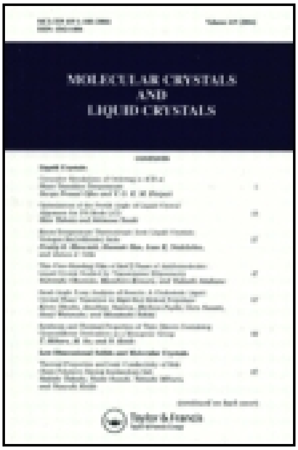

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Mechanical Dynamic Properties of a Main Chain Liquid Crystalline Polyester-Rheological Stationary States

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Mechanical Dynamic Properties of a Main Chain Liquid Crystalline Polyester—Rheological Stationary States

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It is possible to realize rheological stationary states in nematic main chain LC-polymers by prolonged annealing and/or shear which are characterized by reproducible mechanical dynamic data. During the adaption of the stationary states the moduli vary in time until they become constant after several days of annealing and/or shear. By annealing there are developed in the nematic phase structures which show prevailing elastic contributions, i.e. $G' > G''$. During shear the moduli decrease and finally flow tendancies preponderate, i.e. $G'' > G'$. As long as the conditions used in the subsequent measurements are not perturbing the before realized stationary states, the corresponding mechanical dynamic data are time-temperature superposable. Taking into account that neither the thermal nor the mechanical history of the original LC-polymer samples are known, the belonging mechanical data are never reproducible. It is thus suggested to start with the annealing treatment for inducing first an equilibrium nematic structure before the rheological treatments and measurements are carried out.

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

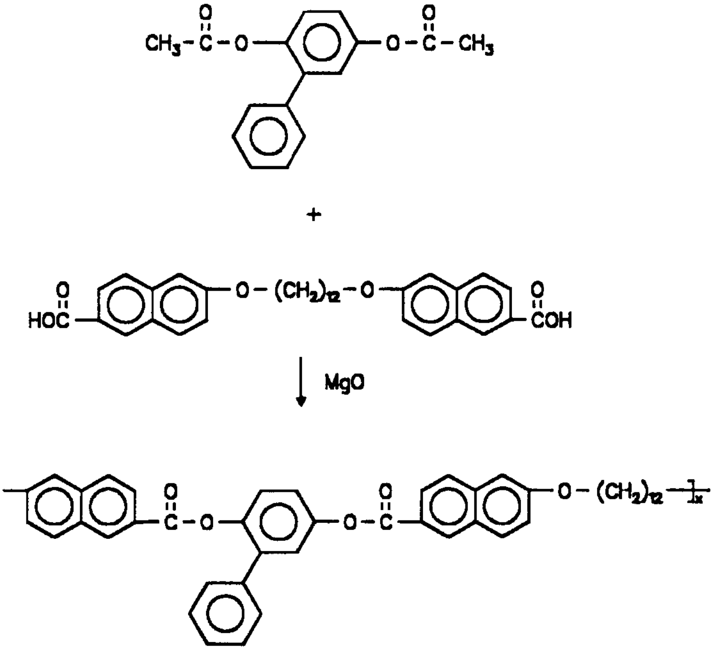
INTRODUCTION

In foregoing studies it has been shown that it is possible to realize rheological stationary states in the nematic phase of a main chain LC-copolyether—poly(4,4′-dihydroxy-α-methylstilbene-hexyl(nonyl)methylene). The stationary states are obtained either by time controlled annealing and/or by subsequent time controlled shear. In the stationary state realized by annealing the storage modulus exceeds the loss modulus, whereas in the stationary state after shear the loss modulus exceeds the storage modulus. Both the stationary states and the belonging mechanical dynamic characteristics are reproducible. Besies the moduli of the stationary state realized by shear after a first annealing obey the time-temperature superposition.[1] The times needed for adaption of the stationary states are molecular weight dependent, ranging from 2 days for the sample M_n = 5,800 to 7 days for the sample M_n = 13,400. Surprisingly the temperature dependence of the shift factors for the time-temperature superposition, which are unusually small, increases also with the molecular weight of the LC-copolyether.[2] The transition from the nematic into the isotropic phase is characterized by the well known jump-like increase of both the moduli and the dynamic viscosity described before by Porter and Johnson.[3]

Extending the study on the mechanical dynamic behaviour of LC-polymers in the nematic phase in this paper we report the results obtained for a nematic main chain LC-polyester.

EXPERIMENTAL

The nematic main chain LC-polyester has been synthesized by MgO catalyzed polycondensation reaction in the melt between acetylated phenylhydrochinone and dodecamethylene-bis-6-hydroxy-2-naphthoic ether.[4]



The intrinsic viscosity of the polymer was of 0.62 dl/g. Due to the reduced solubility of the polymer it was not possible to determine the molecular weight by other methods. For the same reason we have no information on the polydispersity of the LC-polyester.

The presence of the nematic LC-phase has been confirmed by X-ray measure-

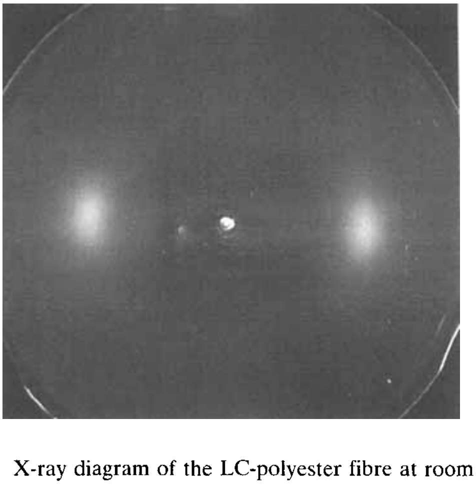


FIGURE 1 X-ray diagram of the LC-polyester fibre at room temperature.

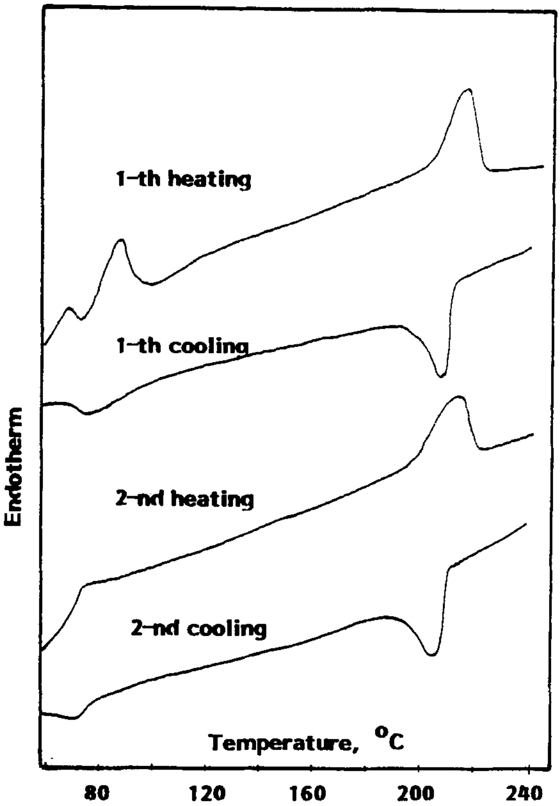


FIGURE 2 DSC thermograms of the LC-polyester. Scans of the first and second heating/cooling cycles in nitrogen at rates of 10 K/min.

ments below Tg on polymer fibers at room temperature (Figure 1). The observed equatorial reflexes indicate a lateral distance of the mesogenes of 4.6 A. Differential scanning calorimetric measurements in the temperature range of 40–260°C have been carried out in nitrogen atmosphere on a PERKIN-ELMER DSC 7 using heating and cooling rates of 10 K/min. After a first heating cooling-cycle the thermograms were reproducible. The recorded DSC scans are shown in Figure 2. The LC-polyester shows no melting transition between the glass and clearing temperature but only an extended nematic range. The glass transition temperature is of about 69°C (midpoint temperature at the heating rate of 10 K/min) and the clearing ranges between 206–230°C with the maximum at 217.1°C.

For the rheological measurements the samples have been prepared by press-moulding for one hour in vacuum at 120°C. The mechanical dynamic measurements have been carried out in the temperature range of 145–260°C on an INSTRON 3250 RHEOMETER using the cone and plate geometry. The diameter of the plate was 40 mm and the cone angle 21 mrad. Isotherm frequency sweeps have been performed in the 0.05–15 Hz range, using a strain amplitude of 2.1 mrad, because a perfect sinusoidal response typical for linear viscoelasticity has been observed only at this small strain amplitude on an oscilloscope connected to the response output of the rheometer. That was not more valid for higher strain amplitudes.

RESULTS AND DISCUSSION

Taking into account the well known sensibility of the mechanical dynamic properties of nematic LC-main chain polymers to thermal and mechanical history which was proved also for the before investigated LC-copolyethers,[1,2] the rheological measurements have been carried out in standard conditions. They have been used also in the investigation of the LC-copolyethers:

I. First the press-moulded sample was melted directly in the rheometer at 145°C. Subsequent isotherm frequency sweeps were carried out in the temperature range of 145–260°C. The frequency isotherms were scanned in temperature steps of 10° in the nematic phase between 145–205°C, and in steps of 5° both in the transition range to the isotropic phase between 205–235°C and in the isotropic phase between 235–260°C.

II. After this first cycle the sample was sheared continuously at 205°C using the freuqency of 1 Hz and a strain amplitude of 7.3 mrad. During shear the moduli decreased substantially suggesting an increased flow tendency, probably due to orientation of the nematic structures. They became constant after at least 30 hours of shear. Then the isotherm frequency sweeps were carried out in steps of 10° downwards in the temperature range of the nematic phase (205–145°C). At each new temperature the sample was sheared again before the measurement for 12 h using the same conditions of 1 Hz and 7.3 mrad, to prevent any relaxation of the shear induced orientation in the nematic phase. The frequency sweeps were then continued in the transition range starting from 205°C upwards and continuing in the isotropic phase to 250°C.

III. After the cycle II shear the sample was annealed at 205°C. During annealing the moduli increased anew. They became constant only after about 6 days of annealing. Subsequently the isotherm frequency sweeps have been executed in the same temperature range as before, starting with 145°C in the nematic phase up to 250°C in the isotropic phase. At each new temperature increment the sample was annealed for 12 h for relaxation of any induced orientation by shear during the previously performed frequency sweep.

IV. For the fourth cycle of measurements, the annealed sample was sheared anew at 205°C using the same conditions as in II. The moduli decreased again during the shear. This time they became constant after 20 h of shear. The frequency sweeps were carried out first in the nematic phase downwards between 205–145°C and then upwards starting with 205°C in the transition region and continuing in the isotropic phase up to 250°C. At each new temperature the sample was sheared again before the measurement for 12 h using 1 Hz and the strain amplitude of 7.3 mrad to prevent the relaxation of the previously shear induced orientation.

The results obtained in the first cycle of the mechanical dynamic investigation of the LC-polyeter press-moulded at 120°C (sample A) are shown in Figure 3. In Figure 3a are illustrated the temperature dependences of the storage (G') and loss moduli (G'') at the lowest (0.05 Hz) and highest (15 Hz) frequency used during the frequency sweeps. The moduli of the nematic phase decrease as usual with increasing temperature between 145–205°C. Then in the transition range from the nematic into the isotropic phase (205–235°C) a jump-like increase is observed which is more accentuated at the lower frequency. In the isotropic phase the moduli decrease again with increasing temperature. It is remarkable that in the nematic phase the loss modulus exceeds the storage modulus suggesting a prevailing flow tendency, whereas in the isotropic phase the storage modulus is the larger. This is much better evidenced by the mastercurves for the nematic (Figure 3b) and the isotropic phase, respectively (Figure 3c).

The validity of the time-temperature superposition, which has been supplementary proved accordingly to Han[5] by the availability of the $\log G'' - \log G'$ correlation (Figure 4), suggests the existence of rheological steady states. The temperature dependence of the shift factors in the nematic phase is, however, unusually small. This is reflected in the values of the corresponding WLF constants (see Table I). In the isotropic phase the shift factors show surprisingly an opposite dependence when compared with the prediction of the WLF relation.

Up to now we have no valid explanation for this strange behaviour of the shift factors of the mechanical dynamic data of the LC-polyester in the isotropic phase. Nevertheless, the inversed dependence of the shift factors suggests the superposition of processes which cover the usual temperature dependence of the mechanical dynamic properties. This supposition is supported by the observation that the slope of the storage modulus curve of the isotropic melt is not decreasing in the low frequency range as it is usually observed for atactic polymer melts, but even seems to increase again slightly (see Figure 3c). A possible explanation could be the prolongation into the isotropic phase of the elimination of the elastic nematic polydomain structures because of their extremely long times of cessation.[6,7]

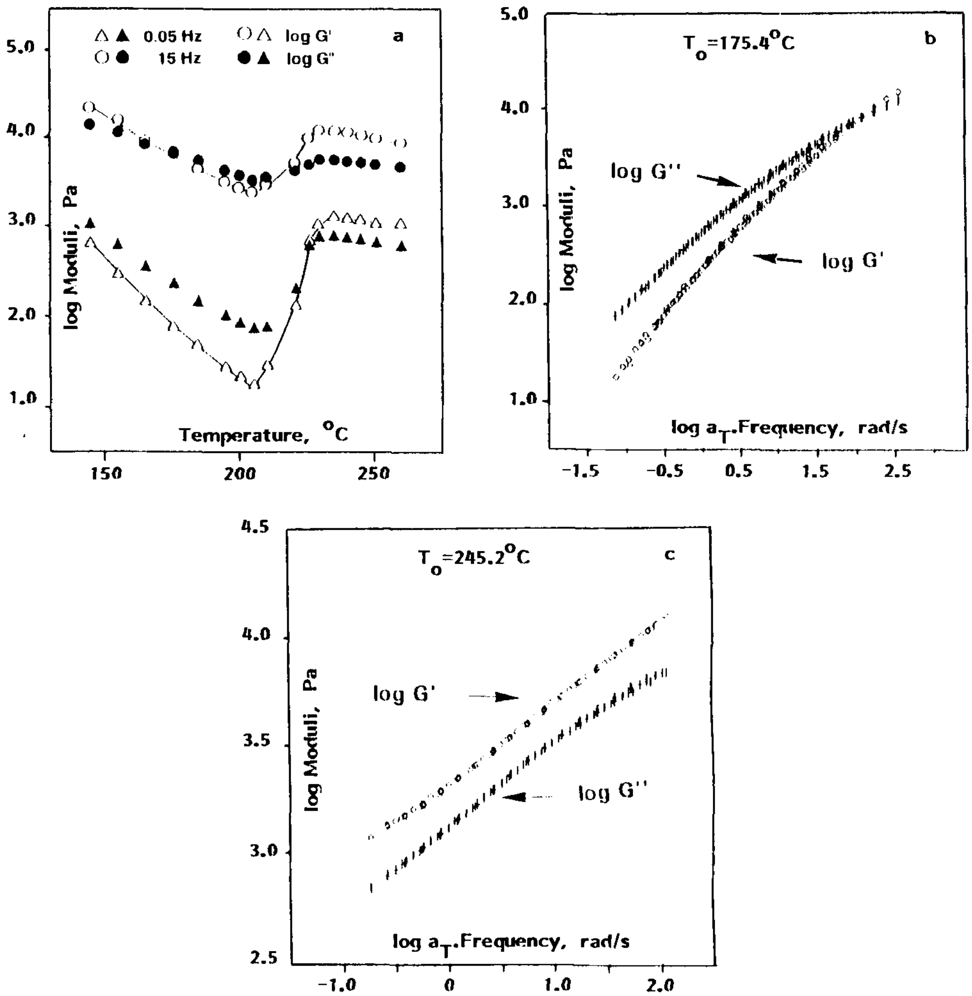


FIGURE 3 Mechanical dynamic data of the untreated LC-polyester sample press-moulded at 120°C. a. Temperature dependence of the storage, G', and loss moduli, G'', at 0.05 Hz and 15 Hz, resp. b. Mastercurves of the moduli in the nematic phase. Reference temperature, T_o = 175.4°C. c. Mastercurves of the moduli in the isotropic phase, T_o = 245.2°C.

It is interesting to notice that in this first cycle of measurements the mechanical dynamic data are dependent on the temperature used for preparation of the sample by press-moulding. Shown in Figure 5a are the respective data for the storage moduli of the LC-polyester obtained by press-moulding at 160°C (sample B) and 180°C (sample C), respectively. The dashed line indicates the position of the corresponding mastercurve of sample A, press-moulded at 120°C (see Figure 3a). With increasing temperature used for press-moulding the data are slightly shifted versus higher values. But much more important is the observation that the time-temperature superposition for the sample C, press-moulded at the highest temperature of 180°C, fails due to increased elastic contributions in the low frequency range starting

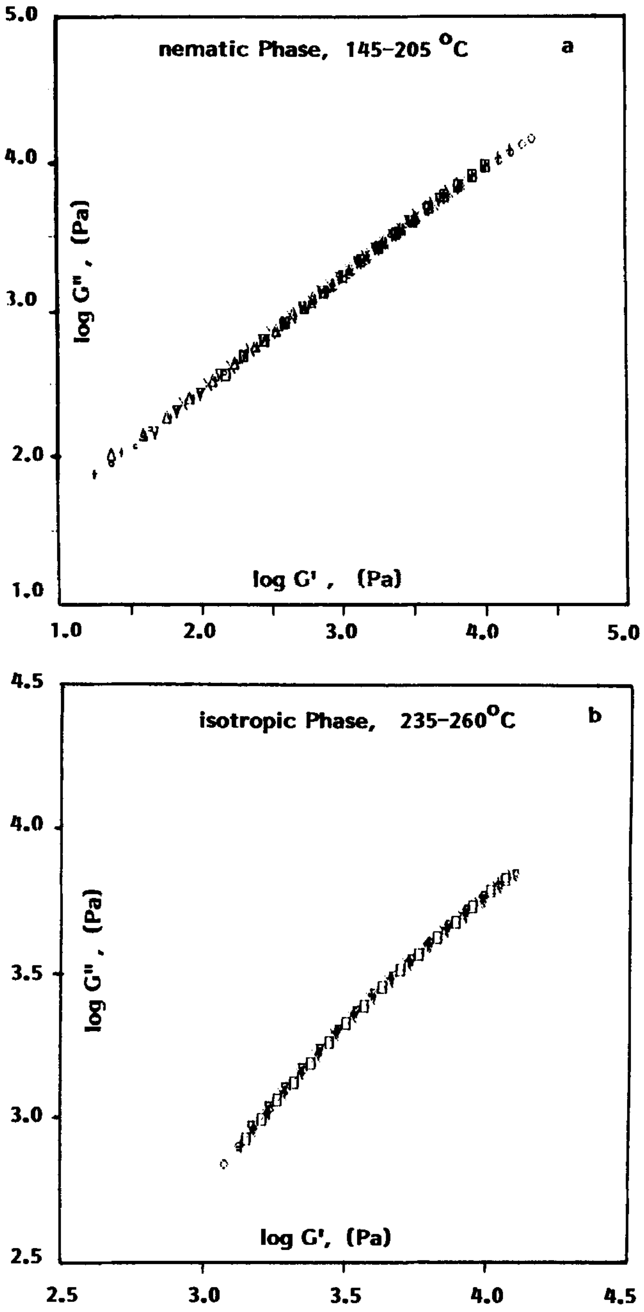


FIGURE 4 Log G″ vs. log G′ plot of the untreated LC-polyester press-moulded at 120°C. a. In the nematic. b. In the isotropic phase.

TABLE I

Values of the WLF constants computed using the experimental shift factors

Sample	T_o, °C	c_1	c_2	c_1c_2
I nematic	175.4	4.0	162.3	649.2
I isotropic	245.2		inversed WLF behaviour	
II nematic	175.0	1.89	88.0	166.3
II isotropic	245.2		identical with I isotropic	
III nematic	—		no time-temperature superposition	
III isotropic	—		no time-temperature superposition	
IV nematic	175.0	5.8	151.8	880.4
IV isotropic	—		no time-temperature superposition	

with the data of the isotherm of 175°C. A pre-relaxation during press-moulding at this high temperature is assumed to be responsible for the observed rheological behaviour of sample C. The increased elasticity of sample C is preserved also in the sheared sample (see Figure 5b). The differences between the rheological behaviour of the samples obtained by press-moulding at different temperatures disappear definitively only in cycle III after annealing to stationary state.

Further discussions of the mechanical dynamic results are restricted for simplification to the LC-polyester sample A, obtained by press-moulding at 120°C. The sample specifications by latin number refer to the conditions applied to the sample before the mechanical dynamic measurements.

The results obtained for the LC-polyester A prepared for the mechanical dynamic investigations according to II are shown in Figure 6. The temperature dependence of the moduli is illustrated in Figure 6a, the mastercurves are shown in Figure 6b and in the log G″ – log G′ correlation in Figure 6c. By shear the moduli are decreased by about one order of magnitude. It is supposed that an induced orientation of the nematic phase is responsible for the increased flow tendency. The shift factors used to construct the mastercurves in Figure 6b were yet smaller than for the sample I (see Table I). In the isotropic phase the moduli were not affected by the applied shear procedure and the mastercurves are identical with those of sample I shown in Figure 3c.

The moduli of the annealed sample III increased by more than 1.5 orders of magnitude comparing with the moduli of the sheared sample II. At the same time the storage moduli of the nematic phase became larger than the loss moduli, suggesting increased elastic contributions. The temperature dependence of the moduli is illustrated in Figure 7a. Surprisingly the time-temperature superposition was not applicable, neither for the data of the nematic phase, nor for that of the isotropic phase, although the mechanical dynamic results were perfectly reproducible (see Figure 7b).

A possible explanation could be related to the modality of execution of the mechanical dynamic measurements. The frequency sweeps were carried out as usual step by step with no waiting time for relaxation between the individual frequencies applied during the frequency sweep. It is thus probable that the initial equilibrium structures realized by relaxation have been perturbed continuously due to shear induced orientation of the nematic phase. It may thus be supposed that the time-temperature superposition would be effective as soon as the time accorded for

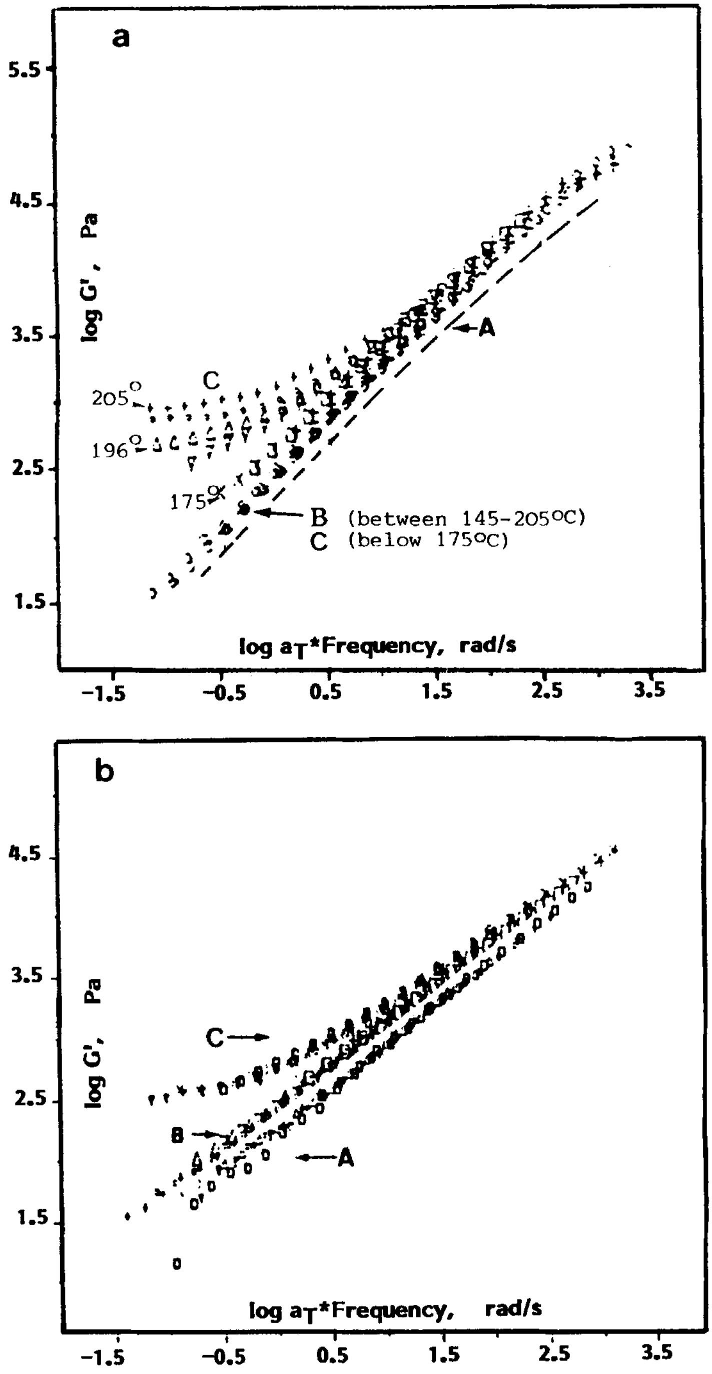


FIGURE 5 Mastercurves of the storage moduli of the LC-polyester samples press-moulded at: A–120°; B–160° and C–180°. a. Untreated samples I. b. Sheared samples II.

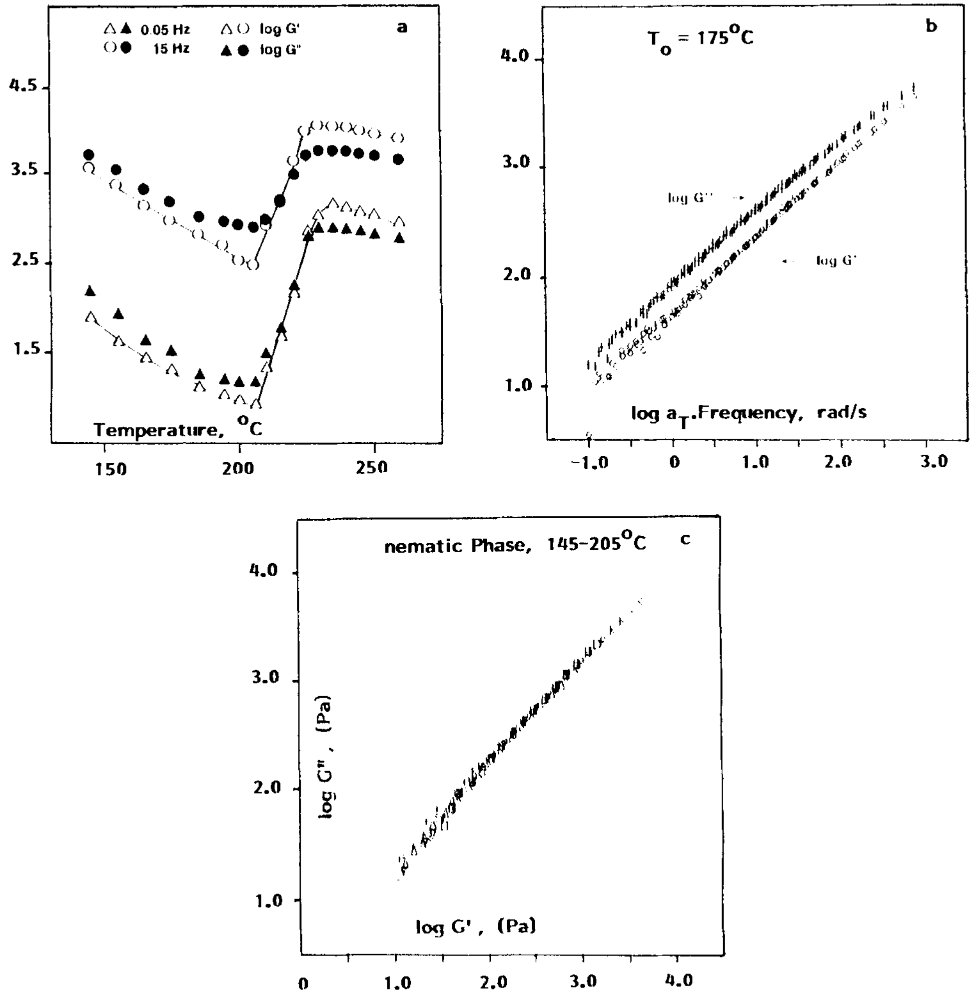


FIGURE 6 Mechanical dynamic date of the sheared LC-polyester II. a. Temperature dependence of the moduli. b. Mastercurves of the moduli of the nematic phase, T_o = 175.0°C. c. Log G'' vs. log G' plot of the moduli of the nematic phase.

relaxation to the initial equilibrium structures realized by annealing was long enough between two subsequent frequency steps.

It is worthwhile to notice that non superposability of the mechanical dynamic data has also been observed in the stationary nematic phase realized by annealing in the LC-copolyethers.[1,2] The time-temperature superposition worked only for the data obtained in the steady nematic phase realized by shear.

Both the higher moduli in the isotropic phase of the annealed sample III when compared with those of untreated sample I, and the invalidity of the time-temperature superposition for the mechanical dynamic data in the isotropic phase of sample III, were unexpected. The measurements were, however, repeated several times and the obtained results were always reproducible. It may thus be supposed

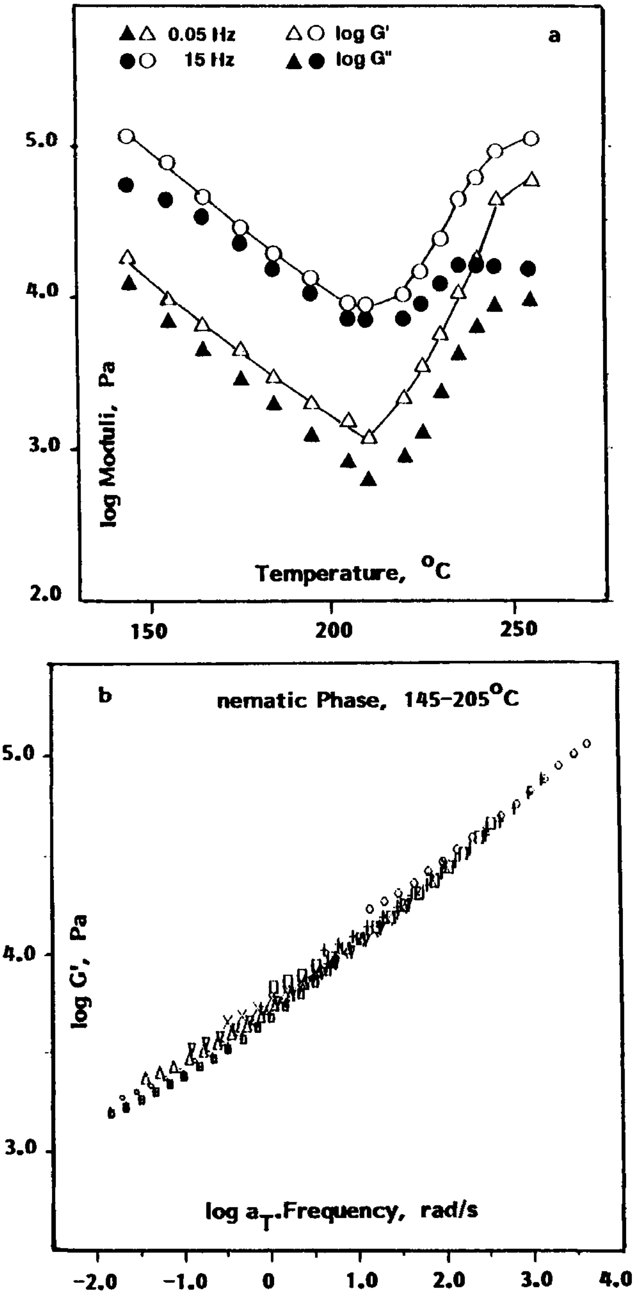


FIGURE 7 Mechanical dynamic data of the annealed LC-polyester III. a. Temperature dependence of the moduli. b. Attempt of constructing the mastercurve of G′ of the nematic phase.

that equilibrium structures of the nematic phase are developed only in the annealed sample III. Probably the untreated samples I were somehow preoriented either by preparation or during press-moulding and except for the sample C press-moulded at the highest temperature they have not started to relax during transition in the isotropic phase.

For the fourth cycle of measurements the annealed sample III was sheared in the same conditions as the untreated sample I. The observed decrease of the moduli was, however, less important as that realized by shear of the untreated sample I. This supports once more the supposition that sample I was from the beginning preoriented so that the same shear treatment induced a better orientation of the nematic phase. This explains the observed higher flow tendency of sample II when compared with sample IV.

The superposability of the mechanical dynamic data was, however, again assured by the shear treatment as illustrated in the mastercurves shown in Figure 8b. In Figure 8a is illustrated the temperature dependence of the moduli, in Figure 8b are shown the mastercurves of the moduli in the nematic phase and in Figure 8c the respective log $G''-\log G'$ correlation confirming the validity of the time-temperature superposition.

The presented rheological data for the four cycles of measurements were perfectly reproducible with the only condition of respecting the conditions and order of annealing and shear treatment. It is surprising that the moduli of the sheared samples II and IV are different although the shearing conditions were the same. An acceptable assumption is that the untreated sample was preoriented and was not completely relaxed during preparation by press-moulding and the melting in the rheometer at 145°C. This suggestion is supported by the observation that the moduli of sample I are smaller when compared with the moduli of the annealed sample III. The fact that when the same shear procedure was applied to the annealed sample III it was not possible to reproduce the data obtained after shearing of the untreated sample I suggests that the strain applied during the shear of sample III was too small for inducing the same orientation in the annealed sample III as in the initial sample I. For illustration, in Figure 9 are compared the storage moduli at the frequency of 1 Hz.

The mastercurves of the storage moduli and of the dynamic viscosities in the nematic phase of the sheared samples II and IV, as well as of the untreated sample I, are compared in Figure 10.

It is interesting to remember that for the LC-copolyethers time-temperature superposable rheological data have been obtained in the nematic phase, also, only for the samples sheared in the same conditions as used for the LC-polyester[1,2] and not for the annealed sample. Nevertheless, the data for the annealed sample were as well reproducible as the data for the annealed LC-polyester III. Also the mechanical dynamic data of the initial sample were never reproducible.

It may thus be assumed that while shear orientation is induced in the nematic phase and the mechanical dynamic data measured after a typical adaption time for realizing of a stationary state the samples obey the time-temperature superposition with the condition that the subsequent measurements are carried out in conditions which do not perturb the before induced orientation by shear.

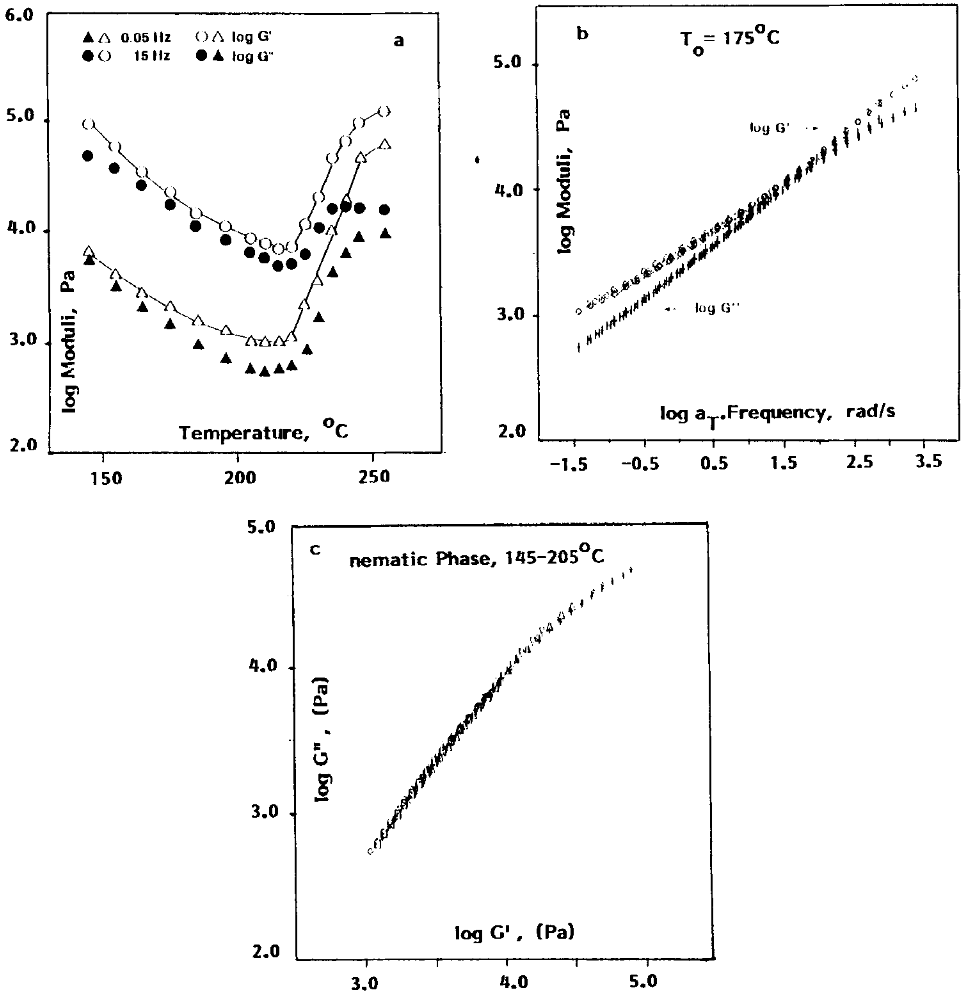


FIGURE 8 Mechanical dynamic data of the LC-polyester IV sheared after annealing. a. Temperature dependence of the moduli. b. Mastercurves of the moduli of the nematic phase. T_o = 175.0°C. c. Log G″ vs. log G′ plot of the moduli of the nematic phase.

During shear the moduli decrease becoming constant after some time of adaption and generally G″ > G′, i.e. the induced orientation in the nematic phase facilitates the flow of the sample. The slopes of the storage and loss moduli curves in the low frequency range are, however, nearly constant and parallel. The order of the slopes is of 0.7, i.e. the slopes are much smaller than the characteristic slopes for atactic polymer melts. A similar flow behaviour is observed for blockcopolymers having a lameller suprastructure. They show in the terminal zone the slope 0.5 for both the moduli curves.[8,9]

Taking into account that the time-temperature superposition of mechanical dynamic data in the nematic phase applies only if the induced stationary state is not perturbed by the measurement, it is not surprising that the data of the samples

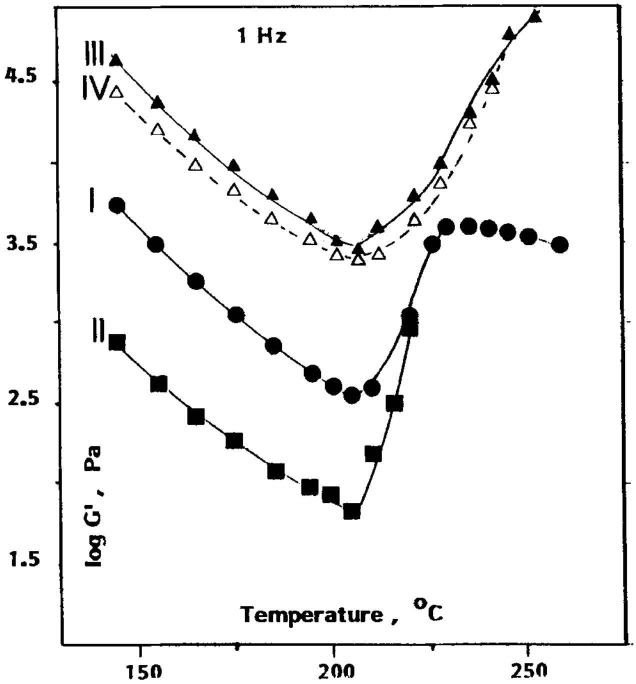
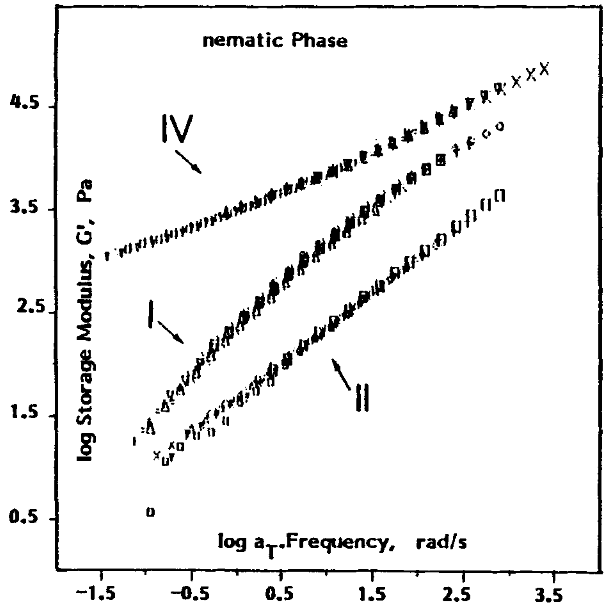


FIGURE 9 Comparison of the temperature dependence of the storage moduli of the different prepared LC-polyester samples at the frequency of 1 Hz.

relaxed by annealing do not obey this principle. With a sufficient long time of annealing any orientation in the nematic phase is completely relaxed, i.e. the overall nematic structure appears random, i.e. polydomain structures prevail.[6,7] The parallel increase of the elastic contribution, so that G' > G", supports this assumption. During the subsequent frequency sweep experiment orientation is induced in the nematic phase even when small strain amplitudes are used. Usual frequency sweeps are executed changing stepwise the applied frequency without waiting for relaxation between the individual steps, thus the shear induced orientation increases also stepwise. If the successive frequency sweeps are carried out in exactly the same manner, in the nematic phase are imposed changeable, but reproducible structures. Consequently the mechanical dynamic data are perfectly reproducible, but not time-temperature superposable. These suppositions are in accord with the present knowledge concerning the rheology of nematic main-chain polymers.[7]

In conclusion it may be supposed that it is possible to obtain reproducible mechanical dynamic data for nematic main chain LC-polymers with the condition that the time of development of stationary states, either by annealing or by shear, is respected. It is supposed that the stationary states are related with induced order in the nematic phase. In the fully relaxed equilibrium polydomain structures prevail over the elastic contributions due to the interdomain interaction, whereas in the oriented structures by shear increased flow tendencies are observed. If the subsequent measurements do not perturb the orientation of the before realized stationary structures, the data obey supplementary the time-temperature super-



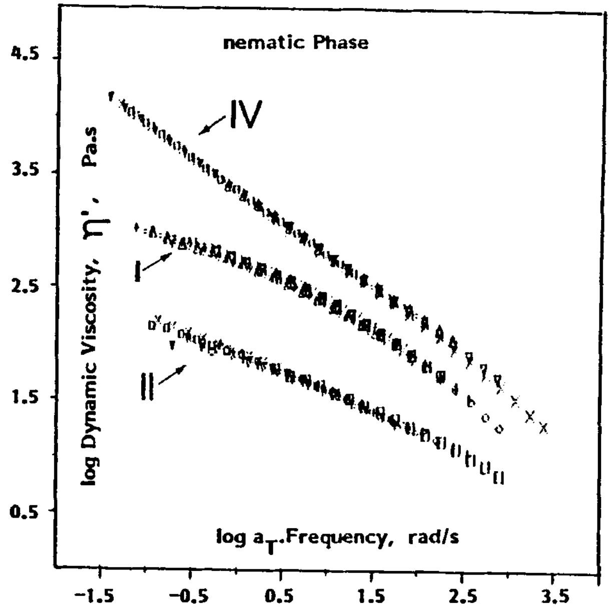


FIGURE 10 Mastercurves of the storage moduli and the dynamic viscosities of the different prepared LC-polyester samples.

position. The WLF constants are, however, small and for further explanations of the mechanical dynamic measurements accompanying texture structure studies are needed. Taking into account that the thermal-mechanical history and thus the degree of orientation of the original LC-polymer sample are not known, it is suggested that in a first step the nematic equilibrium polydomain structure has to be realized by annealing before mechanical dynamic measurements are started.

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