Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 45 (2004) 3505–3510
polymer
www.elsevier.com/locate/polymer

Viscoelastic effects on the phase separation in thermoplastics modified cyanate ester resin

Qingsheng Tao, Wenjun Gan, Yingfeng Yu, Minghai Wang, Xiaolin Tang, Shanjun Li*

Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, Fudan University, Lane 220, Handan RD, Shanghai 200433, China

Received 26 December 2003; received in revised form 11 March 2004; accepted 16 March 2004

Abstract

A high temperature thermosetting bisphenol-A dicyanate, BADCy was blended with a thermoplastic poly(ether imide) (PEI). The phase separation behavior of the blend was investigated by scanning electron microscopy (SEM) and time resolved light scattering (TRLS). It was found by SEM that the blend with 20 and 25 wt% PEI had a phase inversion structure. The results of TRLS displayed clearly that the phase separation took place according to a spinodal decomposition (SD) mechanism and the evolution of both scattering vector q_m and the maximum scattering intensity I_m followed Maxwell-type relaxation equation. The temperature-dependent relaxation time τ for the blends can be described by the Williams–Landel–Ferry equation. It demonstrated experimentally that the phase separation behaviors in PEI/BADCy blends were affected by viscoelastic effect.

Keywords: Cyanate esters; Poly(ether imide); Viscoelastic phase separation

1. Introduction

Cyanate ester resins have been an important thermosetting material for encapsulants of electronic devices, high temperature adhesives, and structural materials of aerospace because of their outstanding mechanical, thermal and adhesive properties. Though cyanate resins are known to be relatively tough compared with other thermosetting polymers, some applications required improved fracture toughness [1,2].

The toughening of polycyanurates has been achieved by the incorporation of thermoplastic without the reduction of polycyanurates' thermal and mechanical properties. These thermoplastics included polysulfone [3–5], poly(ether sulfone) [6,7], polyarylate [8], poly(ether imide) [3,9–10] and so on. Careful control of the morphological structure was necessary to achieve significant toughening. Therefore, the studies on the phase separation of thermosetting/thermoplastic blend were of great importance in toughening thermosetting resins. Various phase morphologies for BADCy/PEI blend could be obtained, depending on the competition between the thermodynamics and kinetics of phase separation and the cross-linking chemical reaction, which are governed by the curing conditions, compositions and PEI molecular weight.

Recently, the viscoelastic phase separation of polymer blend has attracted increasing attention. Most of this attention has been focused on the binary or ternary system of thermoplastic-solvent or thermoplastic–thermoplastic, such as PMMA(poly(methyl methacrylate)/PSAN (poly(styrene-co-acrylonitrile) [11–12], PS(polystyrene)/PVME [13–15], dextran/PEG (poly(ethylene glycol)/H_2O [16] and PS/poly (methylphenylsiloxane) (PMPS) [17]. As these thermoplastic-solvent or thermoplastic–thermoplastic systems were intensively investigated, a series of viscoelastic phase-separation theories were developed to interpret the phenomena taking place in the phase separation process of the above systems. Tanaka first reported unusual phase separation caused by asymmetric molecular dynamics and found that viscoelastic phase separation was a universal phenomenon common to all dynamically asymmetric mixtures; the origin of the dynamic asymmetry might be caused by the size difference in component molecules of a

---

* Corresponding author. Tel.: +86-2165642865; fax: +86-2165640293.
E-mail address: sjli@fudan.edu.cn (S. Li).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.03.043

mixture or the existence of another transition such as a glass transition (T_g). In these cases, domains of a fast dynamic phase appear in a slow dynamic phase matrix, and then networklike or spongelike structures are formed by the domain growth. Finally, a continuous slow dynamic phase develops into a dispersed phase by shrinkage. Therefore, even a minor polymeric component provides network-like continuous or co-continuous phase structures that brought about excellent mechanical properties.

Although there is increasing interest in viscoelastic effect on the phase separation of polymer blends, there are few papers in the literature devoted to the discussion of viscoelastic effect on the phase separation of thermoplastic-thermosetting systems. In our previous work, we first reported experimentally that there existed a viscoelastic phase separation behavior for the PEI/epoxy/methyltetrahydrophthalic anhydride (MTHPA) blend. The time resolved light scattering (TRLS) results displayed clearly that the evolution of scattering vector q_m corresponding to epoxy droplets followed a Maxwell-type relaxation equation [18,19].

The aim of the present work is to study the viscoelastic effect on phase separation of the cyanate ester resins modified with PEI. TRLS was used to trace the evolution of scattering vector q_m and the maximum scattering intensity I_m and discuss the evolution process of phase structure along with the final morphology of the cured blend observed by SEM.

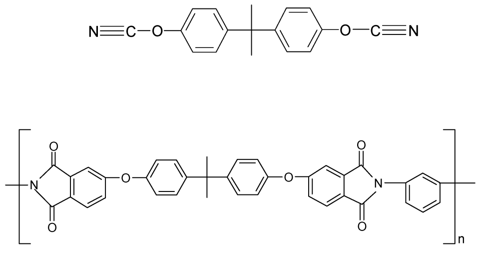
2. Experimental

2.1. Materials

The bisphenol-A dicyanate (BADCy) with a cyanate equivalent of 139 g/equiv. was supplied by Beijing Aeronautical Manufacturing Technology Research Institute. The thermoplastic used in this study was a commercial grade polyetherimide, PEI(Ultem 1000) with a glass transition temperature at ~215 °C from General Electric ($M_n = 12,000$; $W_n = 30,000$). Chemical structures of the above materials were shown in Fig. 1.

2.2. Sample preparation

Modified cyanate resins containing 20 and 25 wt% PEI were prepared as follows. PEI was dissolved in methylene chloride (CH_2Cl_2) and mixed with BADCy at room temperature. The residual solvent was removed under vacuum at 90 °C for 1 h after most of the solvent was evaporated at 40 °C. The mixtures were molded and then cured at different conditions.



(BADCy)

(PEI)

Fig. 1. Chemical structures of BADCy and PEI.

2.3. Time-resolved light-scattering measurements

The specimens for time-resolved light scattering(TRLS) were prepared by solvent casting of a film from a methylene chloride solution (5 wt% of blend). The thin film of the blend was dried under vacuum for two days at room temperature to remove the residual solvent. The phase separation process during curing was observed at real time and in situ on the self-made TRLS with a controllable hot chamber. The TRLS technique is described elsewhere [20]. The change of the light scattering profiles was recorded at appropriate time intervals during isothermally curing.

2.4. Morphology observation

The morphology of the isothermally cured resins was examined under a scanning electron microscope (SEM) (Philip XL 39). The samples were fractured in liquid nitrogen and coated with a fine gold layer before observation.

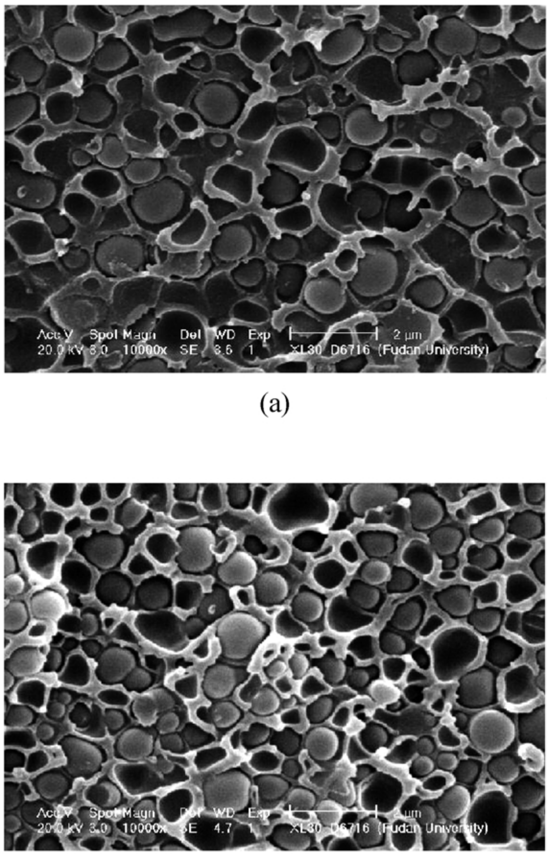
2.5. Glass-transition temperature (T_g) measurement

The glass transition temperature T_gs of BADCy monomer and PEI/BADCy blend were measured using a Perkin–Elmer DSC (Pyris 1). The DSC was calibrated with high-purity indium. Around 10 mg of samples were weighed into small DSC aluminum pans and sealed with aluminum lids. All the experiments were conducted under a nitrogen flow of 40 $cm^3\ min^{-1}$. A first scan was carried out from 20 to 100 °C at 20 °C min^{-1} and then the sample was heated isothermally at 100 °C for 2 min. After cooling at the maximum speed provided by the calorimeter, a second scan was carried out from -60 to 40 °C at 10 °C min^{-1}. T_g was calculated in the second heat flow curve with the program supplied by Perkin–Elmer Corporation and reported as the midpoint temperature of the glass transition.

3. Results and discussion

3.1. Morphology

The morphologies of PEI/BADCy blends cured isothermally at 150 °C were observed with SEM. As shown in Fig. 2, phase-inverted morphology was obtained in the blend with 20 wt% PEI. The continuous PEI-rich phase constituted the matrix and the BADCy-rich particles of around 1 μm diameter dispersed in it. The morphology of the blend



(a)

(b)

Fig. 2. Morphologies of BADCy/PEI blends cured isothermally at 150 °C for 6 h. (a) The blend with 20 wt% PEI (× 10,000), (b) the blend with 25 wt% PEI (× 10,000).

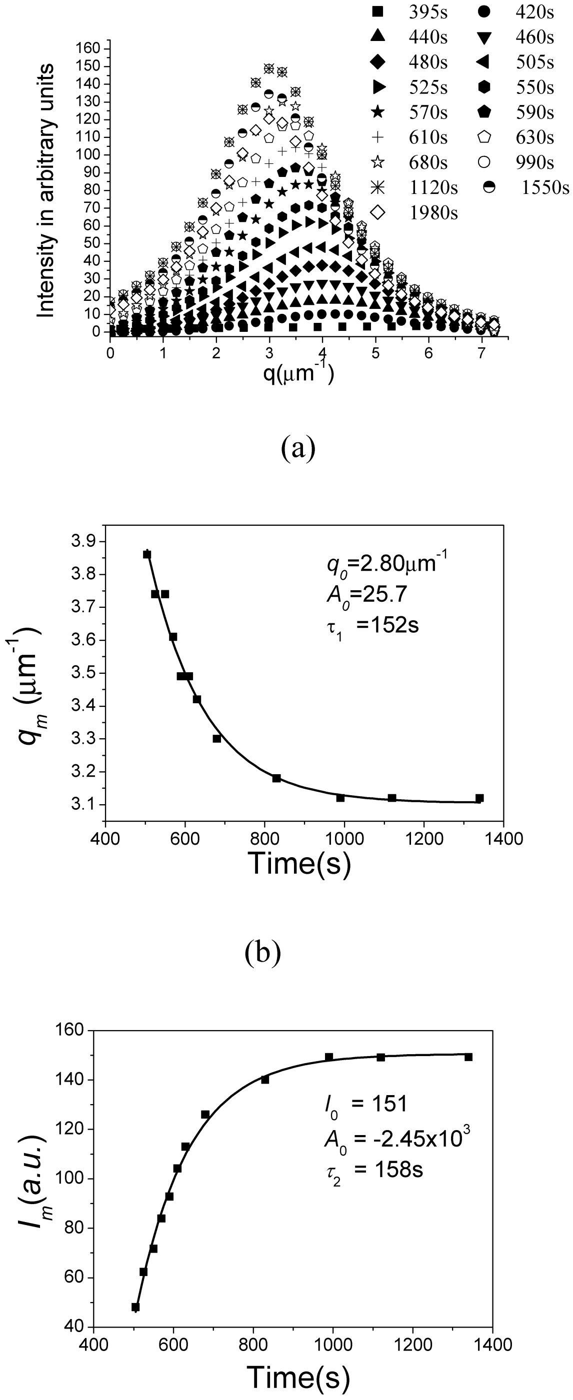
with 25 wt% PEI was similar to that of the blend with 20 wt% PEI. However, the average size of the BADCy particle for the blend with 25 wt% PEI was slightly smaller than the one for the blend with 20 wt% PEI.

3.2. Evolution of $I_m(t)$ and $q_m(t)$ during isothermal process

Phase separation processes of the two blends were traced in situ by TRLS. The change of the light-scattering profiles was recorded at appropriate time intervals during isothermally curing at 120, 130, 140, 150, 160 and 170 °C respectively. Fig. 3(a) shows a typical example of the change in the scattering profile with demixing time t for the blend with 25 wt% PEI cured at 150 °C isothermally. In Fig. 3(a), scattering vector q is defined by Eq. (1),

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{1}$$

where λ is the wavelength of light in the sample and θ is the scattering angle. The peak scattering vector q_m is defined as the q value with an instantaneous maximum scattering intensity I_m in each light profile. The evolution of scattering vector q_m correspond to the coarsening process of BADCy droplets. For the blend with 25 wt% PEI cured at 150 °C isothermally, a light-scattering peak appeared in the profile when curing time was about 7 min. After that, q_m decreased with time continuously and maintained constant eventually. Meanwhile, I_m increased with time continuously, and then reached the maximum value, after that decreased with time and maintained constant at last.



(a)

(b)

(c)

Fig. 3. TRLS profiles of the blend with 25 wt% PEI cured at 150 °C. (a) Intensity versus q_m at different times, (b) q_m versus time, (c) I_m versus time. Symbols correspond to experiment data and lines correspond to the fitting with Eq. (2) or (3).

Table 1
Relaxation time τ for BADCy/PEI blend at different curing temperatures

Sample	Temperature curing T (°C)	120	130	140	150	160	170
BADCy/PEI (80/20)	τ_1 (s)	446	292	190	105	55	32
	τ_2 (s)	437	274	198	96	58	19
BADCy/PEI (75/25)	τ_1 (s)	627	357	225	152	111	67
	τ_2 (s)	599	326	209	158	99.5	42

τ_1 was obtained by the simulation of q_m with Eq. (2); τ_2 was obtained by the simulation of I_m with Eq. (3).

The appearance of the scattering peak should be the indication of the development of a regularly phase-separated morphology via spinodal decomposition. We observed similar characteristics at all the temperatures.

To describe the tendency of the change in q_m with time, time-dependent q_m was fit with a Maxwell-type relaxation (Eq. (2)). The curve in Fig. 3(b) shows that q_m decreases exponentially and fits Eq. (2) well.

$$q_m(t) = q_0 + A_0 \exp(-t/\tau_1) \tag{2}$$

As $t = \infty$, $q_m = q_0$. Here, τ_1 is the relaxation time, and A_0 is the magnifier.

Similarly I_m value was also fit with a Maxwell-type relaxation (Eq. (3)) from the beginning to the maximum value. The curve in Fig. 3(c) shows that I_m value increases exponentially and fits Eq. (3) well.

$$I_m(t) = I_0 + A_0 \exp(-t/\tau_2) \tag{3}$$

According to the simulation of q_m and I_m with Eqs. (2) and (3), the relaxation time τ_1 and τ_2 could be obtained. The meaning of the relaxation time can be explained as follows. Since the cure temperature is far below the T_g of PEI (215 °C), the BADCy monomer acts as a rapid dynamic phase (lower-T_g component), and PEI is a slow dynamic phase (higher-T_g component) and acts as a 'cage effect' [21]. The relaxation time should be the time of escape for the BADCy monomer from the so-called 'cage' of PEI by their relaxation movements.

The time-dependent q_m and the time-dependent I_m fit the Maxwell-type relaxation equation well for both the blend with 20wt% PEI and the blend with 25wt% PEI at different temperatures from 120°C to 170°C. This may suggest that the relaxation movement of the BADCy monomer is a kind of viscoelastic process. All the relaxation time τ obtained by simulation was listed in Table 1. Relaxation time τ decrease drastically with the increase in curing temperature and become progressively less sensitive to the curing temperature. This can be attributed to the acceleration of the relaxation movement at higher temperature. The higher the curing temperature is, the more rapid BADCy monomer escape from the cage of PEI. As shown in Table 1, the relaxation time τ of the blend with 25wt% PEI is higher than that of the blend with 20wt% PEI at the same temperature. The difference in the relaxation time for the two blends should be related to the viscosity variation of the sample. Since viscosity of the former was higher owing to its higher ratio of PEI, there appeared the slower relaxation movement

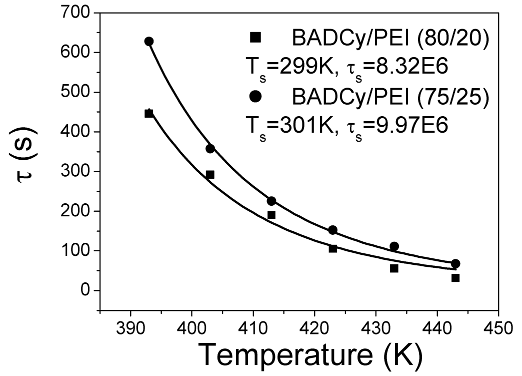


Fig. 4. Plot of relaxation time τ versus temperature. Symbols correspond to experimental data, and lines correspond to the fitting with Eq. (4).

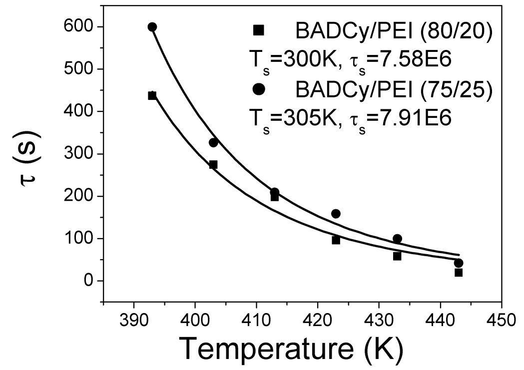


Fig. 5. Plot of relaxation time τ versus temperature. Symbols correspond to experimental data, and lines correspond to the fitting with Eq. (4).

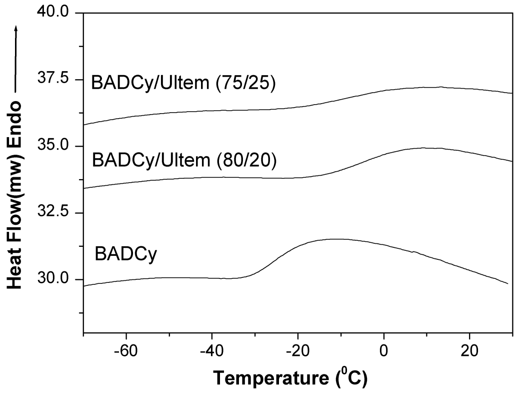


Fig. 6. Glass-transition temperatures of BADCy monomer and the blends.

Table 2
T_s and τ_s obtained from simulation using Eqs. (2) or (3)

	T_s (K)	τ_s (s)
BADCy/PEI(80wt/20wt)	299[a]	8.32×10^6
	300[b]	7.58×10^6
BADCy/PEI(75wt/25wt)	301[a]	9.97×10^6
	305[b]	7.91×10^6

[a] Obtained by the simulation of q_m with Eq. (2).
[b] Obtained by the simulation of I_m with Eq. (3).

of BADCy monomer and the longer relaxation time τ in the blend with 25wt% PEI.

3.3. Fitting with the WLF equation

The temperature superposition principle is usually used to assess the influence of temperature upon the viscoelastic properties of a system. To discuss the viscoelastic effect, relaxation times τ at different temperatures listed in Table 1 were fit with the Williams–Landel–Ferry (WLF) equation:

$$\log\frac{\tau}{\tau_s} = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)}$$

Here, C_1 and C_2 are selected as empirical constants 8.86 and 101.6 K, T_s is the reference temperature (flow temperature of polymer chains or segments, which should be 50 K higher than T_g of the polymer), and τ_s is the corresponding relaxation time at T_s. To simulate the relaxation time τ conveniently, the WLF equation was rewritten in the following form:

$$\tau = \tau_s \exp[-\ln 10 \times 8.86 \times (T - T_s)/(101.6 + (T - T_s))] \quad (4)$$

In Figs. 4 and 5, we find that the simulation results fit the experimental data well, which suggests that relaxation time τ obeys the time-temperature superposition principle and can be described by the Williams–Landel–Ferry (WLF) equation. Furthermore, it can be proved that the coarsening process in phase separation of BADCy/PEI blend is mainly controlled by the viscoelastic flow.

T_s and τ_s obtained from simulation results are listed in Table 2. It is found that T_s or τ_s for the blend with 20 wt% PEI is less than the one for the blend with 25 wt% PEI, which indicates the relaxation movements of BADCy monomer are easier in the former than that in the latter as above discussion indicated.

As indicated above, when C_1 and C_2 in the WLF equation are selected as empirical constants 8.86 and 101.6 K, T_s should be about 50 K higher than T_g. Thus, to discuss the meaning of T_s and corresponding molecular chain or segment which exhibit viscoelastic flow, T_g of BADCy monomer and BADCy/PEI blend were measured by DSC. As shown in Fig. 6, the T_g of the BADCy monomer, the BADCy/PEI (80/20) blend and the BADCy/PEI (75/25) blend are 250, 267 and 268 K, respectively.

In Fig. 6, it is found that T_s is about 50 K higher than T_g of BADCy monomers and about 30 K higher than T_g of BADCy/PEI blend. It is reasonable that T_s is related to the T_g of BADCy/PEI blend because of 'cage effect' of PEI on the relaxation movement of the BADCy monomer. The viscoelastic behavior observed by TRLS should be attributed to the escape movement of BADCy monomers from the so-called 'cage' of PEI through their relaxation movement.

4. Conclusions

Phase separation occurred by a spinodal decomposition (SD) mechanism and final phase inverted morphologies were obtained in the blend with 20 wt% PEI and 25 wt% PEI. The TRLS results indicate that the evolution of scattering vector q_m corresponding to the coarsening process of BADCy droplets follows the viscoelastic relaxation model $q_m(t) = q_0 + A_0\exp(-t/\tau_1)$. Meanwhile, the maximum scattering intensity I_m also follows the viscoelastic relaxation model. $I_m(t) = I_0 + A_0\exp(-t/\tau_2)$. Temperature-dependent relaxation time τ should be the time of escape for the BADCy monomer from the so-called 'cage' of PEI by their relaxation movements. The τ value of the blend with 25 wt% PEI at different temperature is higher than that of the blend with 20 wt% PEI owing to system viscosity variation. The τ value can be described by the WLF equation well, which indicates that the coarsening process in phase separation of BADCy/PEI blend is mainly controlled by relaxation movements. T_s in WLF equation is about 30 K higher than T_g of BADCy/PEI blend and should be related to the T_g of BADCy/PEI blend because of 'cage effect' of PEI on the relaxation movement of the BADCy monomer.

Acknowledgements

This research was supported by the National Nature Science Foundation of China (grant 50273007).

References

[1] Reghunadhan Nair CP, Mathew D, Ninan KN. Adv Polym Sci 2001;155:1.
[2] Fang T, Shimp DA. Prog Polym Sci 1995;20:61.
[3] Woo EM, Shimp DA, Seferis JC. Polymer 1994;35:1658.
[4] Hwang JW, Cho K, Yoon TH, Park CE. J Appl Polym Sci 2000;77:921.
[5] Hwang JW, Cho K, Park CE, Huh W. J Appl Polym Sci 1999;74:33.
[6] Chang JY, Hong JL. Polymer 2000;41:4513.
[7] Chang JY, Hong JL. Polymer 2001;42:1525.
[8] Takao I, Takao K, Toshiyuki O, Masao T. Polym Int 2003;52:773.

[9] Harismendy I, Rio MD, Eceiza A, Gavalda J, Gomez CM, Mondragon I. J Appl Polym Sci 2000;76:1037.

[10] Harismendy I, Rio MD, Marieta C, Gavalda J, Gomez CM, Mondragon I. J Appl Polym Sci 2001;80:2759.

[11] Aoki Y, Tanaka T. Macromolecules 1999;32:8560.

[12] Pathak JA, Colby RH, Kamath SY, Kumar SK, Stadler R. Macromolecules 1998;31:8988.

[13] Tanaka H. J Chem Phys 1995;103:2361.

[14] Polios IS, Soliman M, Lee C, Gido SP, Rohr KS, Winter HH. Macromolecules 1997;30:4470.

[15] Clarke N, McLeish TC, Pavawongsak S, Higgins JS. Macromolecules 1997;30:4459.

[16] Hopkinson I, Myatt M. Macromolecules 2002;35:5153.

[17] Karatasos K, Vlachos G, Vlassopoulos D, Fytas G, Meier G, Du Chesne AJ. Chem Phys 1998;108:5997.

[18] Gan WJ, Yu YF, Wang MH, Tao QS, Li SJ. Macromolecules 2003;36:7746.

[19] Gan WJ, Yu YF, Wang MH, Tao QS, Li SJ. Macromol Rapid Commun 2003;24:952.

[20] Chen WJ, Shen Z, Huang X, Huang J. Macromol Rapid Commun 1997;18:197.

[21] Tanaka H. J Phys: Condens Matter 2000;12:R207.