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Linear viscoelasticity of side chain liquid crystal polymers

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Small amplitude oscillatory shear has been used to study thermotropic liquid-crystalline polymers that have mesogenic groups pendant to flexible backbones. The polymers studied form nematic and smectic glasses, enabling viscoelastic response to be studied over a wide range of frequencies using time-temperature superposition. In contrast to main chain liquid-crystalline polymers, the nematic side chain polymers exhibit linear viscoelastic response over a wide range of strain amplitudes that is independent of thermal and shear histories. Viscoelastic response is very sensitive to smectic-nematic and smectic-isotropic transitions, but insensitive to the nematic-isotropic transition, as time-temperature superposition applies across this transition. We compare viscoelastic data with diffusion data by calculating the time τ that it takes a polymer to diffuse a distance equal to its coil size R ($\tau = R^2/D$). At frequencies lower than $1/\tau$, side chain polymers in their nematic show the terminal response characteristic of viscoelastic liquids. In their smectic, they are still strongly viscoelastic at frequencies lower than $1/\tau$, and approach the terminal response of a viscoelastic solid at the lowest frequencies. Implications of such behaviour are discussed.

1. Introduction

Thermotropic liquid-crystalline polymers comprised of flexible backbones with regularly spaced pendant mesogenic side groups are currently of interest for their potential use as non-linear optical materials [1]. Dynamics in such systems have been studied extensively by nuclear magnetic resonance [2, 3] and dielectric spectroscopy [4, 5]. These techniques are used to monitor the local dynamics of the mesogens. Measurements of viscoelastic properties and self-diffusion can provide information on dynamics of entire polymer chains, but relatively few studies have been made on side chain liquid-crystalline polymers [6–12].

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In this paper we report linear viscoelastic studies on three side chain liquid-crystalline polymers. PAMeAPr forms a nematic glass on cooling and has a nematic–isotropic transition. PMADe forms a smectic A glass on cooling and has a smectic–isotropic transition. PMAM forms a smectic A_2 glass on cooling and has both smectic–nematic and nematic–isotropic transitions. All three polymers become isotropic at quite low temperatures, allowing for thermally stable viscoelastic measurements, and they are soluble in common solvents, enabling molecular characterization.

2. Experimental

The synthesis of the types of liquid-crystalline polymers used in this study has been reported previously [13]. The polymers all have *trans*-azobenzene mesogens attached to acrylate or methacrylate backbones using six-carbon spacers. The structures are shown in figure 1. The smectic interlayer spacings, determined by X-ray diffraction, are 54 Å for PMADe and 63 Å for PMAM.

Molecular characterization was done by T. H. Mourey using size-exclusion chromatography in tetrahydrofuran with refractive index, viscosity, and low angle laser light scattering (LALLS) detectors. This technique provides quantitative determination of weight-average molecular weight, M_w , and intrinsic viscosity, $[\eta]$. We also get an accurate measure of polydispersity, M_z/M_w . Due to low molecular weight tails in

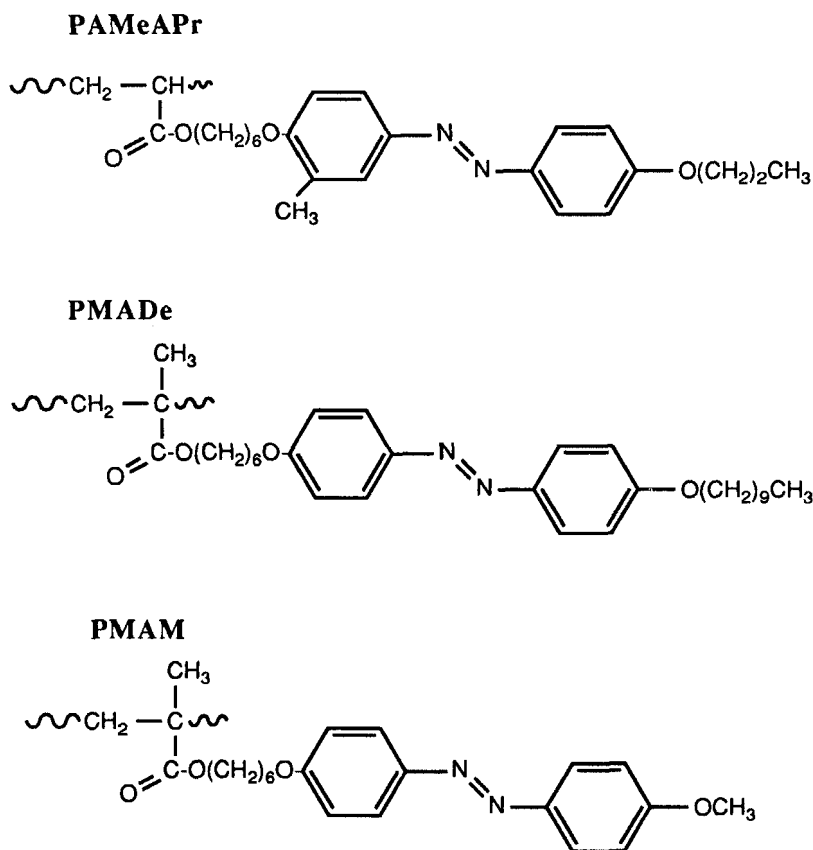


Figure 1. Chemical structures of side chain liquid crystal polymers.

Table 1. Molecular and thermal characterization data.

Polymer	M_w	M_w/M_n	M_z/M_w	$[\eta]/\text{dl g}^{-1}$	$T_g/^\circ\text{C}$	$T_{\text{SI}}/^\circ\text{C}$	$T_{\text{SN}}/^\circ\text{C}$	$T_{\text{NI}}/^\circ\text{C}$
PAMeAPr	34,000	> 1.3	1.4	0.083	22	—	—	82
PMADe	210,000	> 4.5	2.1	0.244	$\sim 110^\dagger$	171	—	—
PMAM	130,000	> 6.0	2.3	0.159	$\sim 70^\dagger$	—	92	132

\dagger Estimated from viscoelastic data (not discernible by DSC).

these samples that extend down to oligomer sizes, we could not get accurate measures of number-average molecular weight, M_n , and thus could not accurately evaluate the standard measure of polydispersity M_w/M_n . We did obtain a lower limit for M_w/M_n from the LALLS detector (which is insensitive to low molecular weight species). All molecular characterization results are listed in table 1. In some cases the distributions are rather broad (PMADe and PMAM). However, we believe the polymers are not branched, as they do not have pronounced high molecular weight tails (as evidenced by fairly small values of M_z/M_w).

Differential scanning calorimetry was done with a Perkin-Elmer DSC-7, using a heating rate of 10 K min^{-1} . Mesophase transition temperatures, taken as the peak apex, are listed in table 1. Phase identification was done by optical microscopy and X-ray scattering. The nematic glass-former (PAMeAPr) showed an obvious glass transition from DSC, the midpoint of which is listed in table 1. The transition was quite broad for a homogenous material (15 K). The smectic glass-formers do not show any obvious glass transitions from DSC. The glass transitions of PMADe and PMAM reported in table 1 were estimated from rheology data.

Two Rheometrics mechanical spectrometers were used for the rheological measurements. The System Four rheometer with a 0–2000 g cm spring transducer and 8 mm diameter parallel plates was used to acquire oscillatory shear data for modulus levels above 10^7 dynes cm^{-2} . The RMS-800 rheometer with a 0–2000 g cm force-rebalanced transducer and 50 mm diameter parallel plates was used to acquire oscillatory shear data for modulus levels below 10^{-3} dynes cm^{-2} . Either rheometer can be used in the intermediate modulus range with 25 mm diameter plates.

Linear viscoelastic response was verified for all data in the nematic and isotropic states, by checking that the measured values of storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, at each frequency, ω , was independent of a strain amplitude variation of at least a factor of two. The range of strain amplitudes corresponding to linear viscoelastic response is in fact quite broad for side chain liquid crystalline polymers in the nematic phase, as it is for ordinary flexible polymers (whereas this is not true for main chain nematic polymers). In the smectic phase, we observe a much narrower range of linear viscoelastic response. As was observed for main chain smectic polymers [14], viscoelastic response is linear up to some critical strain amplitude of (~ 5 per cent), beyond which the response is strongly non-linear, indicating some sort of structure breaking. All data reported here are in the linear viscoelastic range.

All steady-shear data were taken with either 25 or 50 mm diameter parallel plates. The Cox-Merz rule [15], which equates apparent viscosity at a given shear rate to complex viscosity at a given frequency, was found to be obeyed in the nematic and isotropic states. Unfortunately, the comparison was only possible over a narrow range of shear rates because the samples showed edge-fracture effects at shear rates slightly

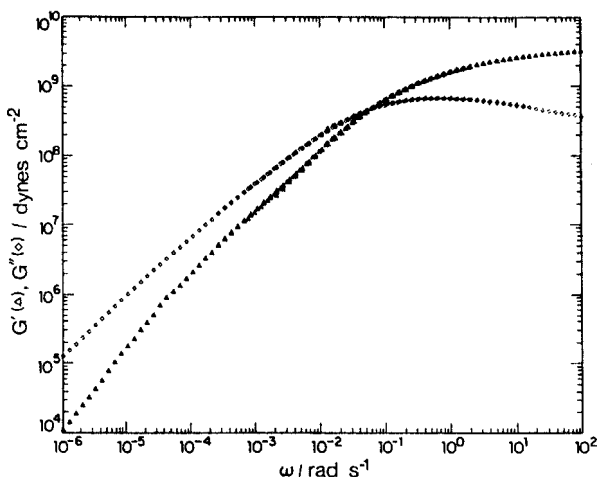


Figure 2. Master curve for PAMeAPr in its nematic phase. $T_{\text{ref}} = 21^\circ\text{C}$.

above the onset of shear thinning, making accurate determinations of apparent viscosity at higher shear rates impossible in our rheometers.

The empirical principle of time–temperature superposition [16] was found to hold over certain temperature ranges, allowing master curves to be made by shifting oscillatory data on the frequency scale. The viscoelastic response of all three polymers obeyed time–temperature superposition from roughly the glass transition up to the lowest mesophase transition. At lower temperatures, superposition failed, as is commonly observed for ordinary flexible polymers in the glass transition zone [17].

3. Results

Data at 21, 24, 27, 30, 35 and 50°C were superimposed to generate the master curve for PAMeAPr shown in figure 2 (referenced to 21°C). This fully characterizes the viscoelastic response of a nematic glass-forming side chain liquid-crystalline polymer above its glass transition. At high frequencies, the data approach a glassy modulus typical for flexible polymers. At intermediate frequencies the data obey a power law with $G^*(\omega) \sim (i\omega)^{0.75}$. At low frequencies the response appears to be approaching the characteristic response of all viscoelastic liquids [16] ($G'(\omega)$ and $G''(\omega)$ approaching their terminal powers in frequency of two and one, respectively). Lower frequencies could not be studied due to crystallization of PAMeAPr ($T_m \cong 80^\circ\text{C}$) when kept for extended periods of time at $50\text{--}80^\circ\text{C}$.

The temperature dependence of the shift factors for PAMeAPr did not obey the WLF equation [16], for unknown reasons. Possibly the temperature dependence of viscoelastic response is coupled to the (unknown) temperature dependence of the order parameter [2, 3, 18]. In any case, the data at the four lowest temperatures ($21\text{--}29^\circ\text{C}$) obeyed an Arrhenius law with an activation energy for flow [16] of 502 J mol^{-1} .

Figure 3 is a master curve for PMADe referenced to 115°C generated by superimposing data at 115, 125, 130, 150 and 160°C . These data also did not obey the WLF equation [16]. From the shift factors required for superposition, we calculate an activation energy for flow of 272 J mol^{-1} for PMADe that applies for the entire smectic phase ($115\text{--}160^\circ\text{C}$). We compare this with the isotropic state, where PMADe has a flow activation energy of 46 kJ mol^{-1} (between 180 and 200°C). The viscosity of PMADe at

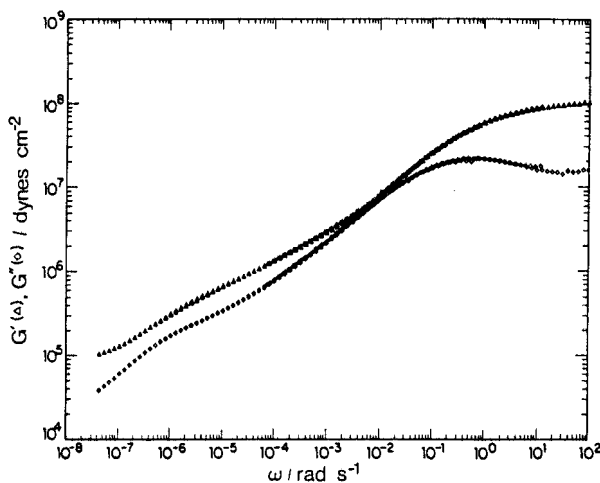


Figure 3. Master curve for PMADe in its smectic phase. $T_{\text{ref}} = 115^\circ\text{C}$.

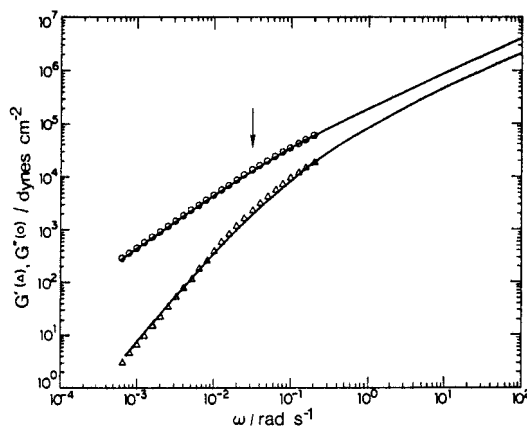


Figure 4. Master curve for PMAM in its nematic phase (solid curves) and its isotropic phase (open symbols). $T_{\text{ref}} = 103^\circ\text{C}$. The arrow indicates $1/\tau$.

180°C (isotropic) is 31.0 P, indicating an abrupt discontinuous change in viscoelastic response at the smectic–isotropic transition, consistent with dielectric data [5].

Figure 3 characterizes the smectic glass-forming side chain liquid-crystalline polymer over as wide a range of frequency as we can cover with our instrumentation. PMADe approaches a glassy modulus at high frequency that is considerably lower than the glassy modulus of flexible polymers. At lower frequencies, smectic side chain polymers exhibit a broad distribution of relaxation times. While never a true power law, the derivative $d(\log G')/d(\log \omega)$ is considerably lower for the smectic polymer than the nematic polymer (see figure 2). The smectic polymer is still highly viscoelastic ($G' \cong G''$) at the lowest frequencies we can probe with our instrumentation, which means the longest relaxation time of PMADe is $> 10^7$ s at 115°C .

PMAM has both smectic and nematic liquid crystal phases. A master curve in the nematic phase, referenced to 103°C is shown as the solid curves in figure 4, generated from data at 103, 113 and 122°C . At low frequencies, the data exhibit the terminal

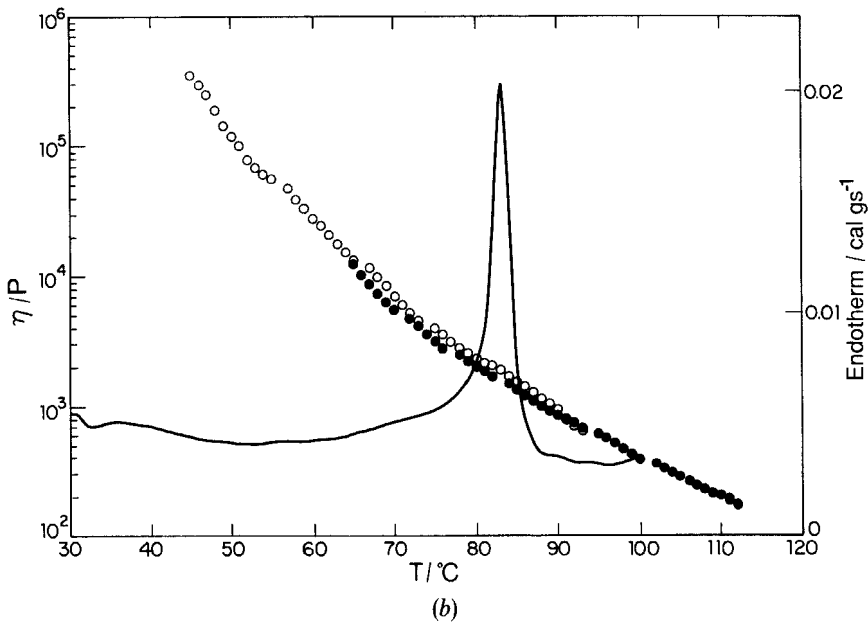
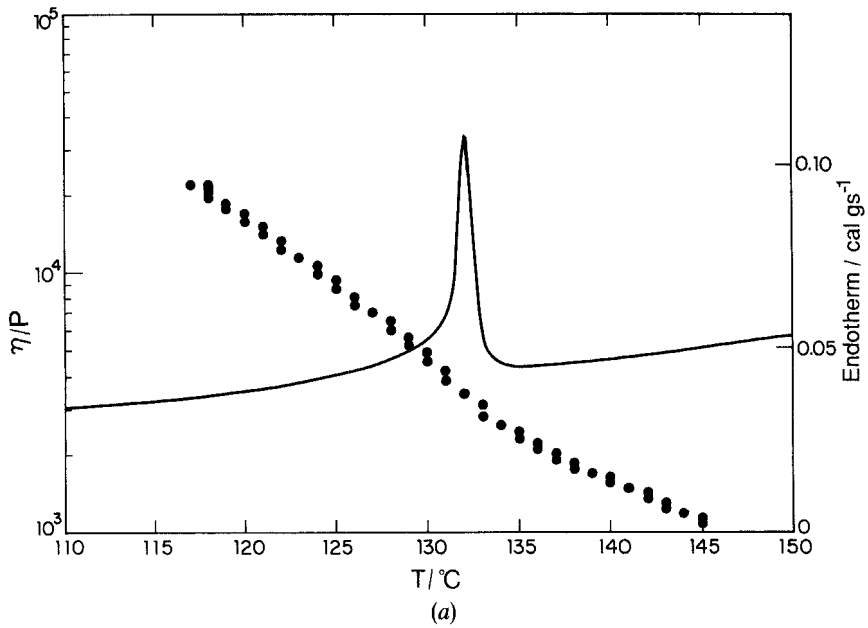


Figure 5. Temperature dependence of apparent viscosity at 1 s^{-1} for (a) PMAM and (b) PAMeAPr. Open circles are 25 mm data, filled circles are 50 mm data. Solid curves are DSC traces for comparison, showing the nematic–isotropic transition.

Table 2. Activation energies for flow near the nematic–isotropic transition.

Polymer	Temperature range	Mesophase	$E_A/\text{kJ mol}^{-1}$
PMAM	117–130°C	Nematic	159
PMAM	135–145°C	Isotropic	105
PAMeAPr	45–73°C	Nematic	138
PAMeAPr	82–112°C	Isotropic	88

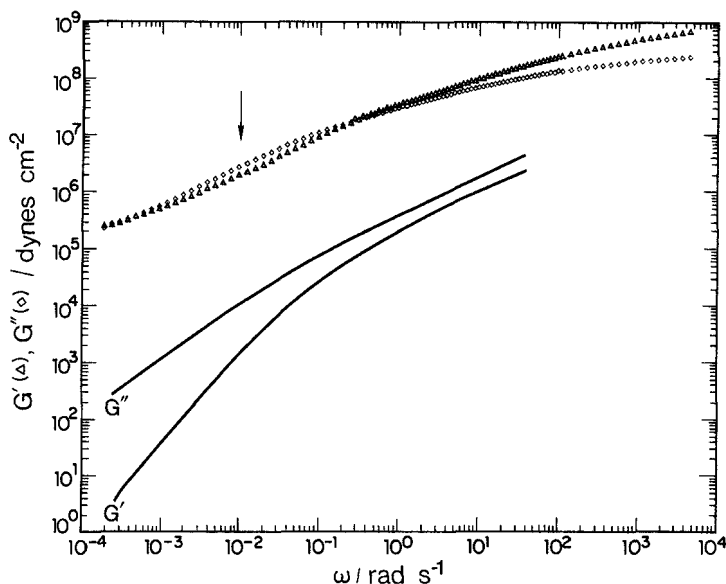


Figure 6. Master curve for PMAM in its smectic phase (open symbols) and nematic phase (solid curves). $T_{\text{ref}} = 84^\circ\text{C}$. The arrow indicates $1/\tau$.

response characteristic of all viscoelastic liquids. For the highest decade in frequency that we can access, the data obey a power law in frequency, $G^*(\omega) \sim (i\omega)^{0.67}$.

Data at 141°C (in the isotropic phase) are shown as the open symbols in figure 4, superimposed on the nematic data. Clearly, time–temperature superposition works across the nematic–isotropic transition for PMAM. In figure 5(a) we plot the temperature dependence of apparent viscosity for PMAM in steady-shear at 1 s^{-1} (for all temperatures shown, this is very nearly the zero shear rate viscosity). The DSC trace for PMAM is also plotted in figure 5(a) for comparison. The apparent viscosity is continuous across the nematic–isotropic transition, with the only effect of the transition being a slight change in slope. The corresponding plot for PAMeAPr is shown in figure 5(b), with qualitatively identical behaviour. The activation energies for flow [16] in the vicinity of the nematic–isotropic transition of these two polymers are summarized in table 2. The activation energy is consistently larger in the nematic phase than in the isotropic phase, as observed for other side chain liquid-crystalline polymers [8]. The continuous nature of the viscosity at the transition is consistent with previous viscosity results [8], and also with dielectric data on side chain liquid-crystalline polymers [5], which clearly show a simple increase in activation energy on cooling into

the nematic phase. This is also consistent with the self-diffusion coefficient of PMAM [12], which is not only continuous through the nematic–isotropic transition, but also insensitive to the smectic–nematic transition! A single activation energy of 92 kJ mol^{-1} describes the temperature dependence of the diffusion coefficient for PMAM between 80 and 160°C [12].

This observation for diffusion is in sharp contrast to the viscoelastic data on PMAM in the smectic mesophase. These data are shown as the open symbols in figure 6, where the data from 84 and 74°C have been superimposed to make a master curve for the smectic mesophase, referenced to 84°C . Judging from the shift required for superposition, the activation energy for PMAM in the smectic mesophase is 389 kJ mol^{-1} . At high frequencies, the data are approaching the glassy modulus of smectic PMAM, which is comparable to ordinary flexible polymers [16]. The data at low frequencies indicate that the longest viscoelastic relaxation time of PMAM in the smectic mesophase at 84°C is $> 10^4 \text{ s}$.

The solid curves in figure 6 are the data for the nematic phase, extrapolated to the smectic phase reference temperature of 84°C using the activation energy of PMAM in the nematic. Thus, figure 6 clearly demonstrates that the viscoelastic response changes dramatically in both magnitude and qualitative character at the smectic–nematic transition.

4. Discussion

4.1. Dynamics in the isotropic and nematic mesophases

The isotropic phase of liquid crystal polymers is generally believed to be essentially the same as an ordinary flexible polymer melt. The fact that the same viscoelastic response is seen in the nematic and isotropic phases for side chain liquid crystal polymers, shown in figure 4, is rather striking. However, since the nematic–isotropic transition is far above the glass transition for PMAM and its molecular weight is not too high (see table 1), the only accessible response is in the terminal region. Thus, we do not know whether the rest of the relaxation time distribution is the same on both sides of the nematic–isotropic transition.

The fact that the only observable rheological change at the nematic–isotropic transition is a change in activation energy (see figure 5 and table 2) is consistent with a modified reptation view of relaxation in the nematic phase. A modified reptation model has already been suggested for dynamics in the smectic mesophase of side chain liquid crystal polymers [19]. In the reptation model [20] the activation energy corresponds to an energy barrier for monomer motion. In the nematic phase the mesogens have no spatial registry, only a preferred direction of alignment. Thus, it seems quite reasonable that the chains have to reptate to relax stress in both the isotropic and nematic phases, with the different constraints on the mesogen imparting different activation energies in the two.

However, there is no evidence of any rubbery plateau, characteristic of entanglement effects [16], in either of the nematic phases studied (see figures 2 and 4). There is instead a broad distribution of relaxation times between the glassy response at high frequencies and the terminal flow (see figure 2). At present we do not know how much of an effect the molecular weight distribution has on the response in this region.

Small angle neutron scattering studies on nematic side chain liquid crystal polymers [21–27] indicate that only subtle changes occur in the radius of gyration when changing from the isotropic phase to the nematic phase, provided that we are far above any smectic transitions [25, 27] and the flexible spacer separating the backbone

from the mesogen is long enough. Six-carbon spacers, used here, are apparently long enough, whereas four-carbon spacers lead to more significant coupling between the backbone and the mesogens [23]. The projections of the end-to-end vector of the coil parallel and perpendicular to an aligning field are essentially equal in the nematic, and unchanged from the isotropic end-to-end distance ($R_{\parallel} \cong R_{\perp} \cong R$).

The neutron scattering results allow us to calculate Flory's characteristic ratio [28],

$$C_{\infty} \equiv R^2/(nl^2), \quad (1)$$

where R is the end-to-end distance of the coil, n is the number of main chain bonds and l is the main chain bond length. Using the recent data on side chain liquid crystal polyacrylates [26] and polymethacrylates [25] in their nematic phases, we calculate $C_{\infty} = 6.0$. This value is typical of ordinary flexible polymers [28], and thus the presence of mesogenic side groups and their alignment in a nematic field does not strongly affect chain dimensions.

Temperature dependence of self-diffusion coefficient of PMAM with $M_w = 74000$ in the range 80–160°C has been reported previously [12]. The self-diffusion coefficient at 103°C (the reference temperature of figure 4) is $D \cong 1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. Assuming reptation, we calculate a self-diffusion coefficient for our molecular weight of PMAM ($M_w = 130000$) as $D \cong (74/130)^2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \cong 3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. In order to compare this result with our viscoelastic measurements, we calculate a diffusion time

$$\tau = R^2/D \quad (2)$$

which is the average time a chain takes to diffuse a distance of order of its coil size. Assuming $C_{\infty} = 6.0$, we calculate the end-to-end distance of the PMAM random coil $R \cong 100 \text{ \AA}$. Using equation (2), we calculate the diffusion time $\tau \cong 30 \text{ s}$ for PMAM at 103°C. The frequency $1/\tau$ is indicated by the arrow in figure 4. At frequencies lower than $1/\tau$, PMAM exhibits the terminal response characteristic of all viscoelastic liquids [16], with $G'(\omega)$ approaching ω^2 scaling and $G''(\omega)$ approaching ω^1 scaling. This means that τ is also the longest viscoelastic relaxation time in the system. Ordinary flexible linear polymers also have the diffusion time equal to the longest viscoelastic time, and thus this is further evidence that chain dynamics in the nematic phase of side chain polymers is very similar to ordinary flexible polymers. At present, it is not clear whether the broad distributions of relaxation times of PMAM at frequencies higher than $1/\tau$ (and the similar effect in PAMeAPr) is due to hindered relaxation due to the nematic ordering field, or simply an effect of the broad molecular weight distribution.

We conclude that both statics and dynamics of side chain liquid crystal polymers in their nematic phase are similar to ordinary flexible linear polymers. Main chain nematic polymers, on the other hand, exhibit markedly different static and dynamic properties. The configuration of main chain liquid crystal polymers is greatly distorted in the nematic phase (with $R_{\parallel} \gg R_{\perp}$) [29]. Viscoelastic response is also much different for main chain polymers [30–47]: Oscillatory data on main chain polymers generally depends on shear and thermal history of the sample. Time–temperature superposition does not work across the nematic–isotropic transition for main chain polymers [37, 44]. Furthermore, a liquid-like response at low frequency has never been observed in the nematic phase of main chain polymers.

4.2. Dynamics in the smectic mesophase

The viscoelastic character of the smectic mesophase of side chain liquid crystal polymers is qualitatively different than the nematic (see figures 3 and 6). The relaxation

time distribution is greatly broadened when in the smectic phase. Since PMAM has both smectic and nematic phases, we can compare viscoelastic response in the two phases for the same polymer (see figure 6), thereby not influencing the comparison with molecular weight distribution effects. While the nematic phase shows a long viscoelastic relaxation time, this was not measurable for either of the smectic phases studied.

Small angle neutron scattering studies on smectic side chain polymethacrylates [25, 27] and polyacrylates [27, 48] indicate that the coil size parallel to an aligning magnetic field, R_{\parallel} , is considerably smaller (by roughly a factor of 2–3) in the smectic phase than in the isotropic phase. The coil size perpendicular to the field, R_{\perp} , is essentially the same as [27, 48], or slightly larger than [27] in the isotropic phase. Similar conclusions are drawn from scattering data on smectic side chain polysiloxanes [49]. Assuming a modified reptation model for diffusion in the smectic phase [19], we expect equation (2) to hold for both the parallel and perpendicular directions (using D_{\parallel} and D_{\perp}) with the same diffusion time τ .

The self-diffusion coefficient [11] for PMAM with $M_w = 74\,000$ at 84°C is $D \cong 3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. Correcting for molecular weight ($M_w = 133\,000$) assuming reptation (as above) we calculate $D \cong 1 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. Since diffusion was measured in a nominally unaligned state, the measured diffusion coefficient should be some average of D_{\parallel} and D_{\perp} . However, for the purposes of this discussion, we will only estimate an upper bound for the diffusion time, using equation (2) with the isotropic coil size of 100 \AA (previously estimated above), keeping in mind that the actual diffusion time could be as much as a factor of ten smaller. This results in a time for PMAM to diffuse a distance of order of its coil size in its smectic phase (at 84°C), $\tau \cong 100 \text{ s}$.

The frequency $1/\tau$ is shown as the arrow in figure 6. Clearly, PMAM in its smectic mesophase is viscoelastic on time scales 100 times longer than τ (at least). Therefore, the viscoelastic response at frequencies lower than $1/\tau$ must be due to structural rearrangements in the smectic phase (corresponding to length scales much larger than the coil size). The smectic phase is akin to a two dimensional crystal, and rearrangement of the structure apparently takes a long time. In this sense the smectic phase is analogous to the lamellar phase of diblock copolymers, where viscoelastic response extends to much longer time scales than the diffusion time [50].

The fact that $G'(\omega)$ appears to be levelling off at low frequencies in figures 3 and 6 indicates that side chain smectic polymers may be viscoelastic solids. This is consistent with results on viscoelasticity of monomeric smectic A liquid crystals [51], which are definitely viscoelastic solids (with $G'(\omega) \gg G''(\omega)$ and independent of frequency) at low strain amplitudes.

Yanovskii and Konstantinov [7] reported viscoelastic response of a smectic B side chain liquid crystal. This polymer showed a broad frequency range of viscoelastic behaviour, with $G' > G''$, similar to the low frequency part of figure 3. They also find viscoelastic response to be very sensitive to the smectic–isotropic transition.

Yamaguchi and Asada [10] also studied viscoelasticity of smectic side chain liquid crystal polymers. Consistent with our findings, they saw no evidence of the rubbery plateau in the smectic mesophase, indicating that entanglements may not be important. Their data also imply a larger activation energy in the smectic phase compared to the isotropic. Dielectric data [5] also indicate a larger activation energy in the smectic phase compared to the isotropic.

Zentel and Wu [8] also report activation energies (from apparent viscosity at a fixed shear rate) in the smectic phase, and also conclude that the activation energy is

larger than in the isotropic phase. For one polymer they report activation energies for both the nematic and smectic A phases. They found the two activation energies to be nearly equal, which sharply contrasts with our results on PMAM. Perhaps the discrepancy is due to the strongly non-linear response of smectic polymers to the steady shear used in [8].

We conclude that the presence of a smectic ordering field has a large effect on the viscoelastic response of side chain liquid crystal polymers. The spectrum of relaxation times is extremely broad, extending well beyond the diffusion time of a chain. The broad relaxation spectrum and the fact that the smectic glasses show no glass transition in DSC seem to indicate a rather gradual and prolonged viscoelastic transition from the glassy state. Perhaps this is related to the temperature dependence of the order parameter, which is expected to increase as temperature decreases. When the order parameter becomes large enough, molecular motion freezes out, resulting in a glass-like modulus.

The few viscoelastic studies on main chain smectic polymers [14, 52, 53] indicate similar effects. Time-temperature superposition apparently works above T_g [14], viscoelastic response is very sensitive to the smectic-nematic transition [52], and the main chain smectics have very broad relaxation time distributions. The only different result for the main chain smectic polymers is that there is a hint of a rubbery plateau [14], possibly indicating that entanglement effects are important.

5. Conclusions

The viscoelastic response of side chain liquid crystal polymers in their nematic phase is qualitatively similar to ordinary flexible linear polymers. On time scales longer than the time it takes the polymers to diffuse a distance equal to their coil size, the nematic polymers flow, like all viscoelastic liquids. The only apparent difference between the nematic and isotropic states is a difference in flow activation energy, which we believe simply reflects the difference in constraints on the mesogen in the two states.

Smectic side chain polymers, on the other hand, show pronounced viscoelastic effects on time scales much longer than the diffusion time. Presumably, this is due to rearrangement of structure (smectic layers) on length scales much larger than the chain size. At the lowest frequencies we could access, the smectic polymers are still viscoelastic. While we cannot be sure from these data whether the smectic phase corresponds to a viscoelastic liquid or a viscoelastic solid, we believe smectics are viscoelastic solids, based on results for monomeric smectic liquid crystals.

We do not see any obvious entanglement effects in any of the phases of the side chain liquid crystal polymers we studied. This is somewhat surprising considering the reasonably high molecular weights. The weight average degrees of polymerization are between 80 and 400, and assuming $C_\infty = 6$, this corresponds to 30–130 Kuhn segments per chain. Flexible polymers typically have 20–40 Kuhn segments in an entanglement strand. Thus, some of the polymers (PMADe and PMAM) might be expected to form entanglements. However, the presence of the pendant mesogens may greatly widen the confining tube, making many more Kuhn segments necessary for entanglement. So, we may have to study higher molecular weight polymers to see entanglement effects.

Future viscoelastic experiments on side chain liquid crystal polymers should focus on varying the molecular weight for a given polymer species, particularly going to higher molecular weights to look for entanglement effects. It would also be useful to prepare samples with narrow molecular weight distributions, as we are not sure whether the broad distributions of relaxation times observed in the nematic phase are

characteristics of that phase, or simply due to polydisperse samples. The nematic–isotropic transition of our two nematic polymers is ~ 60 K above T_g . It would be useful to study a polymer with a smaller temperature difference between T_{NI} and T_g to see whether time–temperature superposition works across the nematic–isotropic transition for parts of the viscoelastic spectrum other than the terminal response.

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