Structure and rheology of twin liquid crystalline polymers

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Addition of short mesogenic segments at the ends of flexible chains alters the mechanical properties by orders of magnitude. Twin liquid crystalline polymers (TLCPs) were synthesized from 4-[(4′-alkoxybenzoyl)oxy]-benzoyl chloride and α,ω-dihydroxy-telechelic polytetrahydrofuran (PTHF) of different molecular weights. With increasing temperature, four equilibrium states of these TLCPs, i.e. crystalline state, phase separated state with mesogenic domains in isotropic PTHF matrix, phase separated amorphous state, and single phase isotropic state, have been observed by dynamic mechanical measurements, differential scanning calorimetry and polarizing microscopy. In the phase separated state, mesogenic domains function as physical crosslinks which give rise to unusually high viscoelastic properties at small strains. Disturbing this state by large amplitude shear resulted in very pronounced shear thinning and slow recovery of structure. At increased temperature, the mesogenic domains become isotropic and their effect as physical crosslinks was significantly reduced, as shown by lower viscoelasticity and weak shear thinning. In the single phase isotropic state above the coexistence temperature T_s, the TLCPs behaved like a common homopolymer of low molecular weight. T_s decreased as the weight ratio of PTHF spacer increased in the experimental range (50–82% PTHF).

(Keywords: thermoplastic elastomer; liquid crystalline polymer; microphase separation; rheology)

INTRODUCTION

The rheological behaviour of phase-separated block copolymers has been studied extensively[1–15]. Compared with homopolymers of similar molecular weight, phase-separated block copolymers often exhibit very high viscoelastic properties and significant shear thinning effect at shear stress or strain[6]. In an earlier paper[13], we reported the specific rheological behaviour of a twin liquid crystalline polymer (TLCP) and attributed it to microphase-separation-induced network structure. The TLCP consisted of a flexible poly(THF) spacer with mesogenic segments on both ends. In the present work, TLCPs were synthesized using poly(THF) of various molecular weights. The phase behaviour and the effects of temperature and shearing, as well as weight ratio of poly(THF) spacer, on the structure and rheology of these TLCPs have been investigated in detail, using dynamic mechanical measurements, differential scanning calorimetry and polarizing microscopy.

EXPERIMENTS

Materials

Four TLCPs were synthesized from 4-[(4′-alkoxybenzoyl)oxy]benzoyl chloride and α,ω-dihydroxy-telechelic polytetrahydrofuran (PTHF) of different molecular weights (650, 1000, 2000, and 2900). The structure shown in *Scheme 1* was determined by nuclear magnetic resonance (n.m.r.)[16]. The weight ratios of PTHF to mesogenic ends were calculated from the molecular weights of the two components.

Apparatus

A Leitz Polarizing Microscope with a Mettler FP-2 hot stage was used for optical studies of phase behaviour and mesophase textures. Differential scanning calorimetry (d.s.c.) was carried out on a Perkin–Elmer DSC-4 instrument under nitrogen atmosphere. The heating rate was 10 K min^{-1}. Dynamic shear flow measurements were made on a Rheometrics Dynamic Spectrometer (RDS), using cone/plate geometry. Samples were moulded in the rheometer at 75°C.

RESULTS AND DISCUSSION

Polarizing microscopy

All four TLCPs were partial crystalline below 25°C. Above this transition temperature, the crystalline structure melted and dispersed liquid crystalline domains formed. It was noted that these liquid crystalline domains were readily deformed when the upper glass slide was touched. The density of the liquid crystalline domains decreased as the weight ratio of PTHF spacer decreased (*Figure 1*). In particular, the TLCP of 82PTHF/18 had much lower domain density than the others. The liquid crystalline domains disappeared above 65°C for all four TLCPs.

Differential scanning calorimetry

The TLCPs displayed two endothermic peaks on heating scan (*Figure 2*). The first peak at about 25°C corresponds to the melting transition of PTHF spacer into amorphous phase and that of mesogenic ends into liquid crystalline phase. The values of Δ*H* for this transition did not show a regular relation with the weight ratio of PTHF spacer; the various molecular weights of

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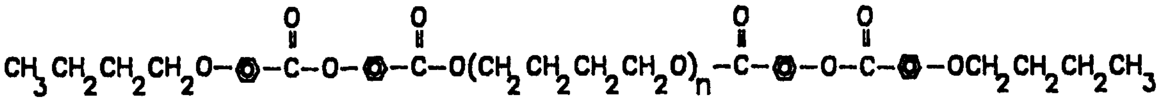

$$CH_3CH_2CH_2CH_2O-\bigodot-\overset{O}{\overset{\|}{C}}-O-\bigodot-\overset{O}{\overset{\|}{C}}-O(CH_2CH_2CH_2CH_2O)_n-\overset{O}{\overset{\|}{C}}-\bigodot-O-\overset{O}{\overset{\|}{C}}-\bigodot-OCH_2CH_2CH_2CH_3$$

No.	n	Mw(PTHF)	Weight Ratio
1	9	650	50PTHF/50
2	14	1000	61PTHF/39
3	28	2000	76PTHF/24
4	40	2900	82PTHF/18

Scheme 1

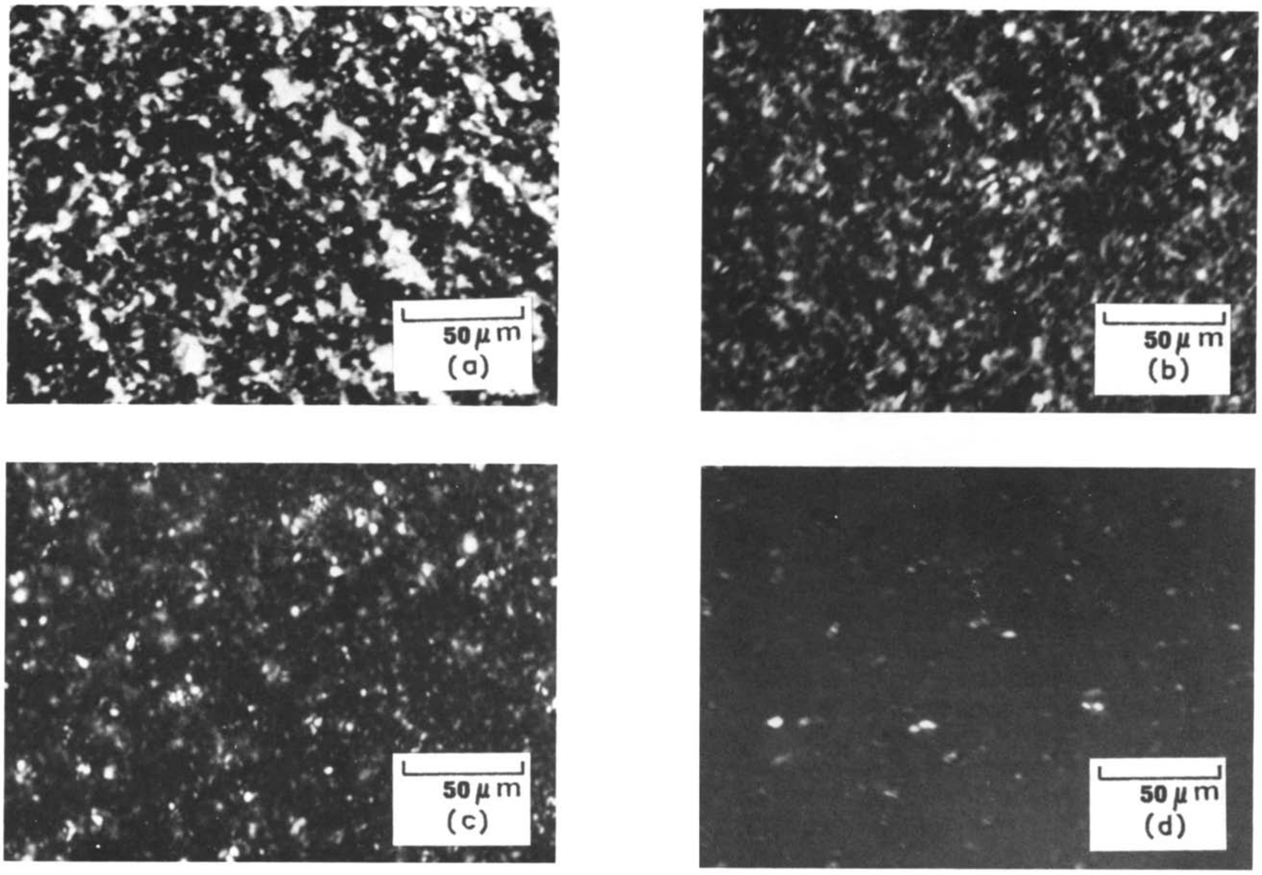

Figure 1 Polarizing microscopy photographs taken at 45°C: (a) 50PTHF/50; (b) 61PTHF/31; (c) 76PTHF/24; (d) 82PTHF/18

the PTHF spacer might affect the crystallinity of the copolymer in different ways.

The second peak at about 55°C originates, as suggested by the polarizing microscopy, at the transition from the mesophase into the isotropic state. ΔH for this transition was 1.25, 0.92 and 0.54 J g^{-1} of copolymer for 50PTHF/50, 61PTHF/39 and 76PTHF/24, respectively. The second endothermic peak of 82PTHF/18 was too small to be determined. Since the PTHF spacer does not seem to make any contribution to this transition, the ΔH value should be based on the weight ratio of mesogen. The recalculated ΔH values of the first three TLCPs, 2.49, 2.34 and 2.25 J g^{-1} of mesogen, are very close together.

According to equilibrium thermodynamics, the energy change between different phase states is independent of path. The phase separation energy of the mesophase state can be regarded as consisting of two parts: first, the energy of the mesophase-isotropic transition within the liquid crystalline domains; and, second, the transition

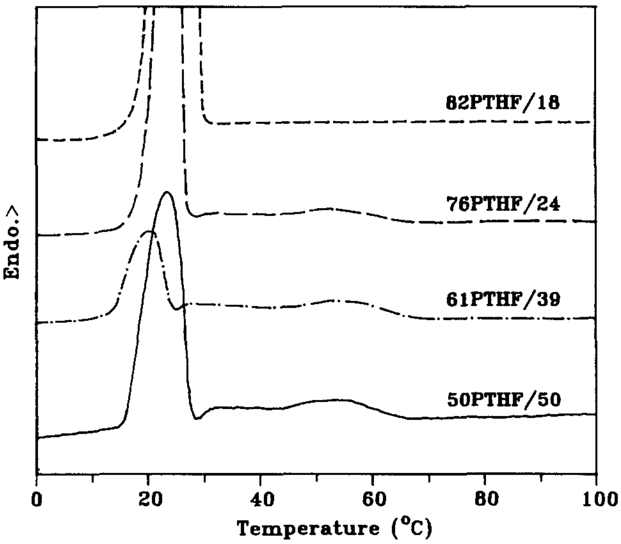

Figure 2 D.s.c. thermograms; heating rate = 10 K min^{-1}

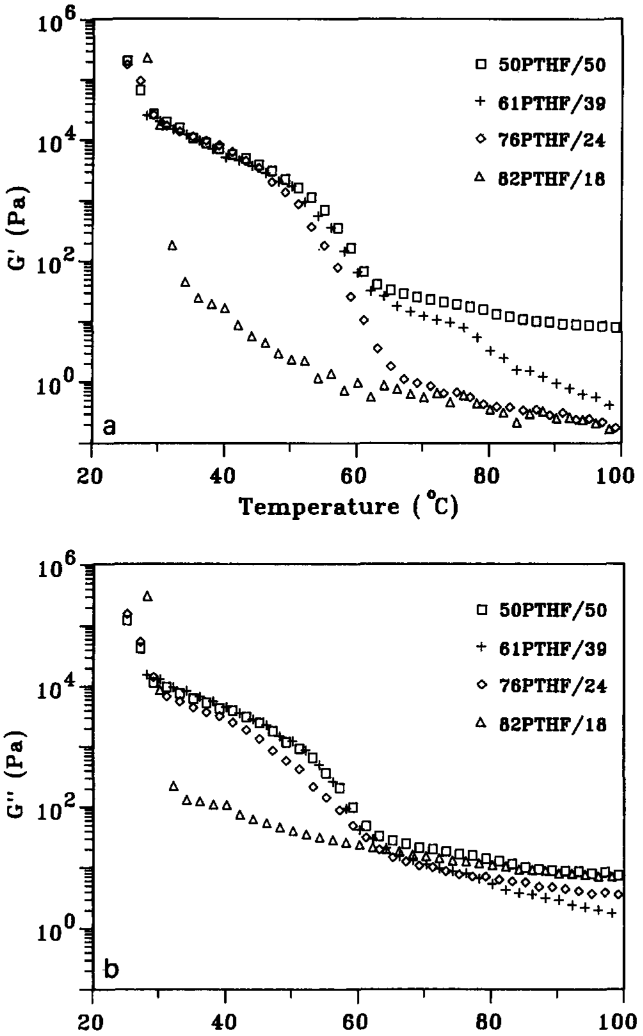

Figure 3 Temperature sweep on RDS; heating rate $= 2\,K\,min^{-1}$; frequency $= 10\,rad\,s^{-1}$; strain amplitude was limited in the linear viscoelastic region

energy for changing from two isotropic phases to a single isotropic phase. The second part is very small and cannot be detected with d.s.c. Therefore, the phase separation energy is essentially equal to the energy for the molecular disordering of the mesophase. It is much larger than the phase separation energy of two isotropic phases.

Dynamic shear measurements

The temperature sweep gave the phase transition temperatures, the strain sweep showed the limit of the linear viscoelastic region and large amplitude shear induced structural changes at some defined temperatures.

In temperature sweep, both storage modulus, G', and loss modulus, G'', were measured at a frequency of $10\,rad\,s^{-1}$ and a heating rate of $2\,K\,min^{-1}$. To avoid any possible flow-induced structural changes, the shear strain amplitude was limited in the linear viscoelasticity region in the whole experimental temperature range. The phase transitions were associated with the significant changes of the dynamic moduli. As shown in *Figure 3*, the transition of crystal melting at about 25°C and the mesophase/isotropic transition at about 55°C resulted in a drastic decrease of the dynamic moduli. The TLCP of 82PTHF/18 showed only a single transition at about 25°C, agreeing well with the d.s.c. thermogram (compare with *Figure 2*). Above 65°C, the mesogen domains, as observed by polarizing microscopy, change to the isotropic state. Microphase separation might still persist in the isotropic state, depending on the weight ratio of PTHF spacer and the temperature. Note that in the temperature range 65–100°C, the storage modulus G' of 50PTHF/50 was relatively high, and that of 76PTHF/24 was two orders of magnitude lower. The TLCP of 61PTHF/39, however, showed a transition between these two phase states at about 80°C.

Strain sweeps were performed isothermally at 45, 70 and 85°C, with a frequency of $10\,rad\,s^{-1}$. *Figure 4* displays the complex viscosity η^*, as a function of strain amplitude. 50PTHF/50 shear thinned in the entire temperature range as long as the strain amplitude increased beyond the linear viscoelastic region (*Figure 4a*). 61PTHF/39 shear thinned at 45 and 70°C, but did not show a significant decrease in η^* at 85°C (*Figure 4b*). 76PTHF/24 shear thinned at 45°C, but not at higher temperatures (*Figure 4c*). For 82PTHF/18, η^* was constant at all experimental shear strains, even at 45°C (*Figure 4d*).

In our earlier paper[13], we defined an average shear rate for oscillatory dynamic shear as $\bar{\dot{\gamma}}_d = 2\gamma_0\omega/\pi$ (γ_0 and ω are strain amplitude and frequency, respectively), and found that the dynamic shear viscosity $\eta^*(\bar{\dot{\gamma}}_d)$ agreed well with the steady shear viscosity $\eta(\dot{\gamma})$. Increasing the shear strain amplitude at a constant frequency has the same effect for the TLCPs as increasing shear rate in steady shear. This shear thinning phenomenon is believed to be due to the fact that large amplitude shear disturbs the microphase separation of TLCPs.

Figure 5 illustrates the structure of the TLCPs for temperature regions and shear stress levels:

(1) Above the crystal melting temperature (T_m), as shown by polarizing microscopy, TLCPs have a two phase domain structure, with dispersed liquid crystalline domains in a continuous matrix of flexible PTHF chains. The probability of TLCP molecules forming connecting chains (tie molecules) between separated domains is much higher than the probability of forming loops (re-entry molecules) with both ends belonging to the same domain. Therefore, the dispersed liquid crystalline domains act as physical crosslinks, tying the flexible PTHF chains into a temporary three-dimensional network. As a result, the whole material displays high elasticity and complex modulus to small amplitude deformations (see *Figure 3*).

Large strain has a drastic effect on the mechanical properties. This might be explained by the following mechanism. As the oscillatory shear strain amplitude increases, the tie molecules suffer from increased shear stress and their mesogenic ends will be pulled out of their respective domains and associate into new phase separated liquid crystalline domains, whereas the increased shear strain amplitude or stress has little effect on the re-entry molecules. Therefore, as the TLCPs were sheared at increased strain amplitude, the ratio of tie to re-entry molecules decreases and the network structure degenerates. This results in a decrease of several orders of magnitude in the complex viscosity (*Figure 4*). It should be noted that, as we reported in a previous paper[13], the recovery of network structure of TLCPs takes of the order of several days after the cessation of severe shear thinning (if the samples are not temporarily heated to above the isotropic transition temperature and then

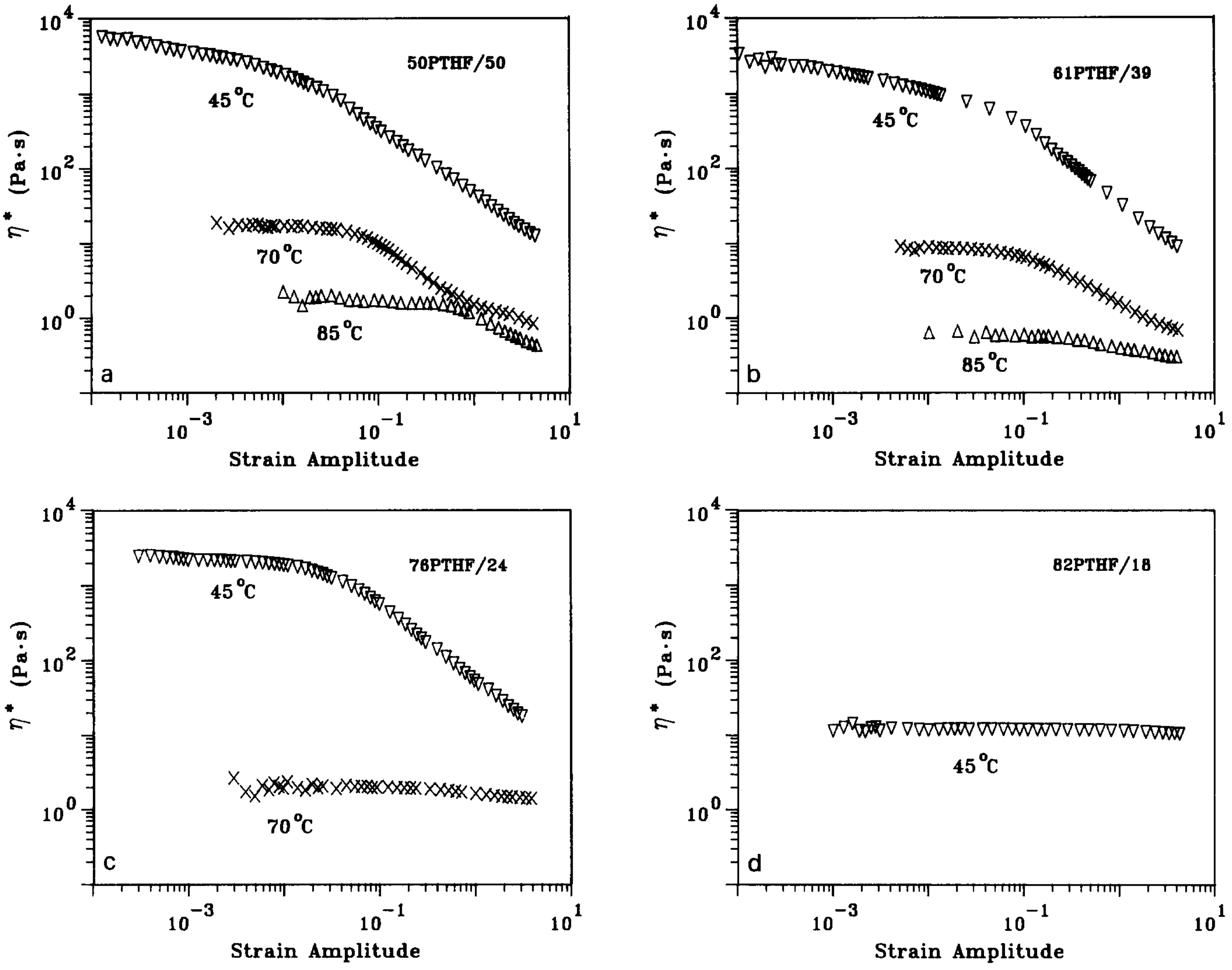

Figure 4 Strain sweep at the indicated temperatures and a frequency of 10 rad s^{-1}

cooled back to the mesophase state). This slow recovery is attributed to a gradual growth of the number of tie molecules. During this process, re-entry molecules must be mobile enough to dissociate from their respective domain. The high phase separation energy of the mesophase state makes it difficult for the mesogenic ends to leave the liquid crystalline domains, and hence results in the low rate of the recovery of network structure.

(2) Above the isotropic transition of the liquid crystalline phase (T_i), TLCPs could retain the microphase separated state, depending on the weight ratio of PTHF spacer. This has been confirmed by n.m.r. measurements[17]. The persistence of network structure is responsible for the relatively high storage modulus at small strains and shear thinning behaviour at large strains of this state (see *Figures 3* and *4*, 50PTHF/50 and 61PTHF/39). However, in this state, the phase separation energy is very low, as it can be seen that the transition of two isotropic phases to a single isotropic phase does not show significant enthalpic change in the d.s.c. thermogram. Therefore, the physical crosslinking effect of the dispersed isotropic domains is very weak. By comparison with the mesophase state, the mechanical dynamic modulus of this state is about two orders of magnitude lower; the critical shear stress to set up shear thinning is about one order of magnitude lower; and the recovery of network structure after severe shearing is much faster (2–5 h).

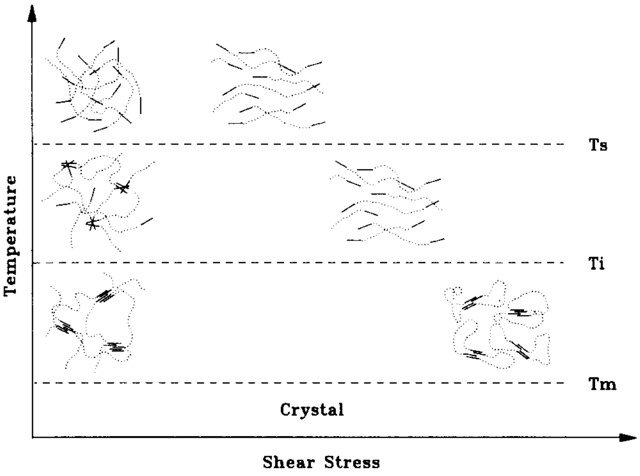

Figure 5 Effects of temperature and shear stress on the structure of TLCPs

(3) Above the coexistence temperature (T_s), the TLCPs become single phased and show very slow viscosity and relative elasticity (see *Figure 3*, 82PTHF/18, 76PTHF/24 and 61PTHF/24). A shear thinning effect can no longer be observed (see *Figure 4*). In short, the TLCPs behave just like a normal polymeric melt of low molecular weight. The coexistence temperature T_s decreases

as the weight ratio of PTHF spacer increases. For 76PTHF/24, the transition of two phases to a single phase occurs simultaneously with the isotropic transition of the liquid crystalline phase, i.e. $T_s = T_i > T_m$; for 82PTHF/18, microphase separation behaviour is negligible above the melting temperature, and we can reasonably assume that $T_s = T_i \approx T_m$.

As shown in the present work, mechanical dynamic measurement is a very sensitive method to detect the phase behaviour of the TLCPs. However, it failed to determine the phase transitions of a di-block liquid crystalline polymer which has only one mesogenic end in the chain. The reasonable explanation for this result is that the microphase separation of a di-block copolymer cannot build up a network structure and hence cannot change significantly the viscoelasticity of the polymer.

CONCLUSION

The microphase separated network structure of TLCPs exhibits unusual rheological behaviour, including strong viscoelasticity and shear thinning which is reversible only after long recovery times. The separated domains have a strong physical crosslinking effect. The strength of the network structure depends essentially on the molecular order in the phase separated domains of the mesogenic ends. In the mesophase state, the phase separation energy is as high as the energy for the mesophase/isotropic transition. Above the mesogenic/isotropic transition temperature, the phase separation energy becomes very low, even below the detection level of the d.s.c. Consequently, although the domain structure could persist in a certain temperature range for the TLCPs with short PTHF spacer, the physical crosslinking effect of the separated domains is largely decreased.

The coexistence temperature of the TLCPs decreases significantly as the weight ratio of PTHF spacer increases. For instance, the TLCP of 82PTHF/18 does not have a complete phase separation behaviour above T_m and displays rheological behaviour typical of a low molecular weight polymeric melt.

The present work is a model study for developing a thermoplastic elastomer of low melt viscosity. It is most interesting that the relatively short mesogenic chain ends give rise to such a large change in the mechanical properties, due to relative highly phase separation energy. The low molecular weight gives the advantage of low viscosity for processing above T_i. On the other hand, the phase separated liquid crystalline domains will form permanent physical crosslinks below T_m of mesogenic segment, giving the whole material elastic behaviour.

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