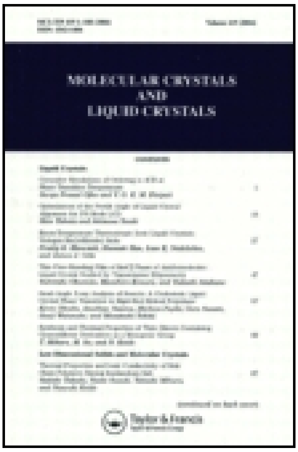

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Mechanical Dynamic Properties of a Main Chain Liquid-Crystalline Copolyether

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The study of the mechanical dynamic properties of the LC copolyether-poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene)—has yielded evidence for the possibility of obtaining stationary states in the nematic phase. These stationary states can be achieved either by annealing at least for four days or by prolonged shear (at least for two days) of the annealed samples by using a given strain amplitude and frequency. The stationary states are characterized by constant and reproducible moduli. The moduli determined after shear obey the time-temperature superposition, but the shift factors are unusually small. The transition from the nematic into the isotropic phase is characterized by an important jump in both the respective moduli and the dynamic viscosity.

INTRODUCTION

Percec *et al.*[1] have shown that the replacement in main chain liquid crystalline polymers—LC-polymers—of thermally sensitive ester units by ether bonds enhances the solubility and reduces the phase transition temperatures. At the same time, the LC-polyethers are free from "crystallization induced reactions" observed for LC-polyesters by Lenz *et al.*[2] The accompanying microstructural changes brought about by crystallization are supposed to be responsible, among other factors, for the observed rheological instabilities of LC-polyesters.[3]

The phase transition temperatures of the LC-polyethers can be controlled by the length and the ratio of the alkyl spacers introduced between the mesogenic units in the main chain. According to Percec,[1] copolyethers show only nematic mesophases, while homopolyethers show both smectic and nematic mesophases.

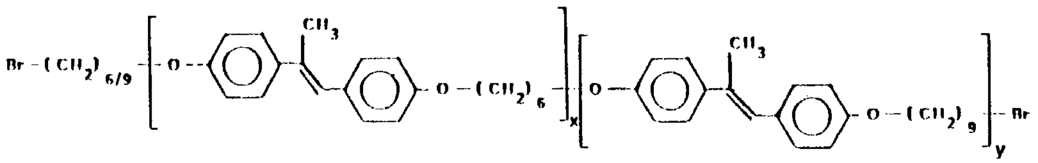
The reason for selecting in the previous study[4] a 6/9 copolyether-poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene)—HMSt(h/n)—with a 20:80 ratio of the hexamethylene/nonamethylene alkyl spacer units (see Table I) was the very favourable phase transition temperatures for mechanical dynamic measurements and the broadness of the nematic phase.

Besides the well known time and temperature dependent instabilities of the rheological properties typical for nematic LC polymers, a characteristic low frequency maximum of tan δ was observed, which is not exhibited by non-LC, amorphorus polymers. As these first mechanical dynamic measurements were restricted

TABLE I

Characteristics of the copolyether HMSt(h/n)

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



Polymer	Molecular Weight M_w by GPC	M_n by GPC	M_w/M_n	M_n vap.pres.osm.	Phase Transition Temperatures, °C Tg	T_m	T_i	hr K/min
HMSt(h/n) - A	41,800	15,900	2.63	9,500	19.0	105.7	184.0	10
HMSt(h/n) - P *)	39,000	—	2.30	–	15.0	86.0	161.0	20

*Copolyether synthesized by Percec and used for rheological measurements in earlier work.[4]

to a single temperature (110°C), in the present study we have extended the investigations to the whole nematic range.

EXPERIMENTAL

The HMSt(h/n) LC copolyether has been synthesized by phase transfer catalyzed polyetherification of 4,4′-dihydroxy-α-methylstilbene in a mixture of *o*-dichlorobenzene-aqueous NaOH in the presence of tetrabutylammoniumhydrogen sulphate (TBAH) as phase transfer catalyst. The ratio of 1,6-dibromohexane to 1,9-dibromononane was, as before, 20:80 mole/mole. Synthesis and purification were carried out as described by Perce *et al.*[1]

The characteristics of the copolyether are shown in Table I. The data for the copolyether prepared by Percec, which has been used in our first rheological study, are also included in Table I. The existence of the nematic mesophase at 140°C has been confirmed by both optical microscopy and X-ray.

Differential scanning calorimetric measurements were carried out under nitrogen using a Perkin-Elmer DSC 7. The heating and cooling rates were both 10 K/min. The thermograms were reproducible after a first heating-cooling cycle. The DSC curves are shown in Figure 1. For comparison there is also shown the second heating scan, at a heating rate of 20 K/min, for the Percec sample HMSt(h/n)-P used in the foregoing study. The phase transition temperatures shown in Table I represent the onset T_g and the maximum T_m and T_i, respectively.

The mechanical dynamic measurements in the oscillatory mode were executed on an Instron Rheometer 3250, using the cone and pate geometry. The diameter of the plates was 40 mm and the cone angle 21 mrad. The measurements were conducted in the frequency range of 0.05-15 Hz and in the temperature range of 120–205°C. To the LC copolyether was added 0.1% w/w of the stabilizer Irganox

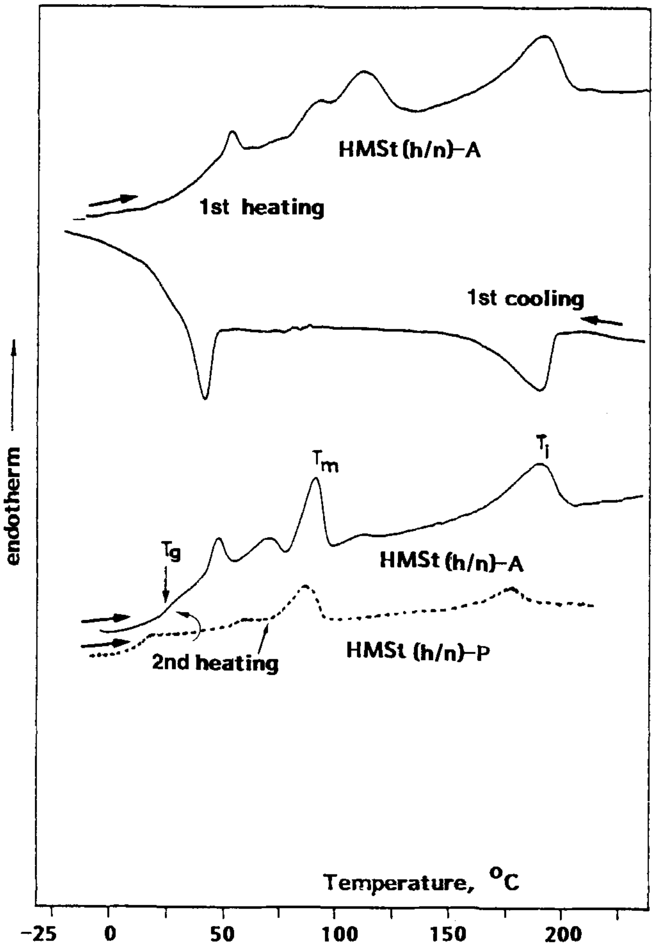


FIGURE 1 DSC curves for the HMSt(h/n) LC-Copolyethers. Full lines: First heating-cooling cycle, resp. second heating scan of HMSt(h/n)-A at rates of 10 K/min; Broken lines: Second heating area at 20 K/min of HMSt(h/n)-P.

1076 (Ciba Geigy), an octadecyl 3-(5,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, to prevent degradation. Measurements with and without stabilizer have confirmed that the mechanical dynamic data are not influenced by the addition of the stabilizer.

RESULTS AND DISCUSSION

We first repeated the measurements relating to the influence of strain amplitude on the mechanical dynamic properties of the HMSt(h/n) LC copolyether. The data obtained for the storage modulus, G′, are shown in Figure 2. The observed dependencies are similar to those reported in our previous paper.[4] The moduli and the dynamic viscosity decrease with increasing strain amplitude. The storage mod-

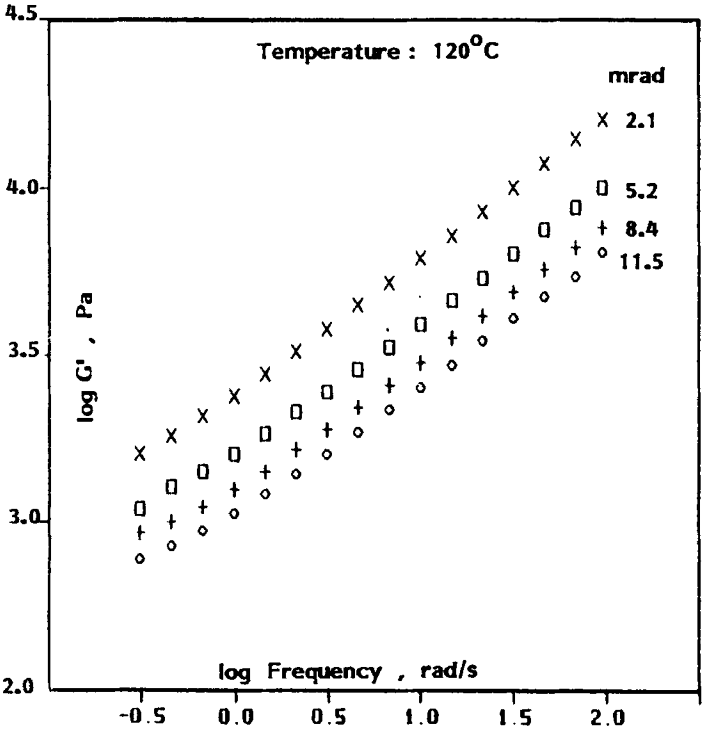


FIGURE 2 Influence of the strain amplitude on the storage modulus, G', of HMSt(h/n)-A. Frequency sweeps (0.05-15 Hz) at 120°C; strain amplitudes indicated.

ulus curve flatten very slightly but consistently, in the lower frequency range. Simultaneous increases occur in the characteristic low frequency maximum of tan δ.

Although the general tendencies are the same, the absolute values are quite different as illustrated, for instance for the dynamic viscosity in Figure 3. The differences are explained by the fact that different conditions were used. In the previous study, the frequency sweep was carried out at 110°C, directly and as soon as the sample had reached the temperature of the rheometer. In the present study the measurements were executed at 120°C on samples annealed for two days.

The strong dependence of the mechanical dynamic data on the strain amplitude is a consequence of the initial poor orientation, because in both cases the samples were not separately oriented during the preparation process. During the frequency sweeps the mechanical shear field acting on the samples produces an orientation which becomes stronger the higher the amplitude. This shear induced orientation during the measurements is responsible for the observed decrease in the moduli.

By connecting an oscilloscope to the response output of the rheometer, it has been observed that a perfect sinusoidal response typical for linear viscoelasticity is obtained only at the lowest strain amplitude of 2.1 mrad. Reproducibility of the data is observed only at this lowest strain amplitude. At higher strain amplitudes reproducibility is achieved solely after prolonged annealing, at least for a minimum of two days.

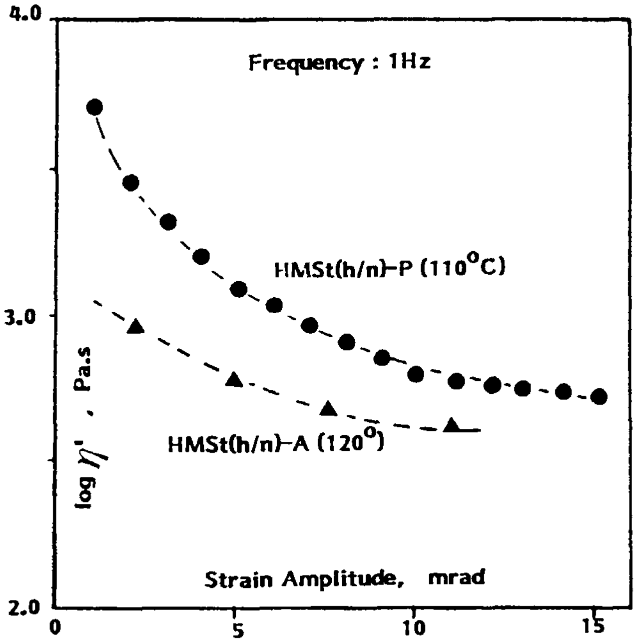


FIGURE 3 Influence of strain amplitude on the dynamic viscosity, HMSt(h/n)-A at 120°C and HMSt(h/n)-P at 110°C.

Three different ways have been used to analyse the instabilities induced by shear in the nematic mesophase of the copolyether.

1. The sample was introduced in the rheometer at 140°C and maintained at this temperature for one day to ensure complete melting of the crystallites. Subsequently frequency sweeps between 0.05 and 15 Hz were carried out directly after the sample had attained the temperature of measurement. The temperature has been varied between 120° and 160°C. The strain amplitude was always 2.1 mrad to ensure linear viscoelasticity.
2. The same sample was then sheared at 160°C with a constant strain amplitude of 7.3 mrad until the moduli became constant. In this way, we realized a reference state of shear-induced orientation which was dependent exclusively on the conditions used. Later, different LC-polymers will be compared in this shear-induced reference state.

   The sample was then annealed at the same temperature at rest and directly in the rheometer. During annealing, frequency sweeps were carried out from time to time between 0.05 and 15 Hz, using a strain amplitude of 2.1 mrad. After four days of annealing, a stationary state was achieved. This was confirmed by the constancy of the moduli. Then the sample was exposed to frequency sweeps as before in the temperature range 120° to 160°C, using the strain amplitude of 2.1 mrad. At each temperature, the sample was annealed for 12 h before starting anew the next frequency sweep.
3. The annealed sample was exposed to shear at 160°C using a frequency of 1 Hz and a strain amplitude of 7.3 mrad. Constancy of the moduli was achieved

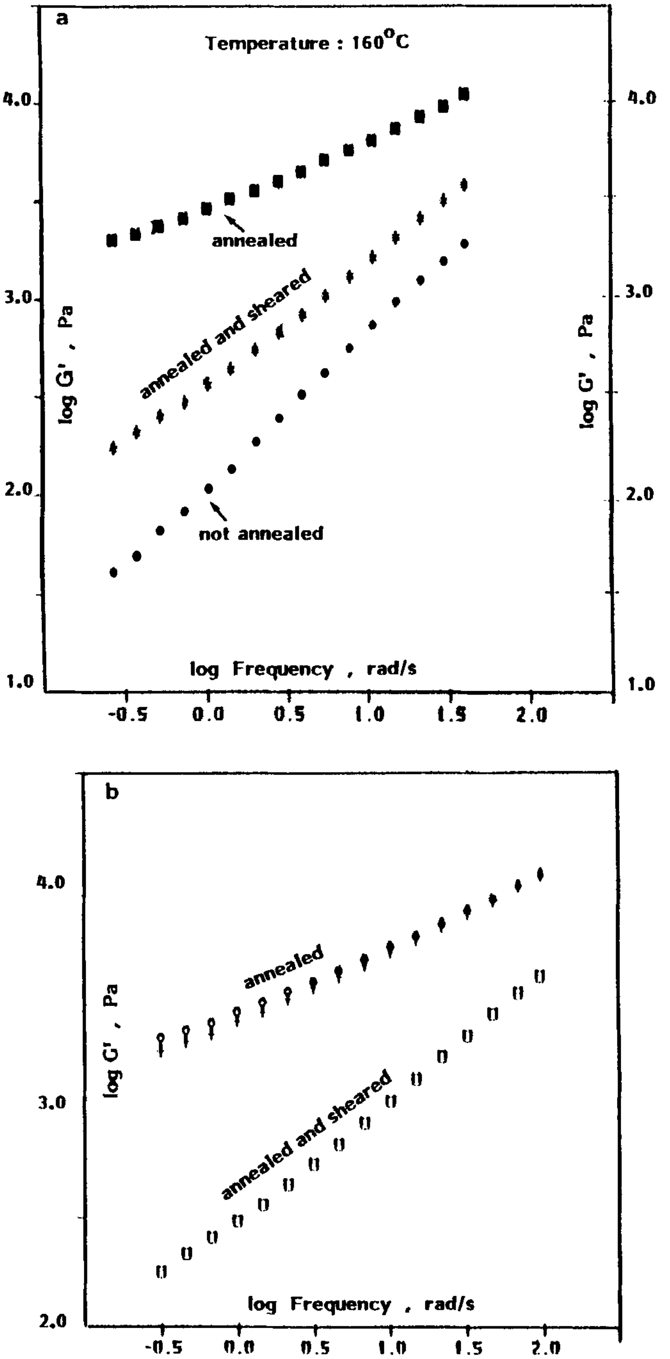


FIGURE 4 Influence of the annealing time and shear on the mechanical dynamic properties of HMSt(h/n)-A; Frequency sweep (0.05-15 Hz) isotherms at 160°C. (a) Storage modulus, G', after different pretreatments of the sample; (b) Reproducibility of the data for the annealed sample: Annealing before (+) and after shear (0).

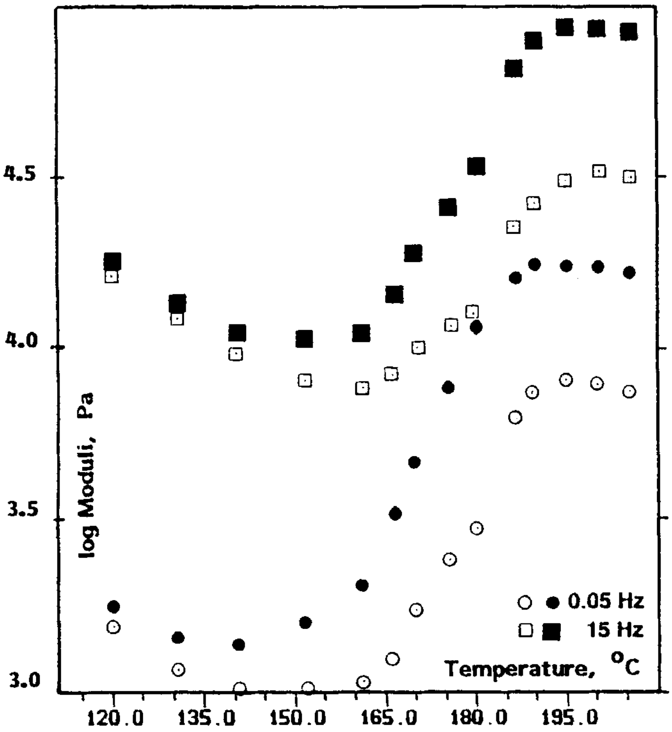


FIGURE 5 Jump in the mechanical dynamic characteristics of annealed HMSt(h/n)-A over the temperature range of the transition from the nematic to the isotropic phase. Storage modulus-G', full points: and loss modulus-G'', open points: at the lower (0.05 Hz) and higher extremes (15 Hz) of the frequency sweep.

after two days of shear. Then the frequency sweeps were renewed in the temperature range 120–160°C and with a strain amplitude of 2.1 mrad. During the shift to a new temperature, the relaxation of the shear induced microstructure caused a general increase of the moduli. To avoid such "temperature effects," the samples were sheared for 12 h each time after changing the temperature, using a frequency of 1 Hz and a strain amplitude of 7.3 mrad, as before.

The curves obtained for the storage modulus at 160°C are shown in Figure 4a. The reproducibility of the data for the annealed sample before and after shear is demonstrated by the curves shown in Figure 4b. The mechanical dynamic data measured at 160°C directly after shear, without subsequent annealing of the sample were never reproducible.

The increase of the moduli during annealing without shear may be explained by the stabilization of mesophase microdomains, the subsequent decrease during shear occurring by an orientation of the molecules in the mesophase, thus promoting flow of the system. This is supported by the observation that in the stationary state realized after annealing $G' > G''$, whereas in the stationary state obtained by shear $G' < G''$.

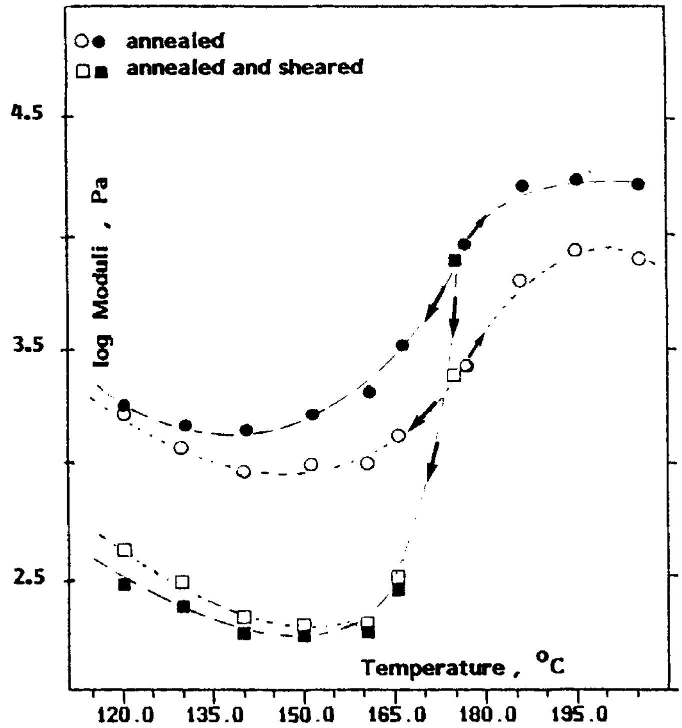


FIGURE 6 Jump in the mechanical dynamic characteristics at 0.05 Hz for HMSt(h/n)-A annealed and sheared after annealing. Full points: storage modulus, G'; open points: loss modulus, G''.

After the cycle of frequency sweeps carried out as described before under the different conditions between 120–160°C, the mechanical dynamic properties of the sample were measured in the two phase nematic/isotropic transition region between 160° and 205°C using the frequencies and strain amplitude as before. Starting at 180°C, no further differences were observed between the viscoelastic moduli of the solely annealed sample and of the sample sheared after annealing.

The influence of temperature on the mechanical dynamic properties of the LC copolyether was investigated while executing frequency sweeps at the strain amplitude of 2.1 mrad for both the annealed sample and the sample sheared after annealing.

The temperature dependence of the moduli at the lowest and highest of the used frequencies, i.e., at 0.05 and 15 Hz, respectively, is illustrated in Figure 5. A steep increase of the values is observed between 160° and 190°C, the temperature range in which the transition from the nematic into the isotropic phase occurs. The observed jump is larger at the lower frequency of 0.05 Hz.

The temperature dependences of the moduli of the annealed and of the sheared sample after annealing are compared in Figure 6 at the lower frequency of 0.05 Hz. The data were always reproducible if the conditions of annealing and shear were strictly respected.

The temperature dependence of the mechanical dynamic moduli of the sample

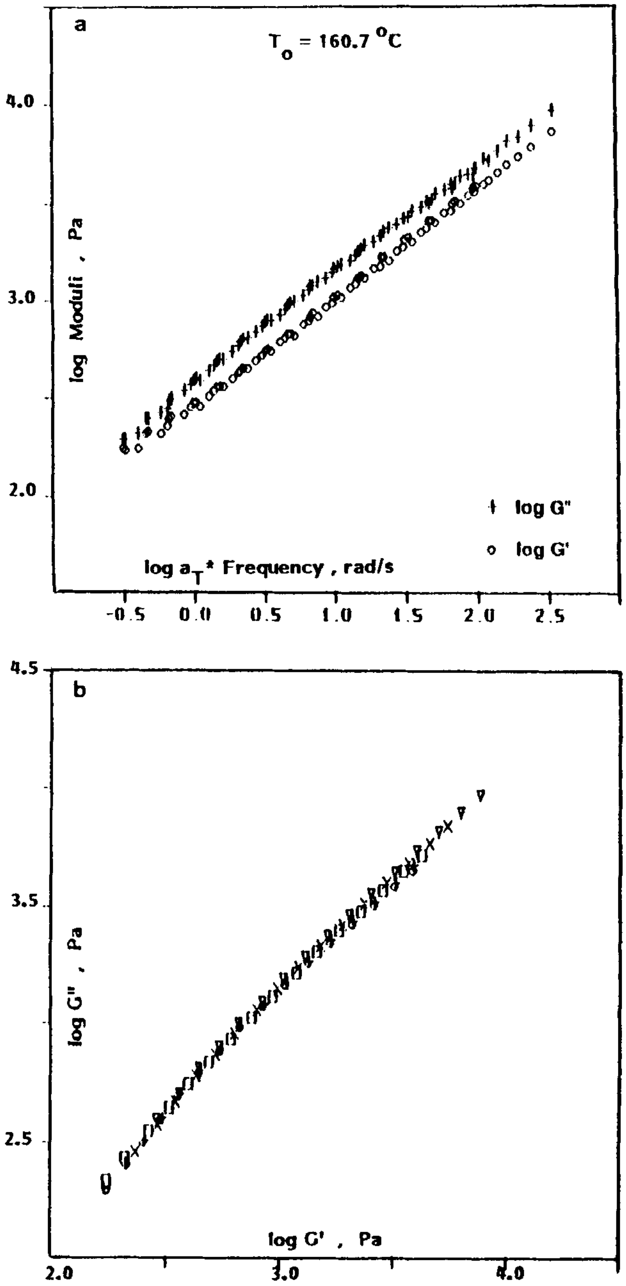


FIGURE 7 Master curves for HMSt(h/n)-A sheared after annealing. Moduli of the nematic phase in the temperature range 120–160°C. (a) G' and G'' at the reference temperature of 160.7°C; (b) log G'' vs. log G' of HMSt(h/n)-A, same temperature range.

TABLE II

Shift factors of the time-temperature superposition for the nematic phase of the polyether HMSt(h/n)-A

Temperature, °C	log a_T
160.7	reference Temperature
150.1	0.05
140.1	0.11
130.1	0.32
120.0	0.55

oriented by shear reflects exactly the data obtained by DSC. On DSC, the onset of the transition from the nematic into the isotropic phase is observed at 161°C, whereas the maximum in the DSC transition peak is situated at T_m = 184°C. The corresponding moduli of the sheared sample show, in the nematic phase, a minimum at 160°C. Then the moduli start to increase at 165°C and show the highest jump between 185° and 190°C. The moduli continue to increase slightly until 200°C; the final temperature of the DSC peak is at 197°C. Above 200°C, in the isotropic phase, the moduli start to decrease anew.

By changing the shear conditions stationary states are realized too, but the values of the measured moduli are different. The typical influence of increasing strain amplitude during shear is observed only up to 180°C. Above 180°C, no further influence of strain amplitude on the measured moduli has been observed.

Taking into account that, according to DSC, the peak maximum is situated at 184°C, it may be supposed that, beginning at that temperature, the LC content of the sample becomes too small for a shear induced orientation, but it is still high enough to determine the further slight increase of the moduli with increasing temperature.

It is remarkable that the mechanical dynamic data for the LC copolyether obey the time-temperature superposition in the stationary states realized in the nematic phase by shear after annealing. This is not valid for the stationary states obtained by annealing only.

A possible explanation for the inapplicability of the time-temperature superposition of the mechanical dynamic data obtained for the sample in the annealed stationary state lies in the mode used for the measurements. During the frequency sweeps, no annealing has been carried out between the different frequencies of measurement. The mechanical shear field acting during the measurements induces an orientation which continously changes the microstructure of the sample. Thus "reproducible non-equilibrium states" are induced which are responsible for the invalidity of the time-temperature superposition. It may be assumed that the validity of the time-temperature superposition can be realised if the annealed sample is again annealed each time before the frequency is changed during the respective frequency sweep.

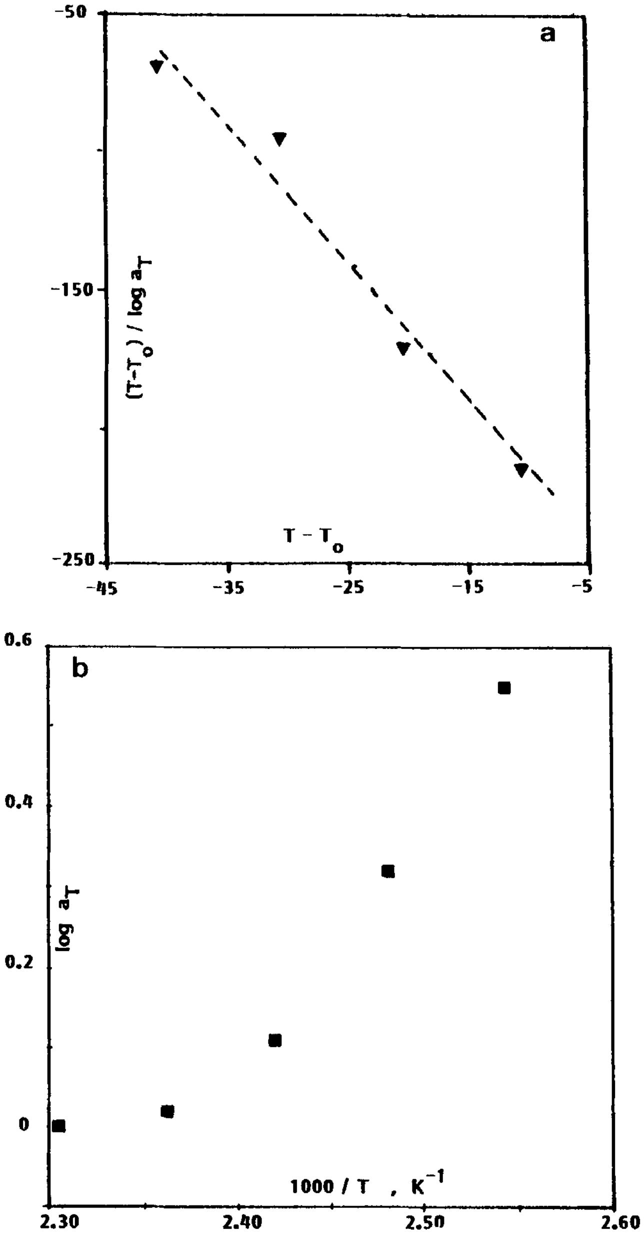


FIGURE 8 Temperature dependence of the shift factors for HMSt(h/n)-A. Temperature range 120–160°C: (a) WLF plot; (b) Arrhenius plot.

The respective master curves for the temperature range of 120–160°C are shown in Figure 7a at the reference temperature of 160.7°C. The validity of the time-temperature superposition has been verified by the temperature invariancy of the log G'' vs. log G' plot shown in Fig. 7b. This proof of the validity of the time-temperature superposition has been first recommended by Chuang and Han.[5]

The temperature dependence of the shift factors is, however, unusually small compared to the respective data for amorphous polymers showing no LC mesophases (see Table II). The values of the corresponding WLF constants[6] obtained using the linearized WLF relation (Figure 8a) are: $C_1 = 0.2$ and $C_2 = 54.3$. Thus the product $C_1 C_2 = 10.9$ is far below the "universal" value of about 900, considered typical for amorphous polymers.

The fact that the temperature dependence of the shift factors do not obey the Arrhenius law (Figure 8b) suggests the simultaneous occurrence of different processes in the nematic phase characterized by different temperature coefficients. The result of the superposition of these processes (at least shear flow and microdomain formation) is the observed extremely small temperature dependence as indicated by the low values of the WLF constants.

CONCLUSIONS

The mechanical dynamic behaviour in the nematic phase of the investigated LC copolyether depends on both the thermal and the shear history. Stationary states can be achieved either by prolonged annealing (at least for 4 days) or by prolonged shear of the before annealed sample. The stationary states are characterized by constant and reproducible values of the moduli.

During annealing an increase of the moduli is observed and it is assumed that stationary nematic polydomainstructures are developed. These structures show the typical behaviour of a physical network characterized by the condition $G' > G''$.

During the subsequent shear after annealing, a substantial decrease in the mechanical dynamic moduli is observed probably due to an orientation of the mesogenic units. This time the stationary states are characterized by the condition $G'' > G'$. It is interesting to notice that in this stationary flow state the moduli obey the time-temperature superposition. The temperature dependence of the shift factors is, however, unusually small.

The transition from the nematic into the isotropic phase is characterized by a large two-phase region in which substantial increases of the moduli.

Acknowledgments

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