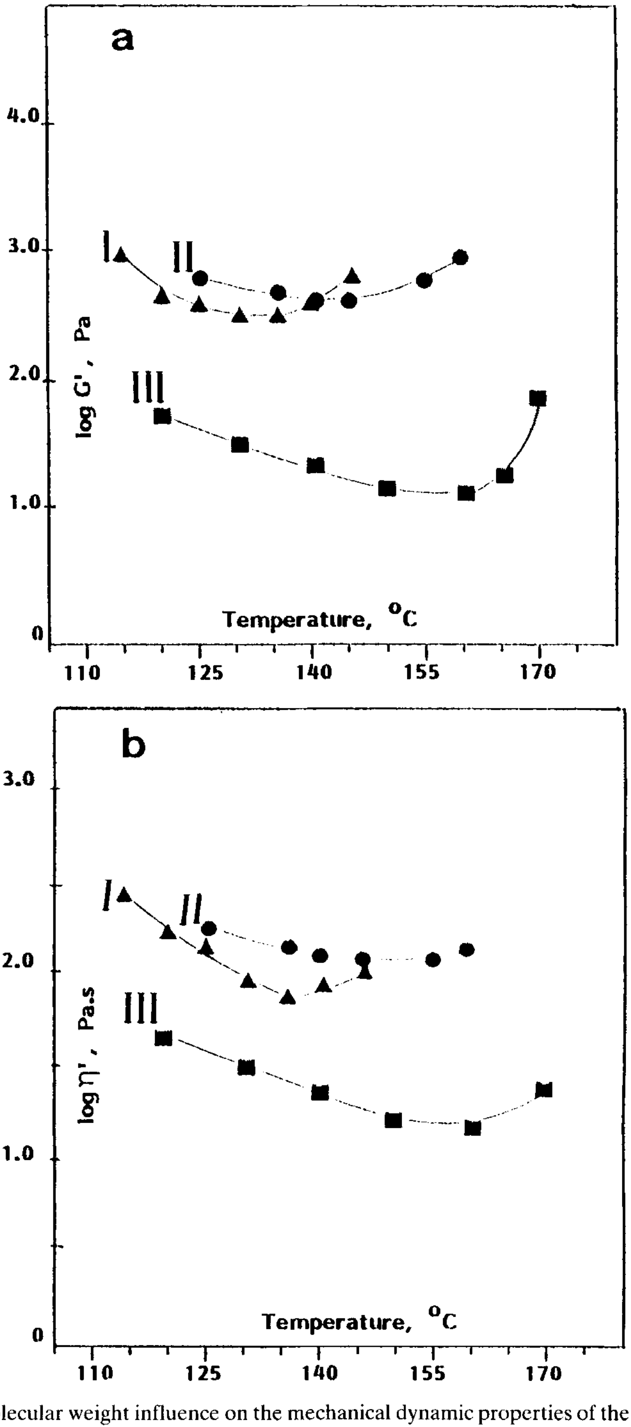

FIGURE 2 Molecular weight influence on the mechanical dynamic properties of the LC-Copolyethers annealed for 24 h at 140°C (significance of latin numbers see Table I) a. Storage modulus, G'; b. Dynamic Viscosity, η'.

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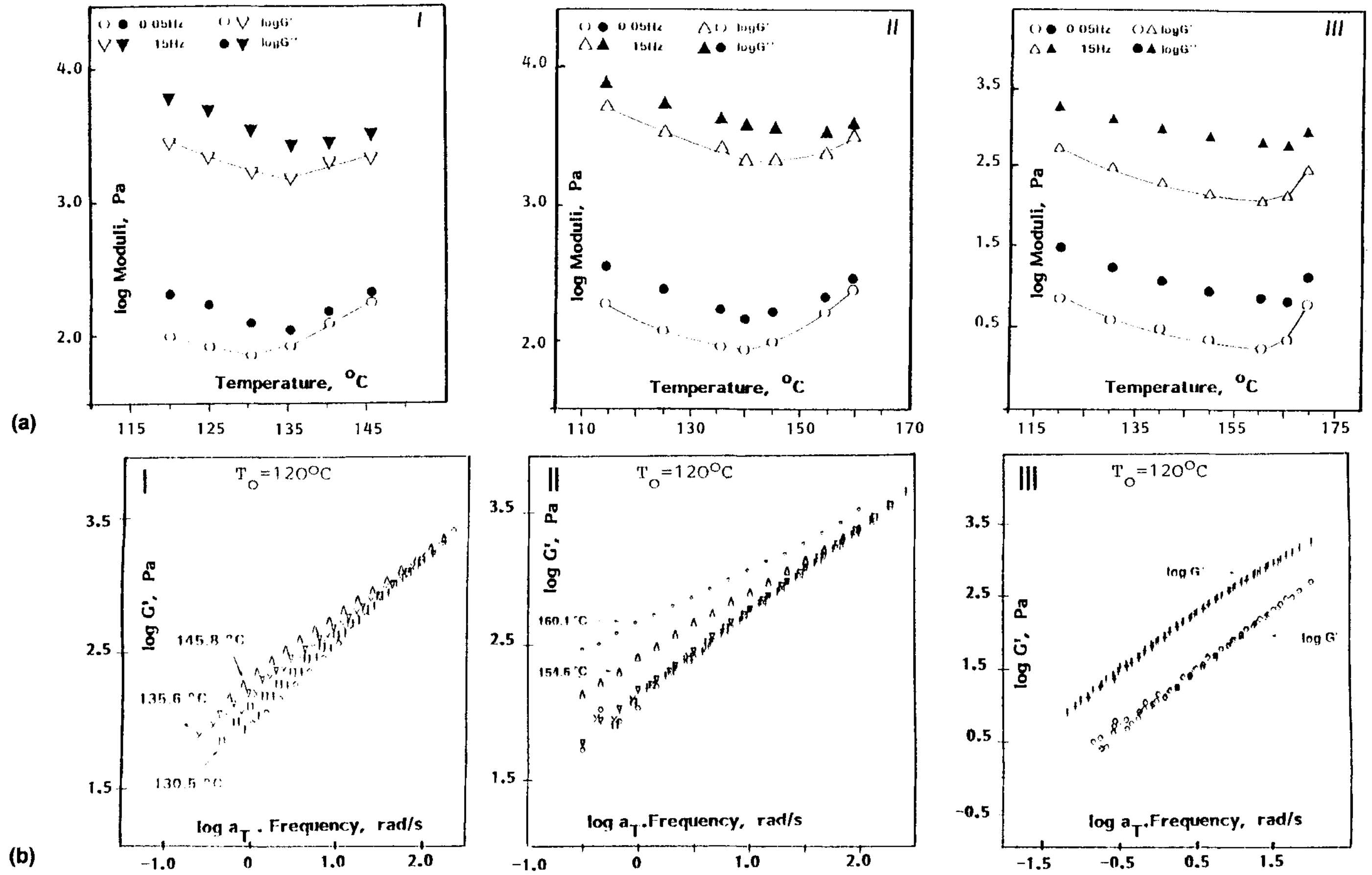

FIGURE 3 a. Storage moduli, G′, and loss moduli, G″, of the LC-copolyethers annealed for 24 h at 140°C. Data for the lowest and highest frequency used during the isotherm frequency sweeps (significance of latin numbers see Table I); b. Attempts to construct mastercurves of the rheological data of the LC-copolyethers annealed for 24 h at 140°C.

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related to the fact that all three polymers were annealed before the measurements for 24 h at the same temperature of 140°C. The analyse of the DSC results shows, however, that the temperature of 140°C is situated for polymer I at the upper temperature end, for polymer II in the middle and for polymer III at the beginning of the nematic phase. It is thus possible that the annealing for 24 h at the same temperature has for the three polymers in the same succession a decreasing influence on their tendency of relaxation.

This supposition has been verified by the subsequent investigation devoted to the influence of the sampling temperature on the mechanical dynamic behaviour of the polymers.

In a first series of experiments the polymers were sheared using a frequency of 1 Hz and a strain amplitude of 7.3 mrad until the moduli became constant. The respective temperatures were chosen on the basis of the DSC curves: 140°C for polymer I, 160°C for polymer II and 170°C for polymer III.

It has been observed that the moduli of polymer III were not affected by this shear procedure, i.e. it is thus probable that the orientation in the nematic phase is not further improved by the used shear conditions. The moduli of polymers I and II, on the contrary, decrease during shear at least by one decade, suggesting an improvement of the orientation. They became constant only after 24 h (I) and 40 h (II) of shear, respectively.

Subsequently the polymers were annealed at the same temperatures as before and the moduli were measured every 12 h in the frequency sweep range of 0.05–15 Hz using the strain ampliude of 2.1 mrad. The measurements were repeated until no further changes of the moduli were detectable. The stationary states were achieved after 2 days for polymer I, 4 days for polymer II and 7 days for polymer III. The observed increase of the moduli during annealing suggests a loss of orientation in the nematic phase.

Using the annealed samples, isotherm frequency sweeps were carried out in the temperature ranges of the respective nematic phases. The strain amplitude was of 2.1 mrad to assure linear viscoelasticity conditions. At each new temperature the samples were first annealed for 12 h before the respective frequency sweep was started. The temperature dependences of the moduli at the lowest and highest of the used frequencies are shown in Figure 4. The before observed dependence $G' < G''$ is still valid for polymer I, but for polymers II and III $G' > G''$ in the entire nematic region. The transition into the nematic-isotropic two phase region is characterized for all three polymers by a jump-like increase of the moduli. $G' > G''$ for all three polymers in the transition region.

The molecular weight dependence of the moduli shows this time the usual behaviour, i.e. the moduli increase with the increasing molecular weight of the polymers (compare Figure 5 with Figure 2a for G').

Although the values were reproducible, the isotherms of the mechanical dynamic data could not be shifted to mastercurves. The invalidity of the time-temperature superposition suggests the presence of non-stationary states in the nematic phase. One possible explanation could be that the experiments were carried out as usual without according time for annealing between two subsequent frequencies.

To assure a reproducible orientation during the measurements, the samples were

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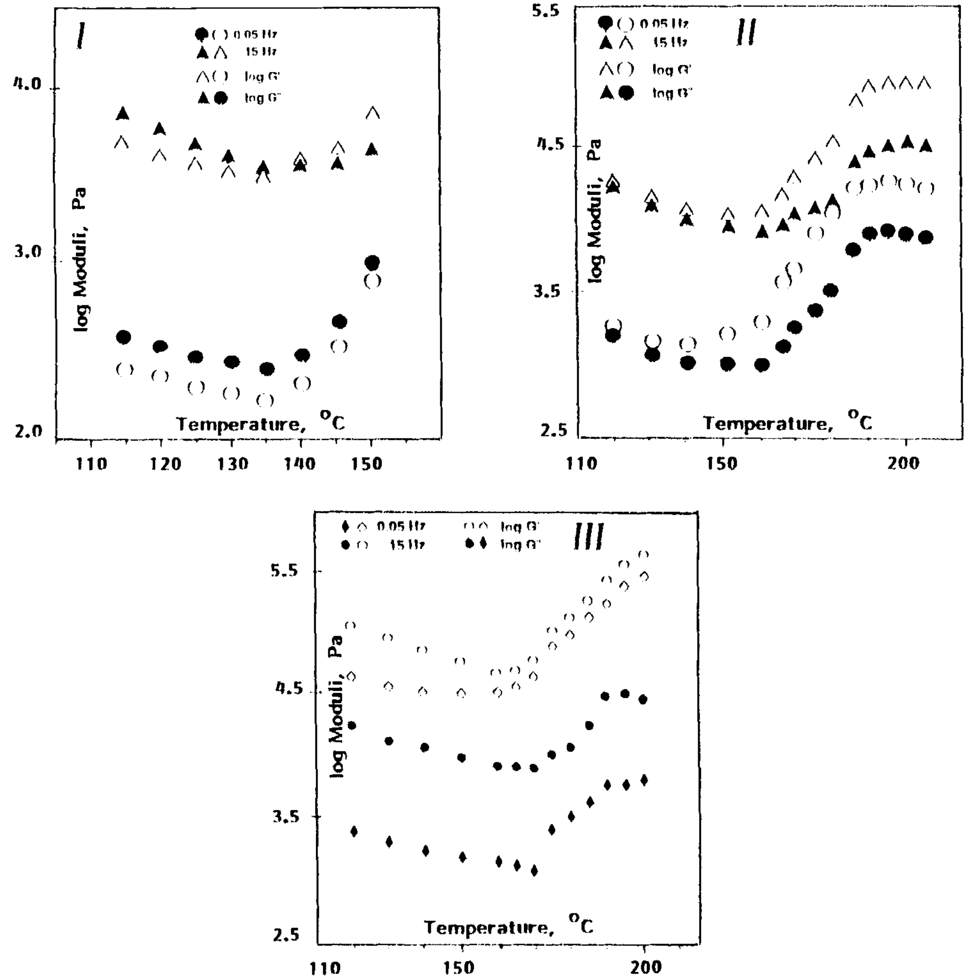

FIGURE 4 Storage moduli, G′, and loss moduli, G″, of the LC-copolyethers annealed to constant values of the moduli. Data for the lowest and highest frequency used during the isotherm frequency sweeps (significance of latin numbers see Table I).

subsequently sheared with a frequency of 1 Hz using the strain amplitude of 7.3 mrad. The shear was conducted until the moduli became constant (1–2 days of shearing) at the same temperature used before for the annealing. Then the respective frequency sweep measurements were executed in the 0.05–15 Hz range with the strain amplitude of 2.1 mrad. To avoid any relaxation of the shear induced orientation, at each new temperature the samples were once more sheared for 12 h using the same frequency of 1 Hz and the strain amplitude of 7.3 mrad. This time the storage modulus was for all three polymers smaller than the loss modulus, i.e. G′ < G″, suggesting an increased flow tendency. For polymers I and II the moduli realized by shear were similar to those of the untreated samples, whereas

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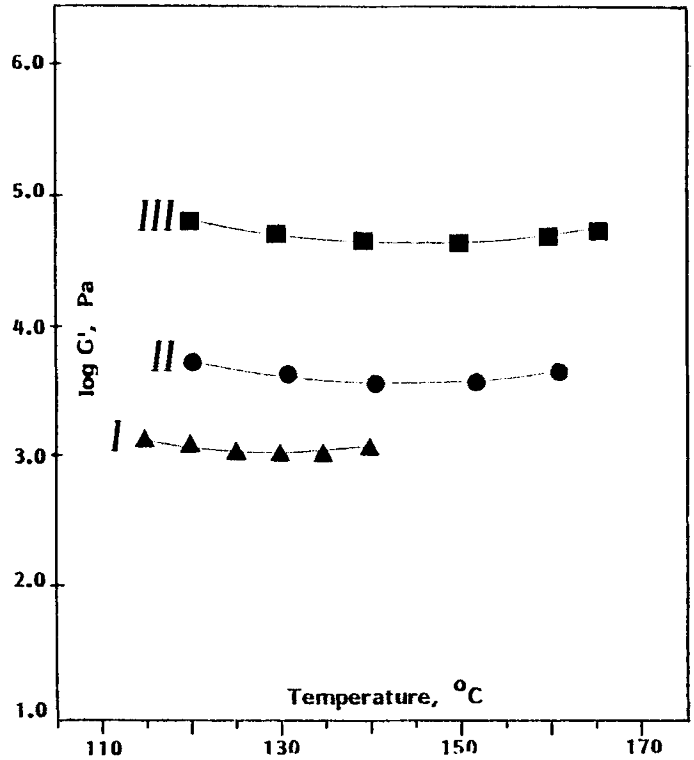

FIGURE 5 Molecular weight influence on the storage modulus of the LC-copolyethers annealed to constant values of the moduli (significance of latin numbers see Table I).

the polymer III the moduli were of about 1.5 order of magnitude higher, suggesting that the initially higher order in the nematic phase of the untreated sample could not be recovered by the subsequent applied annealing and shear conditions.

The time-temperature superposition was, however, this time applicable for all three polymers. The obtained mastercurves are shown in Figure 6. The chosen reference temperatures were 119.0°C for polymer I, 160.7°C for II and 160.0°C for III. But the shift factors were extremely small for the polymers I and II. The following WLF constants were calculated: Polymer I, $C_1 = 0.4$, $C_2 = 10.8$, i.e. $C_1C_2 = 4.3$; Polymer II, $C_1 = 0.8$, $C_2 = 13.6$, i.e. $C_1C_2 = 10.9$; Polymer III, $C_1 = 3.4$, $C_2 = 148.5$, i.e. $C_1C_2 = 504.9$.

In Figure 7 the mastercurves of the dynamic viscosity of the LC-copolyethers at the reference temperature of 120°C are compared. The molecular weight influence was regular, i.e. the viscosity increased with the increasing molecular weight.

It is remarkable that only the low molecular weight polymer I reaches the Newtonian viscosity plateau. Polymer II and polymer III exhibit on the contrary a slope of -0.4 for the log viscosity vs. log frequency plot. Taking into account that the slope was of -0.27 for untreated sample III, which showed the smallest moduli, it may be assumed that the slope of the log viscosity vs. log frequency plot is related to the orientation in the nematic phase.

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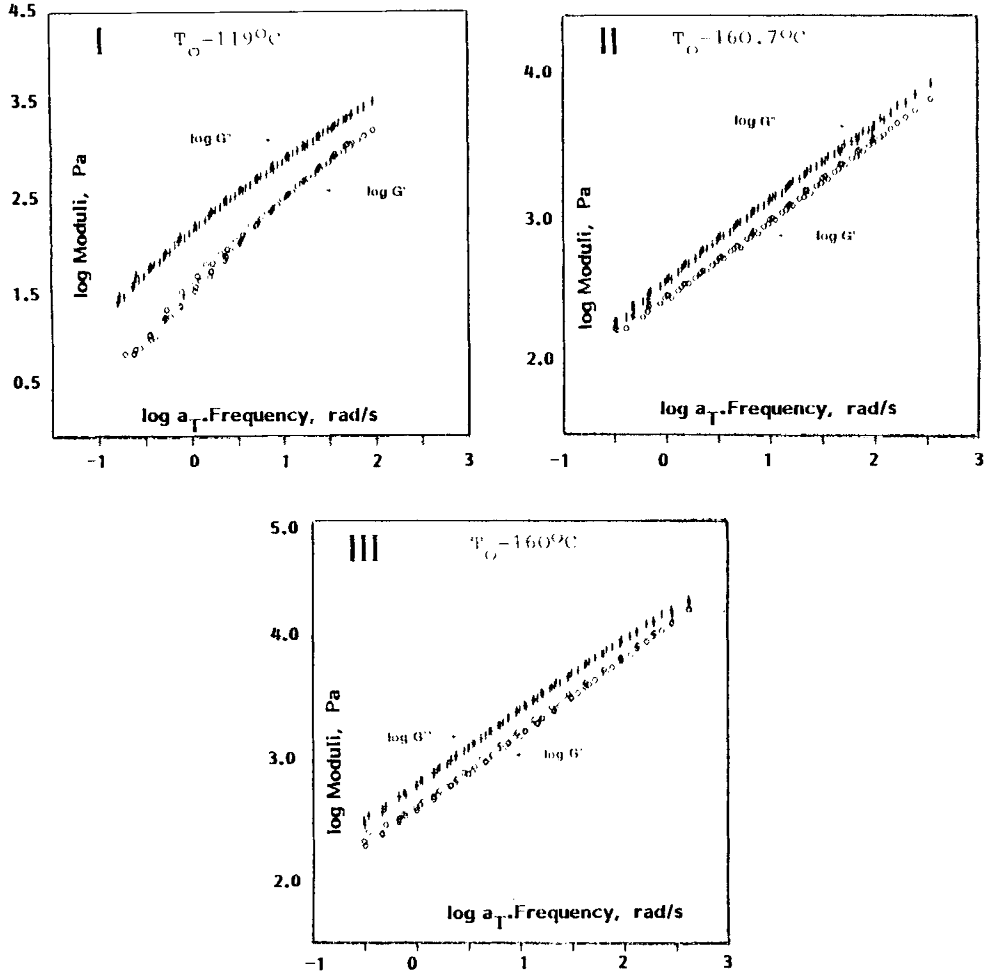

FIGURE 6 Mastercurves of the storage and loss moduli of the LC-copolyethers sheared after annealing to constant values of the moduli (significance of latin numbers see Table I).

CONCLUSION

It has been confirmed that the mechanical dynamic behaviour in the nematic phase of the investigated LC-copolyethers depends on both the thermal and the shear history. By prolonged annealing or by prolonged shear of the before annealed samples, rheological stationary states are realizable which are characterized by constant and reproducible values of the moduli. The required time for adaption of the stationary states increases substantially with the increasing molecular weight of the LC-copolyether: from 2 days for the polymer with $M_n = 5{,}800$ to 7 days for the polymer with $M_n = 16{,}400$. The stationary states of the annealed samples are characterized by $G' > G''$, whereas of the sheared samples by $G' < G''$. The latter data can be superimposed to mastercurves. It is supposed that the observed

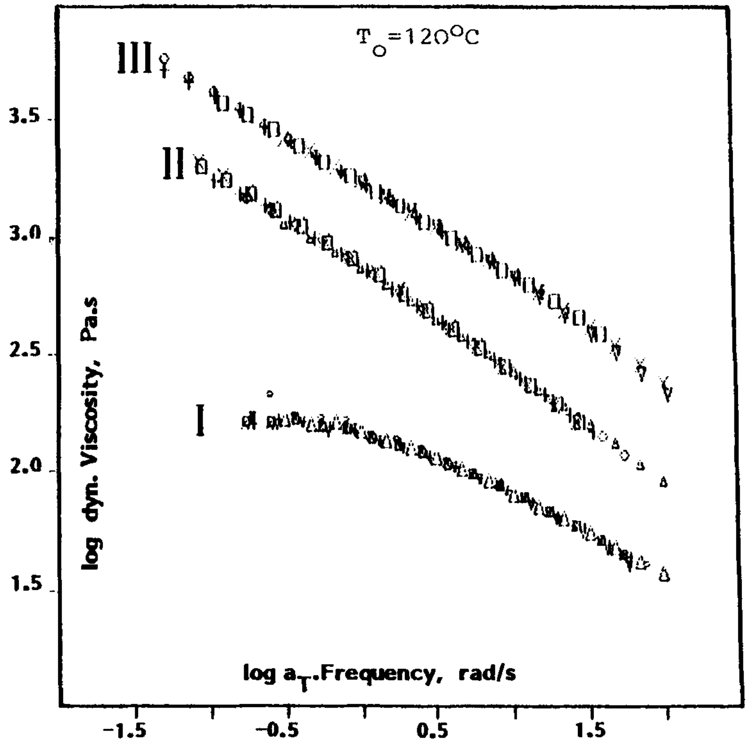

FIGURE 7 Mastercurves of the dynamic viscosity of the LC-copolyethers sheared after annealing to constant values of the moduli (significance of latin numbers see Table I).

increased elasticity tendency during annealing is related to polydomain structures in the nematic phase.

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