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Dynamic mechanical properties of some liquid crystalline polyacrylates

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Summary

The dynamic mechanical properties of some LC (nematic and smectic) polyacrylates with biphenyl mesogens with different spacers and tails are described. From plots of G′ and G″ against frequency and temperature the phase transitions could be clearly detected, in agreement with DSC analysis. Furthermore, the dynamic viscosities of the LC polyacrylates compared with an isotropic model polymer of similar stucture showed a strong shear rate and temperature dependence. Surprisingly it was found that the viscosity of the LC polymers was higher in the nematic phase than in the isotropic phase.

Introduction

Although the flow behaviour of main chain liquid crystalline (abbreviated LC) polymers has been thoroughly investigated in connection with their processing properties (1), relatively few reports are known on the rheology of side chain LC polymers. Opperman et al.(2) have investigated LC polysiloxanes and concluded that the viscoelastic properties of these polymers are largely determined by the properties of the polymer backbone.

Zentel and Wu (3) have investigated the melt viscosity as a function of shear rate and temperature in the isotropic and LC phases of some polyacrylates with arylbenzoate side chain mesogens, with various spacer lengths between backbone and mesogen.

In a recent paper Pakula and Zentel (4) showed dynamic mechanical properties, as a function of temperature and frequency, of a LC polymer with mesogenic groups both in the main chain and the side chain. One of their remarkable results is that the dynamic viscosity, η^*, of the isotropic state is higher than that of the nematic state (but lower than that of the smectic state), although, of course, the isotropic state lies at a higher temperature than the nematic state. In their interpretation the macromolecules are coiled in the isotropic state, whereas they are more or less aligned in the nematic state.

The study of Lin et al.(5) did not concern LC side chain polymers; however, their work on the structure and rheology of twin LC polymers has to be mentioned in the scope of the present paper. These authors reported their study on polytetrahydrofuran of various molecular weights, with mesogenic end groups. In the phase separated state mesogenic domains function as physical crosslinks, thus giving rise to physical gels.

We were interested in the viscoelastic properties in general of side chain LC polyacrylates in comparison with conventional, amorphous polyacrylates with comparable melt viscosity. We investigated these polymers with the aid of dynamic as well as steady shear experiments as a function of temperature.

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Experimental

Materials and methods

Mechanical measurements were performed on a Rheometrics RMS800 mechanical spectrometer. For steady shear measurements use was made of cone/plate geometry (0.1 rad, diameter 25 mm) and for the dynamic mechanical measurements of plate/plate geometry (diameter 25 mm, distance of plates 2 mm, maximum strain amplitude not more than 5%).

An amorphous acrylate copolymer (T_g=50°C, $\bar{M}_w=17.8\times10^3$, $\bar{M}_n=8.6\times10^3$), used for comparison purposes, was a gift of DSM.

Synthesis

The mesogenic group for monomer Ia (Scheme 1), 4-methoxy-4'-(2-hydroxyethoxy)-biphenyl, was prepared from 4-hydroxy-4'-methoxybiphenyl and ethylenecarbonate in dimethylformamide in the presence of tetrapropylammoniumbromide (6). Yield 75% (much higher than that of the reaction with haloethanol (7,8)), mp 172-173°C.

The mesogenic group for monomer Ib, 4-methoxy-4'-(6-hydroxyhexyloxy)-biphenyl, was prepared from 4-hydroxy-4'-methoxybiphenyl and 1-chloro-6-hydroxyhexane (7). Unreacted 4-hydroxy-4'-methoxybiphenyl could be eliminated by washing the crude reaction product with acetone. Yield 85%, mp 147-148°C (recrystallised from ethanol). The side chain of Ic was prepared analogously from 4-hydroxybiphenyl. Yield 68%, mp 103°C (lit (9), 104-105°C).

These side chain alcohols (1 mole) were acylated with acryloyl chloride (2 moles) according to a literature method (10) to yield monomers Ia-Ic. The reaction was carried out in refluxing THF under nitrogen using triethylamine (2.5 moles) as a proton trap. Yield Ia 65%, mp 90-94°C (lit.(8) 94.7-96.4°C). Yield Ib 75%, mp 90-95°C. Yield Ic 70%, mp 52.8-54.0°C (lit. (9) 48°C).

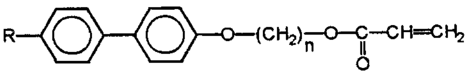
Polymerisations were carried out in refluxing benzene under nitrogen in 15-25% (w/w) solutions using azo-bis-isobutyronitrile or dibenzoylperoxide (0.1-1 mol%) as initiators. The polymers PIa-PIc were isolated by precipitation in cold methanol.

Monomers and polymers were fully characterised by NMR spectroscopy.

Results and discussion

Synthesis and phase behaviour

The polyacrylates PIa (8) and PIc (9) have been prepared before. The phase behaviour of PIc is in accordance with that given in literature (9): it shows no liquid crystallinity. Its structure closely resembles that of the other polymers. Therefore it is very well suited for



Ia, n=2, R=OCH_3
Ib, n=6, R=OCH_3
Ic, n=6, R=H

Scheme 1

TABLE 1

Polymer [a]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	Phase behaviour [b]	T_g(°C) [b]
PIa	14.4	86.9	i 120 n	80
PIb	9.0	22.5	k 129 s_a 140 n 148 i	65
PIc	7.9	22.4	k 57 i	48

[a] MW determined by GPC using polystyrene standards. [b] Determined by a combination of temperature dependent polarisation microscopy and DSC measurements on a Perkin Elmer PE DSC 7.

the comparison of the rheological properties. For PIa no phase behaviour has beendescribed in literature. With hot stage microscopy a monotropic nematic phase, stable over a very small temperature range, could be observed around 120°C. This is in agreement with the observation of an exothermic peak at this temperature in a DSC cooling experiment. In DSC heating measurements the glass-rubber transition appears at 80°C, a double melting peak with maxima at 130°C and 140°C, probably indicates semicrystallinity.
Polymer PIb is new, its LC behaviour is given in Table 1.
For the preparation of the polymers we made use of the synthetic principles, as described for the preparation of PIc (9).

Mechanical measurements

Temperature ranges at which the measurements for the various polymers were carried out, are given in Table 2.
The measurements of the dynamic moduli of PIa and PIb, above 158°C and 143°C, respectively, appeared to be very inaccurate, as a consequence of their low values.

Polymer PIa

Results for the polymer PIa are shown in Figs.1a and b, where the dynamic moduli, G' and G'', are plotted against the angular frequency, ω, on double logarithmic scales for temperatures varying from 111°C to 158°C. Clear gaps between the curves obtained at 127°C and 134°C are perceptible. The dashed curves at 131°C, which, as in general, were measured from high to low frequencies, show that during the measurements a kind of crystallisation takes place (i.e. the transition from the isotropic phase into the nematic phase). This is obvious from the fact that the storage modulus increases with decreasing frequency, which is impossible for a system in equilibrium. The curves at lower temperatures show firstly that the rate of the crystallisation is faster, as apparently no structure changes occur during a frequency sweep, secondly that the amount of crystallinity is higher at lower temperatures and thirdly that the crystallites behave as physic-

TABLE 2

	T range(°C)	T_g(°C)
PIa	111-158	80
PIb	128-158	65
PIc	56- 86	48
cop	95-133	50

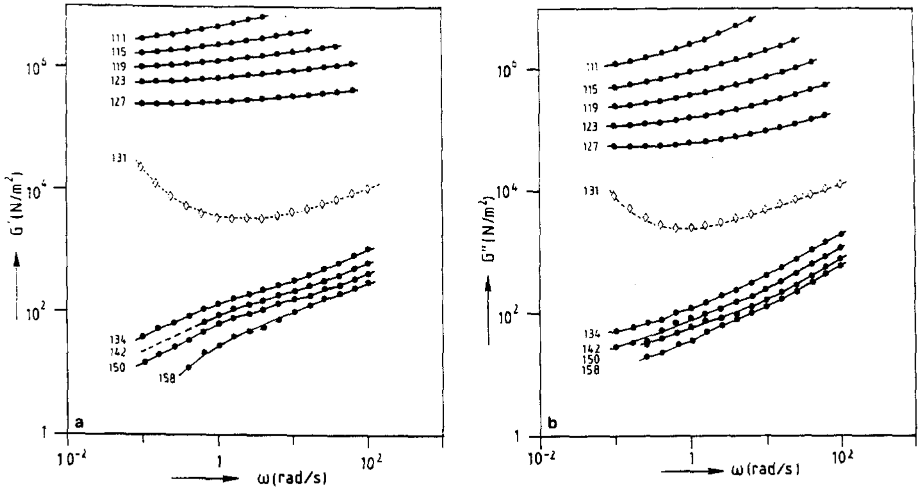


Fig.1 Double logarithmic plots of the dynamic moduli G′ and G″ against angular frequency for the polymer PIa at various temperatures.

al crosslinks, which becomes clear from the rubber-like behaviour, where the values of the storage modulus are relatively independent of frequency. However, the loss moduli are only slightly lower than the storage moduli (tan $\delta \approx 0.2$); this means that the network formed is far from ideal.

The amount of crystallinity was also determined by DSC, it closely agrees with the results found by the mechanical measurements.

A second transition is perceptible, much less clear however, between 146°C and 154°C (in Fig.4 this transition is much more apparent). This is in reasonable agreement with the second transition temperature at 140°C, as measured by DSC (i.e the melting temperature of the crystalline phase). Although the values of the dynamic moduli are rather low at temperatures of 134°C and higher, the polymer does not behave like a Newtonian liquid: the slopes are far from those which are obtained in liquidlike behaviour, where they are 2 and 1 for G′ and G″, respectively. Also from handling the polymer in the hot stage microscope it is obvious that the polymer does not flow easily.

Polymer PIb

For the polymer PIb the storage and loss moduli at various temperatures are shown in Figs 2 a and b. The results at 143°C and higher are rather inaccurate (as a consequence of the inaccuracy of the phase angle); for that reason the curves are smoothed, as indicated by dashed lines at low frequencies. Clear gaps in both moduli are present between 140°C and 143°C and between 128°C and 131°C. These transitions in mechanical behaviour are in agreement with the transition temperatures as determined by DSC: 140°C and 129°C respectively (i.e the transitions from the isotropic into the nematic phase and of the nematic into the smectic phase, respectively). The storage moduli in the temperature range from 128°C to 140°C resemble to some extent a situation of a crosslinked system just after the gel point, where the dynamic moduli are only slightly dependent on frequency.

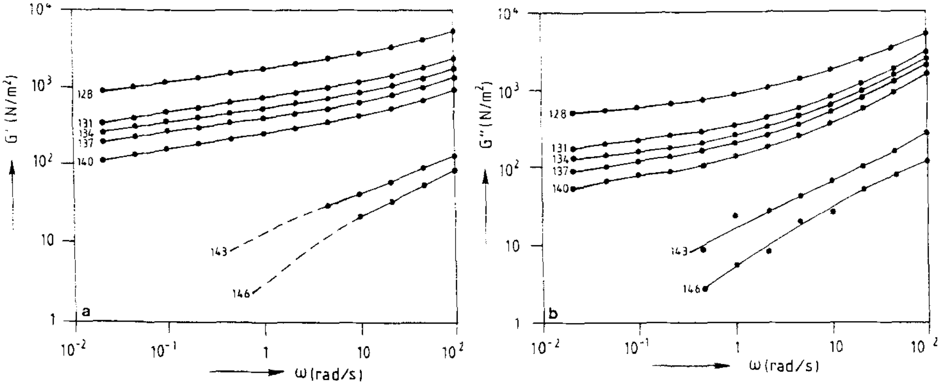


Fig.2 Double logarithmic plots of the dynamic moduli G′ and G″ against angular frequency for the polymer PIb at various temperatures.

Polymer PIc

Results of storage and loss moduli of measurements on polymer PIc are shown in Figs.3a and b. At temperatures of 60°C and higher this polymer shows mechanical behaviour which is comparable with that of normal elastic liquids. The curves of the storage moduli and loss moduli may be shifted according to the WLF equation. However, values of c_1^g and c_2^g are rather unusual: $c_1^g=4.56$ and $c_2^g=35.1$ in stead of the so-called universal values of 17.4 and 51.6, respectively (11). This means that, either both the fraction of free volume at the glass transition temperature and the coefficient of thermal expansion of the free volume, or the constant B in the Doolittle equation are 4 to 5 times as high as usual (11).

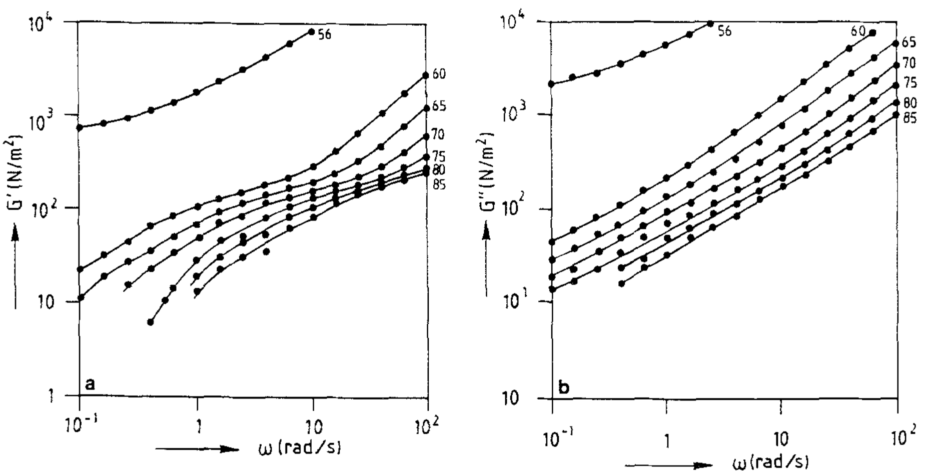


Fig.3 Double logarithmic plots of the dynamic moduli G′ and G″ against angular frequency for the polymer PIc at various temperatures.

As a consequence of the rapid crystallisation, the dynamic moduli could not be measured at temperatures below 56° C. This is in agreement with the crystallisation temperature of 57° C, as determined by DSC measurements.

From the curves of the storage moduli, shown in Fig.3a, it is clear that a relaxation mechanism with a relaxation time around 1 sec is present at 60° C. This relaxation shifts to shorter times (i.e. to higher frequencies) with increasing temperature, according to the normal time temperature superposition. This means that a temporary network structure, probably due to interaction of the rigid biphenyl groups, is present in the liquid state, at least in the temperature range from 60° C to 85° C, but with rather low storage moduli of about 100 N/m². Close inspection of the loss moduli in Fig.3b also points to the presence of a relaxation mechanism, as revealed by the decrease of the slope around the same frequency. The physical crosslinks in this network structure could not be detected by DSC experiments. Again the conclusion is that measurement of the dynamic mechanical behaviour is a strong tool in the determination of the *presence* (only) of such structures. Closer inspection of the storage modulus curves of polymer PIb in Fig.2a also points, although much less clear, to the presence of a temporary network, again probably due to interactions between the rigid biphenyl groups, at temperatures between 134° C and 150° C. These interactions apparently disappear at temperatures above 150° C.

The complex viscosity of the four polymers

In Fig.4 the logarithm of the dynamic viscosity, η^*, of the four polymers, measured at $\omega=1$ rad/s (so that $\eta^* = G^*$), is plotted versus temperature. The amorphous acrylate copolymer behaves quite normally, the crystalline polymer PIc shows normal behav-iour above its melting temperature (the melting temperature is the temperature at which the crystallites consisting of side chains melt). The LC polymers PIa and PIb show a strongly temperature dependent viscosity at their transition temperatures. In contradistinction to the results of Pakula and Zentel (4) the viscosity in the isotropic state is lower than in the nematic state. Apparently side chain LC polymers behave different, in this respect, from main chain LC polymers.

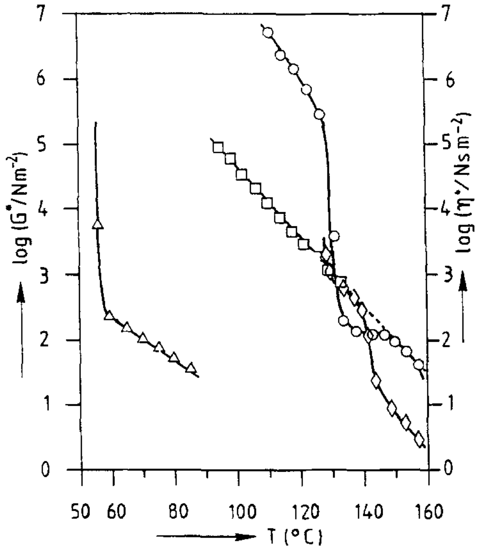


Fig.4 Semi logarithmic plot of the absolute modulus G* and viscosity η^*, measured at $\omega=1$ rad/s, of the four polymers against temperature.

□ amorphous acrylate copolymer;

○ PIa; ◇ PIb; △ PIc

Comparison of the steady shear and the dynamic viscosities of polymer PIb and the acrylate copolymer

In Fig.5 both the dynamic viscosities and steady shear viscosities of the polymer PIb and the acrylate copolymer are plotted against angular frequency, ω, and shear rate, q, respectively, on double logarithmic scales at a temperature of 140°C. The results of the acrylate copolymer (DSM) are obtained by extrapolation of the measurements at 95°C to 133°C with the aid of the time-temperature-reduction. For this polymer both viscosities follow the empirical, so-called Cox-Merz-rule, as η^* and η plotted against ω and q, respectively, follow the same line, as long as the ω and q are not too high. At low shear rates and frequencies the polymer shows Newtonian behaviour.

On the other hand, the flow behaviour of the PIb polymer is completely different:

a) no Newtonian region is perceptible, even not at the rather low shear rates and frequencies of 0.01 s^{-1};

b) both viscosities differ, even at low rates, by a factor of 2.5. However, as appears from Figs.2, the viscosity is strongly dependent on temperature (1.1 decade per 3°C, or about a factor 2.5 per °C), so the difference between the dynamic and steady shear viscosities could be an artefact only, as the temperature control in the mechanical spectrometer is not better than 1°C;

c) in the shear rate range around 0.1 s^{-1} the viscosity decreases faster, but at high shear rates a new region is reached with the same shear rate dependence as that at lower shear rates;

d) the steady state viscosity was measured with increasing shear rate; on subsequent decrease of the shear rate, the viscosity increased in accordance with the high shear rate dependence, thus forming a gap with the original viscosity; apparently the former increase of the shear rate resulted in a degradation of the physical structure of the LC polymer, which was not recovered in the relatively short measuring time.

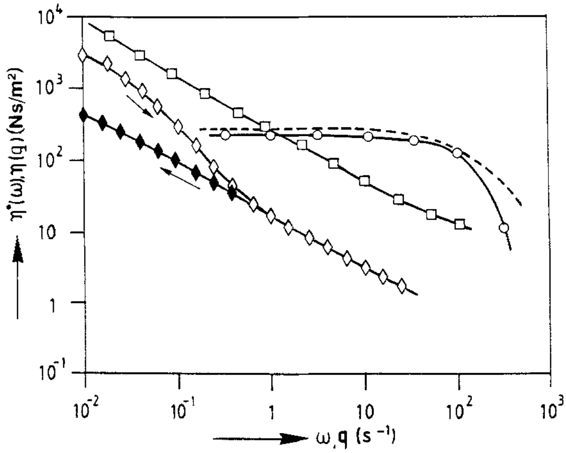


Fig.5 Double logarithmic plot of the abolute viscosity η^* and the steady state viscosity η of the amorphous acrylate copolymer and polymer PIb against angular frequency ω and shear rate q, respectively, at 140°C.

Δ and --- η^* and η, respectively, of the amorphous acrylate copolymer; □ and ◇ η^* and η, respectively, of PIb.

Conclusions

Measurements of the temperature dependence of the viscoelastic properties, especially of the dynamic moduli as a function of frequency, has proven to be a strong tool, also in this study, in the determination of the **presence** of certain structures (or molecular interactions) and phase transitions in LC polymers (determination of the presence only, not of the structures themselves). In fact, dynamic functions can change tremendously by the creation of crosslinks, whether chemical or physical, at least when measured in the appropriate frequency window. Hence, small changes indicate the appearance (or disappearance) of only a small amount of structures or crosslinks. From both phenomena examples are shown in this study: large changes are in agreement with DSC measurements, whereas small changes in general could not be detected by this calorimetric technique.

Our aim was to compare the viscoelastic properties of side chain LC polyacrylates with an amorphous polyacrylate of comparable melt viscosity. Three polyacrylates with mesogenic side groups were synthesized; two of them showed LC behaviour, whereas the third one did not: this polymer shows only a glass transition temperature and a melting temperature. The melting transition of this polymer is characterised by a very small melting enthalpy of less than 2 J/g; above that temperature relatively strong interactions are still present, as revealed by a transition present in the viscoelastic behaviour.

The LC polymers have viscosities that resemble that of the amorphous polyacrylate to some extent, but their shear rate dependencies are much more pronounced. The same holds for their temperature dependencies, as a consequence of the various LC transitions.

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