Colloid Polym Sci (2005) 283: 1143–1148
DOI 10.1007/s00396-004-1214-0

SHORT COMMUNICATIONS

Bao-Yan Zhang
Lu-Mei Liu
Dan-Shu Yao
Li-Feng Zhang

Phase behavior of liquid crystalline elastomers based on a tri-vinyl mesogenic cross-linker

Received: 24 March 2004
Accepted: 30 August 2004

B.-Y. Zhang (✉) · L.-M. Liu
D.-S. Yao · L.-F. Zhang
The Centre for Molecular Science and Engineering, Northeastern University, Shenyang, 110004, China
E-mail: baoyanzhang@hotmail.com
Tel.: +86-24-83687446

Abstract A series of cross-linked liquid crystalline polymers are prepared by graft copolymerization, and their liquid crystalline properties are characterized by DSC and POM. The results show that low levels of cross-linking do not obviously affect the phase behavior of the network polymers; in contrast, high levels of cross-linking may have more drastic influences, and liquid crystalline phases may lose, and more marked variation in phase transition will occur in materials with more direct coupling through a shorter or stiffer coupling chain between mesogenic side units and polymer backbone. At the same time, the coupling between the polymer chain and sidegroups results in stress-induced orientation in LCEs.

Keywords Liquid crystalline elastomer · Thermotropic · Coupling

Introduction

In recent years, much attention has been paid to the liquid crystalline network polymers, which are also called liquid crystalline elastomers (LCEs). Slightly cross-linked LC elastomers offer the possibility of combining the rubber elasticity of polymer networks with LC phases. LC elastomers are of great interest in the academic area with basic questions concerning the interaction of the LC director and the polymer network [1–6] So, since the first synthesis in 1981[7], LCEs based on polysiloxane, polyacrylate and epoxy and also combined main chain/side chain polymers have been realized [8–13], and most cross-linking monomers are bifunctional compounds.

Some LCEs have been investigated in our previous studies, [14–22] while in this paper, a mesogenic tri-vinyl compound is used as a cross-linking monomer to prepare a series of network liquid crystalline polymers. The phase behavior of the monomers and elastomers obtained are characterized by DSC and POM, and the influence of the content of cross-linking unit on the phase behavior of the elastomers is discussed through the coupling of the mesogenic side units and polymer chain.

Experimental

Materials

Polymethylhydrosiloxane (PMHS) with Mn = 700~800 was purchased from Jilin Chemical Industry Company and used without any further purification. 4-Allyloxybenzoyl-4′-(4-*n*-amylbenzoyl)-*p*-benzenediol bisate (**M1**), which is a nematic monomer with a broad mesomorphic phase from 109.6 to 224.7 °C, and 4-[3,5-di(acryloyloxy)-benzoyl]-4′-(4-allyloxy-benzoyl)-*p*- benzendiol bisate (**M2**), a smectic tri-vinyl monomer, used as a cross-linking unit are prepared in our lab.

M1: IR (KBr, cm^{-1}): 3,080(=C–H), 2,960~2,850 (CH_3– and –CH_2–); 1,735(C=O); 1,645 (C=C); 1,605~1,507()

^{1}H-NMR (DMSO-d_6, δ/ppm): 0.95(t, 3H), 1.35–1.63 (m, 6H), 2.71 (t, 2H), 4.65 (m, 2H), 5.32–5.47 (d, 2H), 6.11 (m, 1H), 6.91–7.31 (m, 8H), 8.10–8.18 (m, 4H).

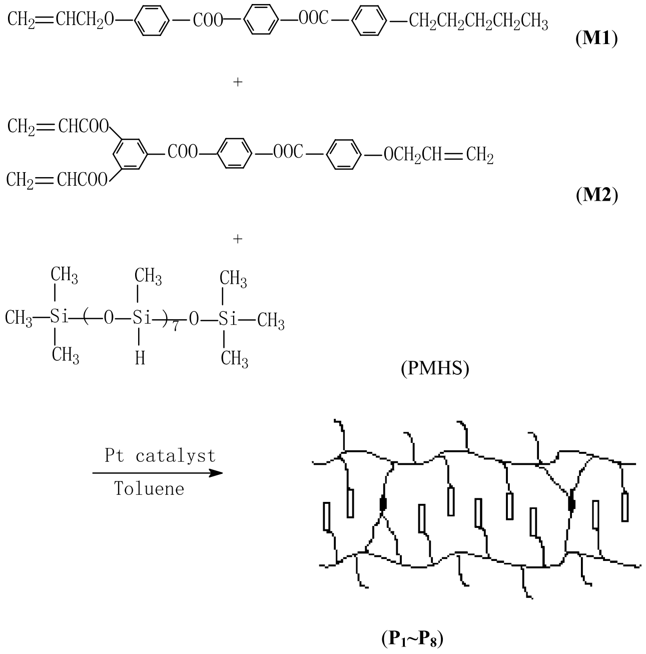
M2: IR (KBr, cm^{-1}): 3,068(=C–H), 2,933 (–CH$_2$–), 1,721 (C=O); 1,601∼1,509().

^{1}H-NMR (DMSO-d$_6$, δ/ppm): 4.64 (d, 2H), 4.98 (d, 2H), 5.82 (m, 1H), 5.96–6.10 (m, 6H), 7.01–8.16 (m, 11H).

All other solvents and reagents are purified before use.

Characterization

FTIR spectra are measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI, USA). The polymer sample films are obtained via casting on a KBr table. Thermal transitions were measured with a Netzsch DSC 204 (Netzsch, Germany) equipped with a liquid nitrogen cooling system at a heating rate of 20 °C/min under nitrogen atmosphere. Phase transition temperatures were collected during the second heating scans. The textures of the liquid crystalline phases were observed with a Leica DMRX (Leica, Germany) polarizing optical microscope equipped with a LinkaMTHMSE-600 (Linkam, England) hot stage.



Scheme 1 Synthesis Routes of the LCEs

Polymer synthesis

The cross-linked liquid crystalline polymers are synthesized according to the description in Scheme 1, and the polymerization experiments are summarized in Table 1.

The cross-linked polymers **P**$_1$∼**P**$_8$ are prepared by a graft copolymerization of mesogenic monomer 4-allyloxybenzoyl-4′-(4-it n-amylbenzoyl)-*p*-benzenediol bisate (**M1**) and tri-vinyl cross-linking monomer 4-[3,5-di(acryloyloxy)-benzoyl]-4′-(4-allyloxy-benzoyl)-*p*-benzendiol bisate (**M2**) upon polymethylhydrosiloxane (PMHS) with different proportions, using dry toluene as the solvent and hydrogenhexchloroplatinate hydrate as the catalyst. The reaction was carried out at 60∼70 °C until the IR spectra showed that the Si–H absorption peak of PMHS at 2,160 cm^{-1} disappeared. The solvent was removed under reduced pressure, and the crude polymer was purified by precipitation from solution in methanol by the addition of THF. After filtration and evaporation of the solvent, the product was dried at 50 °C for 10 h under vacuum.

Results and discussion

The phase behaviors of the monomers **M1**, **M2** and polymers **P**$_0$∼ **P**$_8$ are determined by differential scanning colorimetry (DSC) and polarizing optical micrograph (POM). The thermal behaviors determined by DSC are consistent with POM observation results. The phase transition temperatures and corresponding enthalpy changes are listed in Table 1 and 2, respectively.

Phase behavior of **M1** and **M2**

The POM observation results show that **M1** exhibits enantiotropic nematic thread-like texture, and **M2**reveals a smectic fan-shaped texture in heating and cooling cycles. Photomicrographs of M1 and M2 are shown in Fig. 1a, b.

According to Table 2, a melting transition and a nematic to isotropic phase transition for **M1** appear at 109.6 and 224.7 °C, an isotropic to LC phase transition appears at 207.5 °C and a crystallization temperature at 80.9 °C. While for **M2** the melting temperature and the smectic to isotropic phase transition occur at 59.6 and 124.2 °C, there is not an endothermic peak for crystallization but an inflexion for glass transition appears at 42.3 °C, and the isotropic to smectic phase transition at 99.5 °C in the cooling scan. We attribute the appearance of T_g in the cooling scan to the polymerization of the **M2** during the heating scan.

The enthalpy change (ΔH) of mesophase to isotropic phase transition of **M1** is much bigger than that of **M2** (3.88 J/g for **M1** and 0.43 J/g for **M2**), which means **M1** will contribute more to the mesomorphic property of the LCEs prepared because the intermolecular force is much bigger for M1, and the energy required to distort its anisotropic phase is larger than that of **M2**.

Table 1 Polymerization and the thermal analysis results of the polymers

Polymer	Feed		DSC			
	PMHS/**M1**/**M2** (mmol)	**M2**[a] (mol%)	T_g (°C)	T_c[b] (°C)	ΔH[c] (J g^{-1})	ΔT[d] (°C)
$\mathbf{P}_0$	1.00/7.00/0.00	0.0	42.3	222.3	2.03	180.3
$\mathbf{P}_1$	1.00/6.70/0.10	1.5	38.6	193.8	0.38	155.2
$\mathbf{P}_2$	1.00/6.10/0.30	4.7	38.3	190.7	0.29	152.4
$\mathbf{P}_3$	1.00/5.50/0.50	8.3	40.4	163.9	0.15	123.5
$\mathbf{P}_4$	1.00/4.90/0.70	12.5	41.2	–	–	–
$\mathbf{P}_5$	1.00/4.30/0.90	17.3	43.7	–	–	–
$\mathbf{P}_6$	1.00/3.70/1.10	22.9	47.4	–	–	–
$\mathbf{P}_7$	1.00/3.10/1.30	29.6	54.2	–	–	–
$\mathbf{P}_8$	1.00/1.90/1.70	47.2	70.6	–	–	–

[a] Mole percent of **M2** based on **M1** + **M2**

[b] Clearing point temperature

[c] Enthalpy change of mesophase to isotropic phase transition

[d] $\Delta T = T_c - T_g$

Phase behavior of LCEs

Thermal analysis

Side-chain LC polymers are composed of two, more or less independent, subsystems: the polymer chain and the mesogenic side groups, which linked to the polymer chain though a decoupling element, usually called as a flexible spacer, and assumed that the orientation of polymer chains and mesogenic side groups are largely decoupled from each other, so both subsystems are able to follow their inherent orientational tendencies. However, there are some couplings between the polymer chain and the mesogenic side groups; in particular, in our present work, the flexible spacers of **M1** and **M2** are too short to completely decouple the side groups and polymer backbone, and with the addition of the tri-vinyl in **M2**, quite direct coupling results from the cross-link sites in the product. As a consequence, the introduction of cross-link units **M2** in to the LCEs produced obviously affects their phase behavior.

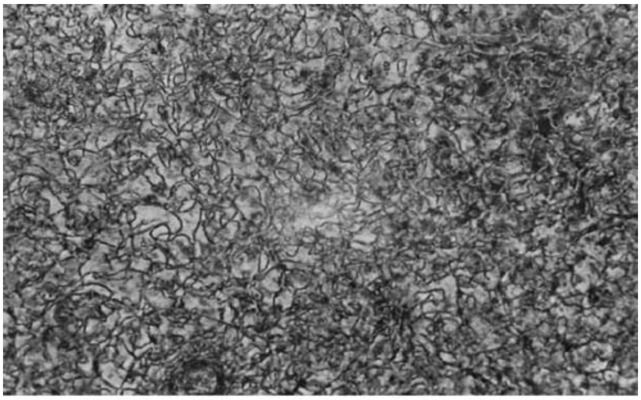
Generally, cross-linking imposes additional constraints on the segmental motion of polymer chains; therefore, the increase of the glass transition temperatures T_g might be expected. However, experimental results show that this effect is relatively small in the case of lightly cross-linked polymers. This implies that another role has been played by the flexible cross-linking units simultaneously: plasticizer. The existence of plasticizer causes the decrease of T_g of lightly cross-linked

Table 2 Phase transitions of the monomers

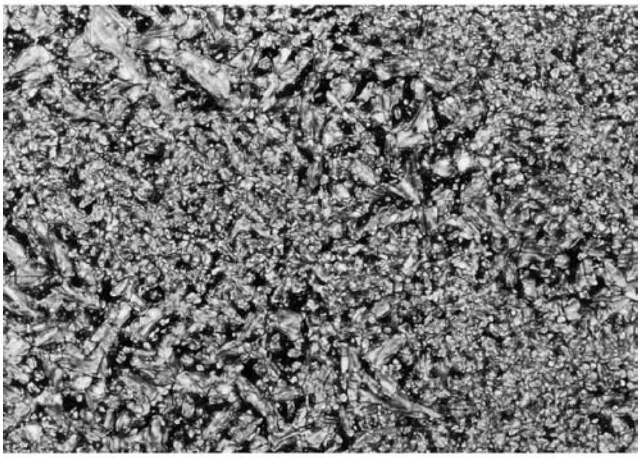
Monomers	Phase transitions in °C (corresponding enthalpy changes in J/g)
M1	Heating: K 109.6 (52.92) N 224.7 (3.88) I Cooling: I 207.5 (−2.87) N 80.9 (−34.93) K
M2	Heating: K 59.6 (36.95) S 124.2 (0.43) I Cooling: I 99.5 (−0.75) S 42.3[a] K

K solid, *N* nematic, *S* smectic, *I* isotropic

[a] A glass transition appears on the DSC cooling scan



(a) M1 at 217°C



(b) M2 at 114°C

Fig. 1 Polarized optical micrograph of **M1** and **M2** (200×)

polymers. In these two controversial functions, cross-linkers act against each other, so the T_g of the LCEs is dominated by the preponderant function. Taking the cross-linking effect and plasticization effect into account, T_g is given by [22]

$$T_g = T_{go} - K_x \cdot \rho_x \tag{1}$$

$$T_g = T_{go} + K_x \cdot \rho_x \tag{2}$$

where T_g and T_{go} are the glass transition temperatures of cross-linked and uncross-linked polymers, K_x is a constant, and ρ_x is the cross-link density. When the cross-link density is less than certain critical value, and the plasticization effect of flexible cross-linking chains is predominant, Eq. 1 is adopted. Conversely, when the cross-linking effect is predominant, Eq. 2 is adopted.

Figure 2 shows the effect of the concentration of cross-linking **M2** units on phase transition temperatures of $\mathbf{P}_1 \sim \mathbf{P}_8$: T_g of $\mathbf{P}_1 \sim \mathbf{P}_4$ are a little lower than that of the precursor polymer $\mathbf{P}_0$ and the lowest T_g belongs to $\mathbf{P}_2$; however, the general tendency of a cross-link to increase T_g and the slight plasticization of the short flexible units in M2 caused T_g to increase from 38.3 to 70.6 °C when the concentration of cross-linking **M2** units increases from 4.7 to 47.2 mol%.

Similar to T_g, chemical cross-linking affects the isotropization temperature (T_c) of LCEs: chemical cross-linking could prevent the motion and orientation of polymer chains at and in the vicinity of the cross-linking sites, and so not it is not in favor of the formation of mesogenic orientation order in the networks, because the LCEs are cross-linked in the nonmesogenic state. Although the rigid mesogenic core of cross-linking units may promote the formation of mesophase in network polymers, it is very faint, because the intermolecular force is weak for **M2** implied by its small enthalpy change (δH) of mesophase to isotropic phase transition (0.43 J/g).

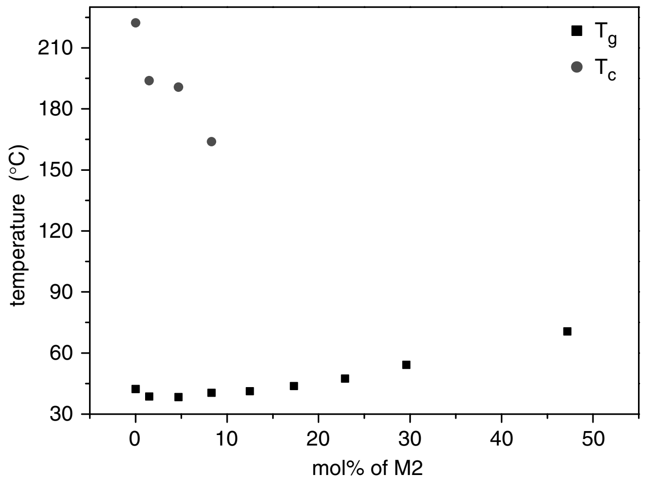


Fig. 2 Phase transition temperatures of cross-linked polymers as a function of **M2** content

The theory given by Warner et al. [23] suggests how the coupling might affect the phase transition behavior of LCEs: although there is some flexibility in the chain between network points, for the LCEs cross-linked in the isotropic phase, the effect of cross-linking is to stabilize the random polymer conformations typical of the isotropic phase. Thus, to achieve the conformational arrangements required for LC ordering, the elastomer must be distorted, and the elastic energy of the modulus must be overcome. The LC phase is thus reduced in stability for the LC ordering is in direct conflict with the entropy-driven desire for the polymer to take up random conformations.

According to Table 1, the T_c-value and the enthalpy change (δH) of $\mathbf{P}_0 \sim \mathbf{P}_3$ decrease from 222.3 to 163.9 °C and 2.03 to 0.15 J g^{-1} when the content of cross-linking units increase from 0 to 8.3 mol%. Besides, T_c disappears when the content of the cross-linking unit is greater than 12.5 mol%. This result accords with the theory of Warner et al. [23], and we attribute the swift disappearance of the mesophase to the formation of the network structure in the nonmesogenic state, as cross-linking obtained in the nonmesogenic state tends to maintain the polymer backbones at isotropic random coil states, and it will reduce the energy of disorientation of mesogenic units in the liquid crystalline phase with the increase of cross-linking densities.

The effect of cross-linking to the T_c of LCEs can be understood by the form of the free energy change at the clearing point,[24]

$$\Delta G = 0 = \Delta H - T_{c0}\Delta S \tag{3}$$

$$\Delta G = 0 = \Delta H + \Delta F - T_c\Delta S \tag{4}$$

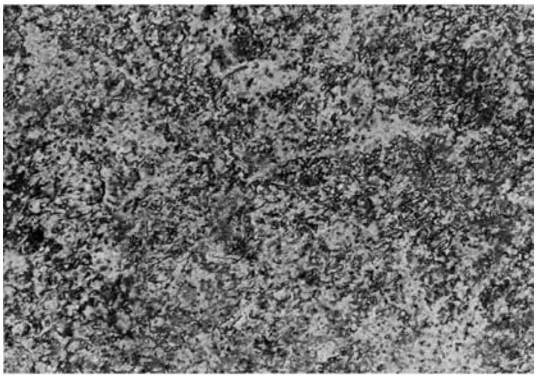
Equation 3 is the free energy change for the uncross-linked material at anisotropic to isotropic transition. In the cross-linked case, there is an additional term to be considered: ΔF represents the energy required to transform the network configuration in the LC phase to that of the isotropic phase, so the form of the free energy change is given as Eq. 4. If the system was cross-linked in the LC phase, ΔF is a positive contribution, whereas for an elastomer prepared in the isotropic phase, ΔF is of the opposite sense for the anisotropic to isotropic transition and will be favorable.

Combining Eqs. 3 and 4 and assuming that the enthalpy change is unaffected by the cross-linking gives:

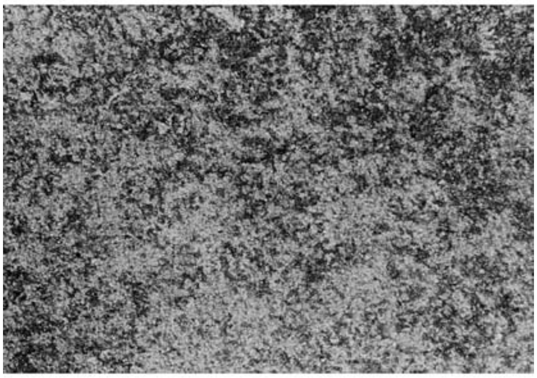
$$T_c = T_{c0} + \Delta F / \Delta S \tag{5}$$

Clearly, low levels of cross-linking do not obviously affect the phase behavior of the network polymers; in contrast, high levels of cross-linking may have more

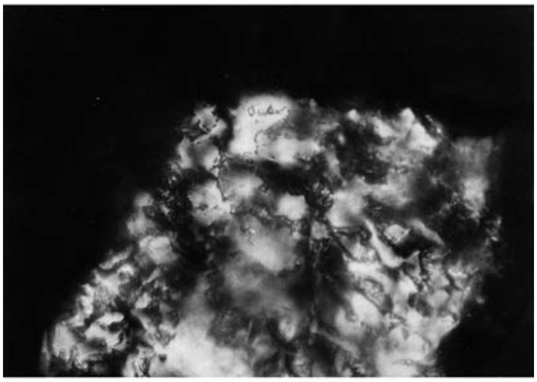
(a) **P_0** at 110°C



(b) **P_1** at 94°C



(c) **P_3** at 121°C



(d) stree-inducde texture of **P_4** at 87°C

◀

Fig. 3 Polarized optical micrographs of polymers (200×)

drastic influences, and liquid crystalline phases may lose, while materials with more direct coupling through a shorter or stiffer coupling chain will exhibit a more marked variation in T_c upon cross-linking.

Texture analysis

The phase behavior of polymers **P_0**~**P_8** observed with POM is consistent with the results obtained using DSC, and the observation of POM suggests that the introduction of closs-linking to polymer remarkably changes its textures: the un-cross-linked polymer **P_0** exhibits typical nematic thread-like textures just as **M1** does (see Fig. 3a), while the lightly cross-linked polymers **P_1**~**P_3** display the texture shown in Fig. 3b, c instead of the nematic thread-like texture.

As suggested by the DSC curves, **P_4**~**P_8** do not show any texture under crossed polarizers; however, **P_4** and **P_5** reveal stress-induced birefringence at temperature higher than T_g: **P_4** and **P_5** exhibit colored textures (see Fig. 3d) under stress, and immediately bounce up leading to the vanishment of the textures when removing the stress. While pressing **P_4** and **P_5** to form semitransparent thin films at room temperature, the birefringence also can be observed under POM.

Just like shifts in phase transition temperature, the stress-induced birefringence of LCEs also can be understood by the coupling in network structure: these properties can be considered to be manifestations of coupling between the polymer chain and side groups; the network acting to allow the observation of such effects by restricting the relative motion of polymer chains. Thus, a macroscopic deformation of the cross-linked sample leads to an equilibrium deformation the polymer chains, and results in the orientation of mesogenic side groups [25].

Conclusion

A series of cross-linked liquid crystalline polymers were prepared by graft copolymerization. Their phase behavior shows that low levels of cross-linking do not obviously affect the phase behavior of the network polymers; in contrast, high levels of cross-linking may have more drastic influences, and liquid crystalline phases may lose and more marked variation in phase transition will occur in materials with more direct coupling through a shorter or stiffer coupling chain between mesogenic side units and polymer backbone. At the same time, the coupling between the polymer chain and sidegroups results in stress-induced orientation in CLEs.

Acknowledgements The authors are grateful to National Natural Science Fundamental Committee of China and HI-Tech Research and development program (863) of China, National Basic Research Priorities Programme (973) of China and Science and Technology Research Major Project of Ministry of Education of China for financial support of this work.

References

1. Schuring H, Stannarius R, Tolksdorf C, Zentel R (2001) Macromolecules 34:3962
2. Hotta A, Terentjev EM (2001) J Phys Condens Matter 13:11453
3. Zanna JJ, Stein P, Marty JD, Mauzac M, Martinoty P (2002) Macromolecules 35: 5459
4. Stein P, Assfalg N, Finkelmann H, Martinoty P (2001) Eur Phys J E 4:255
5. Kim ST, Finkelmann H (2001) Macromol Rapid Commun 22:429
6. Assfalg N, Finkelmann H (2001) Macromol Chem Phys 202:794
7. Finkelmann H, Kock H, Rehage G (1981) Makromol Chem Rapid Commun 2:317
8. Zentel R, Reckert G (1986) Makromol Chem 187:1915
9. Zentel R, Benalia M (1987) Makromol Chem 188:665
10. Zentel R (1992) Polymer 33:4040
11. Osada S, Tsunashima K (1996) Polymer 37:1925
12. Talroze R, Zubarev E (1999) React Funct Polym 41:1
13. Espinosa M, Cadiz V (2001) J Polym Sci Polym Chem 39:2847
14. Jia YG, Zhang BY, Zhou EL, Feng ZL (2002) J Appl Polym Sci 85:1104
15. Zhang BY, Meng FB, Zang BL, Hu JS (2003) Macromolecules 36:3320
16. Meng FB, Zhang BY, Liu LM, Zang BL (2003) Polymer 44:3935
17. Zhang BY, Hu JS, Wang Y, Qian JH (2003) Polym J 35:476
18. Zhang BY, Liu LM, Feng ZL, Jia YG (2003) Liq Cryst 30:1015
19. Hu JS, Zhang BY, Sun K, Li QY (2003) Liq Cryst 30:1267
20. Zhang BY, Hu JS, Jia YG, Du BG (2003) Macromol Chem Phys 204:2123
21. Liu LM, Zhang BY, Cheng CS, Zhen YY (2004) J Appl Polym Sci 91:773
22. Hu JS, Zhang BY, Jia YG, Chen S (2003) Macromolecules 36:9060
23. Warner M, Gelling KP, Vilgis TA (1988) J Chem Phys 88:4008
24. Davis FJ, Mitchell G R (1996) Polymer 37:1345
25. Hirschmann H, Roberts PMS, Davis FJ, Guo W, Mitchell GR (2001) Polymer 42:7063