

Effects of Chain Entanglement on Liquid-Liquid Phase Separation Behavior of LCST-type Polymer Blends: Cloud Point and Decomposition Rate^{*}

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Abstract By preparing homogenous blend samples with different degrees of chain entanglement, we report an anomalous contribution of chain entanglement to phase separation temperature and rate of poly(methyl methacrylate)/poly(styrene-*co*-maleic anhydride) (PMMA/SMA) blends presenting a typical lower critical solution temperature (LCST) behavior. The melt-mixed PMMA/SMA blends with a higher chain entanglement density present a lower cloud point (T_c) and shorter delay time, but lower phase separation rate at the given temperature than solution-cast ones, suggesting that for the polymer blends with different condensed state structure, thermodynamically more facilitation to phase separation (lower T_c) is not necessarily equivalent to faster kinetics (decomposition rate). The experimental results indicate that the lower T_c of melt-mixed sample is ascribed to smaller concentration fluctuation wavelength (λ_m) induced by higher entanglement degree, while higher entanglement degree in melt-mixed sample leads to a confined segmental dynamics and consequently a slower kinetics (decomposition rate) dominated by macromolecular diffusion at a comparable quench depth. These results reveal that the chain packing in polymer blends can remarkably influence the liquid-liquid phase separation behavior, which is a significant difference from decomposition of small molecular mixtures.

Keywords: Chain entanglement; Spinodal decomposition; Concentration fluctuation; Segmental dynamics.

INTRODUCTION

Miscibility/compatibility and phase separation behavior of polymer blends having lower critical solution temperature (LCST) or upper critical solution temperature (UCST) have been investigated extensively^[1–4]. In the past several decades, researchers' attention has been focused on the phase separation mechanism including spinodal decomposition (SD) and nucleation and growth (NG)^[2, 5, 6], thermodynamics of phase separation^[7], kinetics of phase separation^[8, 9] and phase morphology evolution of polymer blends^[10, 11]. The effects of external conditions (shear and electric field *etc.*) on phase separation behavior of polymer blends have also been investigated systematically^[4–6]. Recently, the influence of incorporation of nanoparticles on the phase behavior of polymer blends has also gradually attracted considerable attention^[12–14]. In addition, the viscoelastic phase

^{*} This work was financially supported by the National Natural Science Foundation of China (No. 51173165) and the Fundamental Research Funds for the Central Universities (No. 2013QNA4048).

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Received October 8, 2014; Revised November 26, 2014; Accepted December 15, 2014

doi: 10.1007/s10118-015-1637-8

separation behavior has been widely studied recently owing to its special characteristic resulting from dynamic asymmetry^[15, 16]. Tanaka^[17, 18] investigated this unusual phase separation in polymer solutions systematically by experiments and computer simulations, and the phase inversion in the final stage could be observed. Shi *et al.*^[19, 20] reported the dynamic competition between crystallization and phase separation in dynamically asymmetric amorphous/crystalline polymer blends, and found that viscoelastic phase separation may frustrate crystallization. Although people have made great achievements as mentioned above in the field of liquid-liquid phase separation of polymer blends, there are still some problems unknown and indistinct.

Considering the long-chain nature of macromolecules, it is reasonable that a homogeneous polymer blend may present different chain packings, such as entanglement, orientation *etc.*, which are absent in small molecule mixtures. Although the viscoelastic phase separation behavior has partially demonstrated the differences between macromolecular blend and small molecule mixture systems due to the viscoelasticity of macromolecules^[16, 18], the effect of chain packing on phase separation behavior of polymer blends is ignored and subsequently is still unknown. In our previous work^[21], we have reported that the difference in chain entanglement could lead to a different relaxation and subsequently a different decomposition kinetics in a weakly dynamic asymmetric blend of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-maleic anhydride) (SMA) presenting LCST characteristic. It is generally accepted that the kinetics of phase separation strongly depends on quench depth ($\Delta T = T - T_s$)^[2, 3, 8, 9, 22, 23], where T and T_s are unstable temperature and equilibrium SD temperature, respectively, *i.e.*, the larger the quench depth is, the faster the kinetics of phase separation is. In other words, for LCST-type polymer blends with various compositions, at a given temperature the blend sample with a lower cloud point (T_c) or T_s presents a higher phase separation rate^[24, 25]. Therefore, some questions arise: in the case of polymer blends with the same composition having different condensed state structures, could chain entanglement affect the phase separation temperature? Shall thermodynamically lower T_s be necessarily equivalent to faster decomposition in kinetics under the same phase separation temperature? Without question these are important and unsolved theoretical questions which need further studies to be done.

In this paper, the binary blends composed of PMMA/SMA exhibiting LCST behavior^[26–29] are selected as a model system. As pointed out previously^[21], the blend samples with different degrees of chain entanglement could be prepared through two routes (melt mixing and solution casting). In particular, a 80/20 composition in weight was mainly discussed due to the same trend in other compositions. Considering PMMA/SMA blend is a weakly dynamic asymmetric system, the influence of chain entanglement on phase separation behavior may be obvious and important. Herein we focus on the effects of chain entanglement on T_c and decomposition rate of phase separation in PMMA/SMA blends. Some seemingly anomalous results were reported and discussed on the basis of thermodynamics and kinetics. In addition, the dominant factors of thermodynamics and kinetics difference induced by chain entanglement are also discussed.

EXPERIMENTAL

Materials and Sample Preparation

Poly(methyl methacrylate) (PMMA) (IF850, $M_w = 8.1 \times 10^4$, $M_w/M_n = 1.9$) was purchased from LG Co. Ltd, South Korea, and poly(styrene-*co*-maleic anhydride) (SMA) (210, $M_w = 2.6 \times 10^5$, $M_w/M_n = 3.7$) with MA content of 10 wt% was kindly supplied by SINOPEC Shanghai Research Institute of Petrochemical Technology, China. PMMA/SMA blend films with the weight ratio of 80/20 were prepared by solution casting (marked as “SC”) and melt mixing (labeled as “MM”) respectively. The details of sample preparation about these two routes were described in our previous papers elsewhere^[21, 29]. The films with thickness of about 20 μm were used for light scattering tests and phase contrast microscopy observation, and the ones with about 100 μm in thickness were used for dielectric measurements. All the resultant films were optical transparent, characteristic of homogeneous structure.

Small-angle Laser Light Scattering (SALLS)

Light scattering measurements were carried out on a home-made, time-resolved small-angle laser light scattering

(SALLS) apparatus. The principle and details of the SALLS system are presented in many published papers elsewhere^[22–24]. To determine the cloud point, non-isothermal phase separation measurements were adopted. The film samples were put on a hot stage to be annealed at 160 °C for 10 min, and then heated to 250 °C at various heating rates. Furthermore, isothermal phase separation processes were applied to obtain the delay time and kinetics. The films were first preheated at 160 °C for 10 min, then jumped to the appointed temperatures for isothermal measurements with various time lengths.

Phase Morphology Observation

The phase morphology evolution during isothermal phase separation was observed on phase contrast optical microscope (PCM, BX51, Olympus, Japan) equipped with an Olympus camera. And the temperature was monitored using a temperature-controlled hot stage (THMS600, Linkam Co. UK) with the accuracy about (± 0.1) K. The phase morphology evolution was recorded in real time when the film samples were annealed at 230 °C for various time lengths. All the measurements were performed under nitrogen atmosphere to avoid possible degradation.

Broadband Dielectric Spectroscopy

Dielectric measurements for the blend films were conducted on a Novocontrol Alpha high resolution dielectric analyzer (Novocontrol GmbH Concept 40, Novocontrol Technology, Germany), equipped with a Novocool cryogenic system for temperature control with a precision of (± 0.1) K. The films of approximately 100 μm in thickness were sandwiched between two circular gold electrodes with a diameter of 20 mm. Isothermal frequency sweeps were carried out over a wide frequency range of 10^{-1} – 10^7 Hz in the temperature range of 90–160 °C.

THEORETICAL BACKGROUND

The linear Cahn-Hilliard theory can be used to describe the scattering intensity evolution at the early stage of phase-separation for binary polymer blends^[30, 31]. Considering the thermal fluctuation of stable binary polymer blends, Cook^[32] modified the Cahn-Hilliard function into

$$I(q, t) = I_s(q, 0) + [I(q, 0) - I_s(q, 0)] \exp[2R(q)t] \quad (1)$$

where $I_s(q, 0)$ is the scattering intensity of the stable system, $q = (4\pi/\lambda)\sin(\theta/2)$ is the wavenumber of the spatial composition fluctuation, λ is the corresponding wavelength and θ is the scattering angle. The relaxation rate or amplification factor, $R(q)$, is further related by

$$R(q) = -Mq^2 \left(\frac{\partial^2 f_m}{\partial \phi^2} + 2\kappa q^2 \right) \quad (2)$$

in which, M , ϕ , κ , f_m are the mobility coefficient of molecules, the volume fraction, the gradient energy coefficient and the mean field free energy of mixing, respectively.

Equation (2) includes the apparent diffusion coefficient D_{app} , which describes the uphill diffusion during spinodal decomposition.

$$D_{\text{app}} = -M \frac{\partial^2 f_m}{\partial \phi^2} \quad (3)$$

From Eq. (1), one can find that plots of $\ln(I(q, t) - I_s(q, 0))$ versus t yields $R(q)$, and then from Eq. (2) and Eq. (3), one can obtain the values of D_{app} from the intercepts of the plots of $R(q)/q^2$ versus q^2 .

RESULTS AND DISCUSSION

Homogenous PMMA/SMA Blends with Different Degrees of Chain Entanglement

We prepared two PMMA/SMA (80/20) blend samples with different degrees of chain entanglement to explore

the influence of chain packing on liquid-liquid phase separation. As discussed in our previous work^[21], the plateau modulus $G_{N\text{exp}}^0$ and crossover modulus G_x are higher for melt-mixed blends than solution-cast ones, corresponding to lower entanglement molecular weight and higher chain entanglement density. It is generally accepted that the polymer chains are entangled each other in molten state, provided that the molecular weight is higher than the critical entanglement molecular weight. On the other hand, as discussed in our previous study^[33], the polymer chain architecture is likely to be in an extended conformation in a good solvent, and then the resultant dried films can carry some memory of the polymer chain conformation from the original solution due to the fact that polymer chains may not have enough time to relax and approach equilibrium during the rapid drying process in solution casting. Accordingly, the films prepared by solution casting present a lower entanglement density compared to the melt-mixed samples, which can be ascribed to the salvation and memory effects. In order to guarantee all the test results are comparable, the initial state of PMMA/SMA blend samples should be homogenous and consistent in whole. Figure 1 shows the scattering patterns and the relative intensity versus q for as-prepared blend films. It can be found that for the initial samples, the scattering intensity is almost equal to zero and independent of q . Once there exists a weak inhomogeneity of the samples, a scattering peak can be detected, such as the early stage of SD for PMMA/SMA blends, as shown in the inlay of Fig. 1. Hence, it is meaning that the blends prepared by solution casting and melt mixing are homogeneous. Moreover, these results can be further confirmed from the phase morphology observation by PCM (Figs. 7a and 7a'), which will be discussed in the following section. Therefore, based on the above results, considering the wavelength of laser light (632.8 nm) and measurement limitation of SALLS, one can conclude that the initial structure of solution casting and melt mixing PMMA/SMA blends are consistent. In other words, there is no difference in the initial heterogeneity of samples, so the phase separation temperature and kinetics in the following discussion are comparable and reliable.

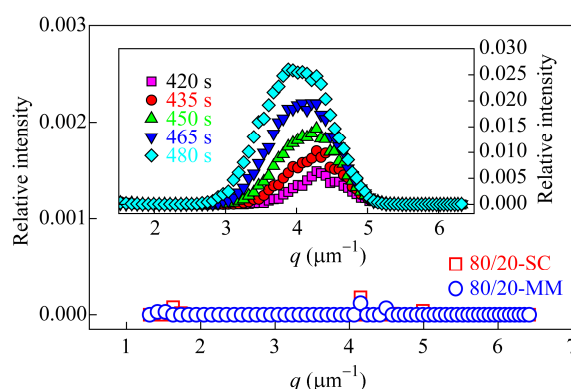


Fig. 1 The relative intensity versus q for initial PMMA/SMA blend films measured at 30 °C. The inlay presents the time evolution of relative intensity for PMMA/SMA blends during the isothermal phase separation at 230 °C.

Phase Separation Temperature

First, the effect of chain entanglement on the cloud point (T_c) of PMMA/SMA blends during heating phase separation was investigated. Figure 2 shows the heating rate dependence of T_c for PMMA/SMA blends. As described in our previous finding^[29], in order to exactly compare the scattering intensity and avoid the negative effect of sample diversity, the normalized scattering intensity $I_N(t)$ at a given scattering vector $q(t)$ is used to determine T_c . From Fig. 2, an obviously nonlinear relationship between T_c and heating rate is observed, indicating that the actual equilibrium value of T_c can not be obtained from conventional linear extrapolation, as pointed out by previous literatures^[34, 35]. However, an interesting phenomenon is noted that T_c of melt-mixed blends is lower than that of solution-cast ones at all heating rates under investigation, meaning that phase separation in melt-mixed samples is more inclined to take place. This may be mainly ascribed to the critical

concentration fluctuations differences induced by chain entanglement at the early stage of SD, which will be discussed in detail in next section. This is similar to the result reported by Clarke *et al.*^[36], who found that the phase diagrams of entangled polymer blends could be changed in the presence of shear flow. Besides, the inhomogeneity degree might be also considered, unfortunately, the extremely little difference is detected.

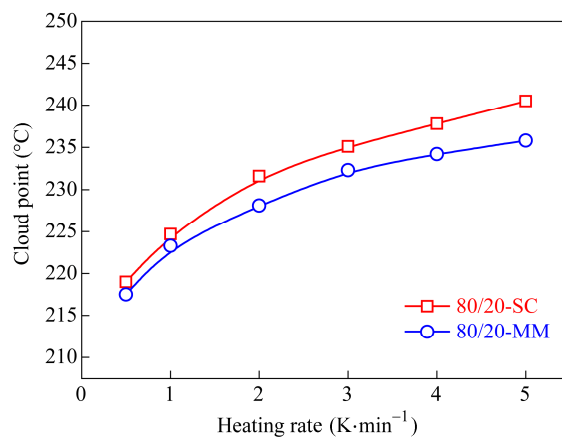


Fig. 2 Heating rate dependence of cloud point for PMMA/SMA (80/20) blends

In polymer solutions, Yang *et al.*^[37] reported that the entanglement of poly(vinyl methyl ether) (PVME) obviously affected the phase separation of poly(ethylene oxide) (PEO) in PVME/PEO aqueous solutions. In polymer blends, Kumar *et al.*^[38] found that brominated isobutylene-*co-p*-methylstyrene rubber and phenol formaldehyde resin blends exhibit very limited compatibility with each other and even phase separation takes place due to increasing the entanglement and network density, which is consistent with our result of lower T_c in melt-mixed blends corresponding to higher entanglement density. Additionally, more complicated effect could be found in hyperbranched polymer/linear polymer/solvent ternary blends, namely, the increase of entanglement does not monotonously reduce the compatibility^[39]. Considering the above results, one can conclude that the compatibility or phase separation temperature could be affected by chain entanglement.

The initial concentration fluctuations could affect the equilibrium phase separation temperature and phase kinetics^[40–43]. As pointed out above, the distinct T_c between two blends at the same heating rate clearly reflects some difference in macromolecular entanglement of PMMA/SMA blends. Hence, it is proposed that the different degrees of macromolecular entanglement have a remarkable effect on critical concentration fluctuations and subsequently lead to the different T_c . Moreover, the difference of T_c gap between two blends is becoming smaller with decreasing heating rate, which can be attributed to long time annealing effects. Sauer *et al.*^[44] reported that melt preannealing at temperatures above glass transition temperature (T_g) is required to attain an equilibrium entanglement density. In our previous work, we also found that PMMA/SMA blends annealed at $T > T_g$ could make them approach the equilibrium state^[21, 33, 45]. Low heating rate indicates a longer annealing time, and both systems approach the equilibrium state, hence, the T_c differences between two blends decrease.

Delay Time of Phase Separation

As discussed above, T_c is much different for PMMA/SMA blends with different chain entanglement structures during non-isothermal phase separation experiments. What is the situation in isothermal phase separation? Figures 3(a) and 3(b) show the time evolution of $I_N(t)$ for PMMA/SMA (80/20) blends during isothermal annealing at 230 °C and corresponding delay time under various isothermal tests. The delay time (τ_d) is defined as a period from jumping to a given temperature to the time when apparent phase separation occurs, *i.e.*, a scattering circle appears and the scattering intensity begins to increase, as shown in Fig. 3(a). The delay time can be theoretically predicted^[46], and Pavawongsak *et al.*^[47] suggest that this is due to the formation of a temporary network of the well entangled polymer which needs to relax before phase separation can occur. It can be noted

that τ_d of melt-mixed blends is shorter than that of solution-cast samples under all temperatures investigated, meaning that melt mixed blends are more inclined to phase separation, consistent with the T_c results. This is also similar to the result of the effect of mesoscopic fillers on the polymerization induced viscoelastic phase separation, a significant enhancement effect can be found due to the strong polymer chain entanglement resulted in enwrapped mesoscopic fillers^[48].

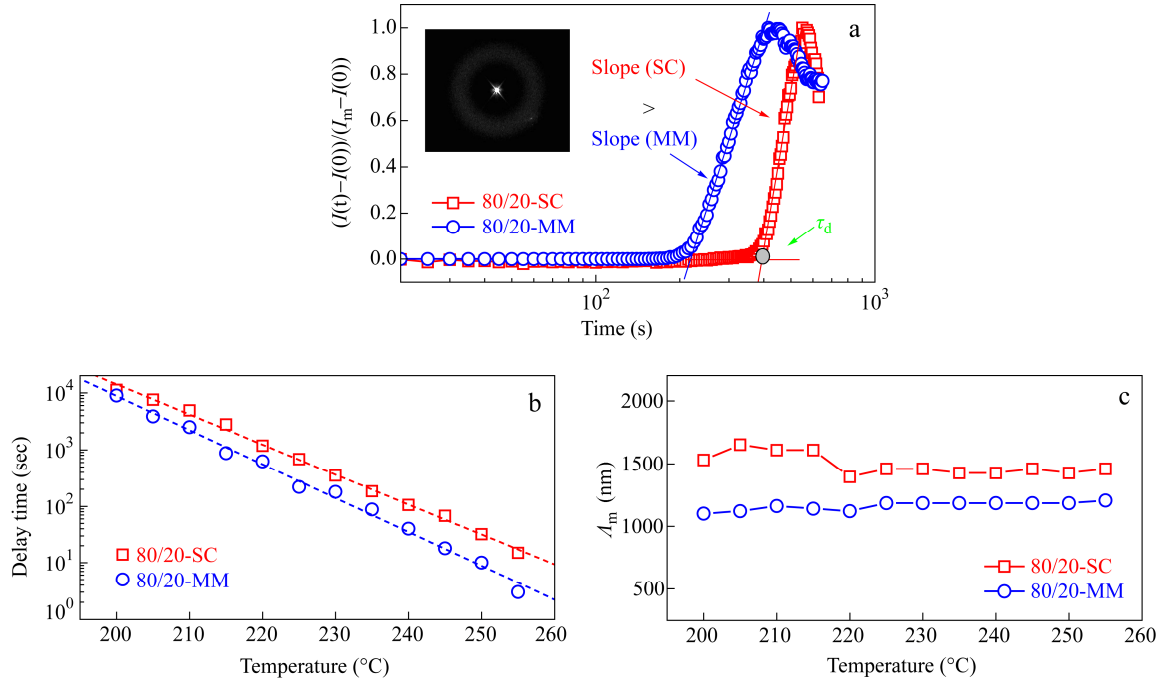


Fig. 3 (a) Time evolution of normalized scattering intensity for PMMA/SMA (80/20) blends at 230 °C (The inlay presents the scattering pattern at the early stage of phase separation for PMMA/SMA (80/20-SC) blend at 230 °C.); (b) Semi logarithmic plots of delay time against isothermal phase separation temperature for PMMA/SMA blends; (c) Concentration fluctuation wavelength λ_m of PMMA/SMA blends at the early stage of SD

At the early stage of SD, the time evolution of the concentration fluctuations follows the linear theory proposed by Cahn^[31]. The concentration fluctuation wavelength λ_m ($\lambda_m = 2\pi/q_m$, where q_m is the maximum scattering vector) keeps constant and the amplitude of concentration fluctuations $\Delta\phi(t)$ grows with time. Pincus^[42] predicted that the unstable wavelength $2\pi/q$ is on the order of ideal chain radius (R_0). de Gennes^[40] reported that the fluctuations of long wavelength $2\pi/q$ are expected to relax by a reptation process. λ_m values of PMMA/SMA (80/20) blends at the early stage of SD under various isothermal temperatures are presented in Fig. 3(c). It can be seen that λ_m of melt-mixed blends is lower, which could reflect the thermodynamic differences of phase separation, indicating that the fluctuation period is shorter and phase separation is more inclined to take place for melt-mixed blends, in good agreement with the T_c and τ_d results. Moreover, the equilibrium SD temperatures are closely related to the contributions of critical concentration fluctuations^[49, 50]. Hence, based on the above results and discussion, due to the chain entanglement differences, we can conclude that the critical concentration fluctuations and wavelength of melt-mixed blends are lower, subsequently, phase separation is more inclined to take place, corresponding to lower T_c and shorter τ_d . Additionally, λ_m is virtually independent of quench depth for both melt-mixed and solution-cast blends, the same as the apparent independence of q_m from quench depth reported in other blend system^[7].

Phase Separation Kinetics

Furthermore, as shown in Fig. 3(a), it should be pointed out that the slopes of scattering intensity growth are much different between melt-mixed and solution-cast PMMA/SMA blends, suggesting that the kinetics of phase

separation are inconsistent. Hence, the effect of chain entanglement on kinetics of phase separation should be discussed in detail. The linear Cahn-Hilliard theory modified by Cook (as shown in the Section 3) can be used to describe the kinetics at the early stage of SD for binary polymer blends^[30–32]. According to Eq. (1), the values of $R(q)$ can be obtained from the initial slopes of $\ln(I - I_s)$ versus time curves. In accordance with Eq. (2), $D_{app}(T)$ at various temperatures can be obtained from the intercepts of the plots of $R(q)/q^2$ against q^2 . The details of these plots are not presented herein, while can be seen in our previous work^[29]. Figure 4 represents the temperature dependence of apparent diffusion coefficient ($D_{app}(T)$) for PMMA/SMA blends. It is obvious that $D_{app}(T)$ strongly depends on quench depth, nearly exponential functions can be observed, indicating that it is impossible to obtain equilibrium SD temperature *via* linear extrapolation of $D_{app}(T)$ to zero reported in other blend systems^[22, 51]. Furthermore, it should be noted that $D_{app}(T)$ of melt-mixed blends is lower than that of solution-cast samples, meaning a lower phase separation rate, which seemingly contradicts with the results of lower T_c and shorter τ_d for melt-mixed blends. Actually, these results are reasonable because T_c and τ_d depend on thermodynamics, while kinetics of phase separation is dominated by diffusion related to segment motion. The result of phase separation kinetics is consistent with the entanglement effect reported in the previous literatures^[52, 53]. Furthermore, phase separation kinetics is influenced by quench depth ($\Delta T = T - T_s$). Herein T_s is replaced by T_c at the lowest heating rate (T_{c0}) because T_s is impossible to be obtained by linear extrapolation mentioned above. Provided that the temperature is identical, ΔT is larger for melt-mixed blends due to lower T_{c0} , but the value of D_{app} is lower than solution-cast ones. Hence, the phase separation rate of melt-mixed blends is much lower at a same given quench depth, further verified that the phase separation rate is lower for melt-mixed blends than solution-cast ones.

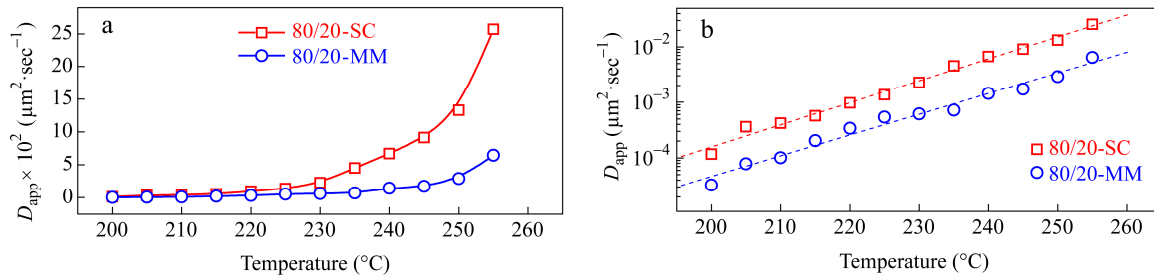


Fig. 4 (a) Temperature dependence of D_{app} and (b) semi logarithmic curve of temperature dependence of D_{app} for PMMA/SMA (80/20) blends (Reprinted from Ref.[21]; Copyright (2012), with permission from Elsevier)

It is generally accepted that the phase separation is indeed a synchronous process containing disentanglement and diffusion *via* segment motion. Hence, to further discriminate the essence of kinetics differences, the segmental dynamics of PMMA/SMA blends was investigated using broadband dielectric spectroscopy. The empirical Havriliak-Negami (HN) function was used to analyze the dielectric loss of the complex dielectric function^[54].

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{HN})^{\alpha_{HN}}\right]^{\beta_{HN}}} \quad (4)$$

where ω is angular frequency ($\omega = 2\pi f$), $\Delta\varepsilon$ is the dielectric strength, ε_∞ is the unrelaxed ($\omega = \infty$) value of the dielectric constant, and τ_{HN} is the HN characteristic relaxation time. The exponents α_{HN} and β_{HN} ($0 < \alpha_{HN}, \alpha_{HN}\beta_{HN} \leq 1$) are shape parameters which describe the symmetric and asymmetric broadening of the relaxation time distribution, respectively. Furthermore, τ_{HN} is related to τ_{max} corresponding to the maximum of the dielectric loss by the equation

$$\tau_{\max} = \tau_{\text{HN}} \left(\sin \frac{\alpha_{\text{HN}} \beta_{\text{HN}} \pi}{2(\beta_{\text{HN}} + 1)} \right)^{1/\alpha_{\text{HN}}} \left(\sin \frac{\alpha_{\text{HN}} \pi}{2(\beta_{\text{HN}} + 1)} \right)^{-1/\alpha_{\text{HN}}} \quad (5)$$

The quantitative information from the isothermal dielectric spectra can be extracted by HN fittings, as shown in Fig. 5. It can be seen that the α -relaxation peak associated with segment motion shifts to lower frequency for melt-mixed PMMA/SMA blends, meaning an increased relaxation time and decreased segment motion ability. Figure 6 shows the temperature dependence of $\tau_{\max}$ of the α -relaxation for PMMA/SMA blends. It can be observed that $\tau_{\max}$ in solution-cast blends is shorter under various temperatures, which is ascribed to the lower chain entanglement density^[21]. Considering the above discussions, the chain entanglement density is higher in melt-mixed blends and the segment motion should overcome the chain entanglement resistance, subsequently the segment motion decreases. On the other hand, the diffusion rate is dominated by segment motion, accordingly, the kinetics of phase separation in melt-mixed blends is lower due to the higher chain entanglement density and lower segmental dynamics.

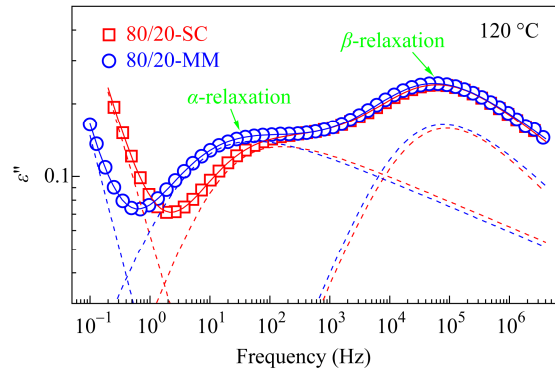


Fig. 5 Dielectric loss ε'' as a function of frequency for PMMA/SMA (80/20) blends at 120 °C (The short dash curves represent HN fittings of the experimental data.)

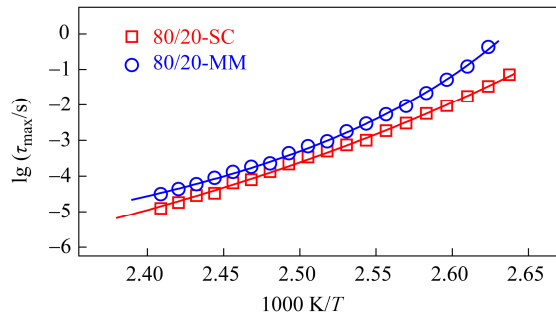


Fig. 6 Relaxation time of the α -relaxation process as a function of temperature for PMMA/SMA (80/20) blends

It is well known that strong dynamic asymmetry between two components of polymer solutions^[17, 18] or binary polymer blends^[15, 16, 19, 20] could lead to unusual phase separation (viscoelastic phase separation) behavior, which is essentially different from the conventional classification of phase separation. Subsequently, the thermodynamics and kinetics of phase separation might be inconsistent. However, the PMMA/SMA blend investigated here is a weak dynamic asymmetry system^[28, 33, 45]. In this study, chain condensed structure is mainly focused, and dynamic asymmetry is not a key factor herein. Hence, considering the above results and discussion, the thermodynamics and kinetics of liquid-liquid phase separation in PMMA/SMA blends are mainly influenced by chain entanglement.

Phase Morphology Evolution

In order to further verify the thermodynamics and kinetics differences of phase separation between melt-mixed and solution-cast PMMA/SMA blends, the phase morphology evolution was observed during isothermal phase separation, as shown in Fig. 7. The initial morphology of blend is uniform, and homogeneous structure can be observed (Figs. 7a and 7a'). The bicontinuous phase structure could be observed when apparent phase separation occurs (Figs. 7b and 7b'). With phase separation proceeding, bicontinuous structure remains and the domain size grows (Figs. 7c and 7c'), characteristic of SD mechanism. Finally, the sea-island structure forms at the later stage of SD (Figs. 7d and 7d'). Additionally, it should be pointed out that the time is shorter when apparent phase separation could be detected by PCM (Figs. 7b and 7b') in melt-mixed blends, consistent with the lower T_c and shorter τ_d results discussed above. However, the time is longer for melt-mixed blends when the phase structure reaches the same domain sizes (Figs. 7c, 7c', 7d and 7d'), suggesting that the phase separation rate is slower in melt-mixed blends, in good agreement with the above kinetics results. Through numerical simulations,

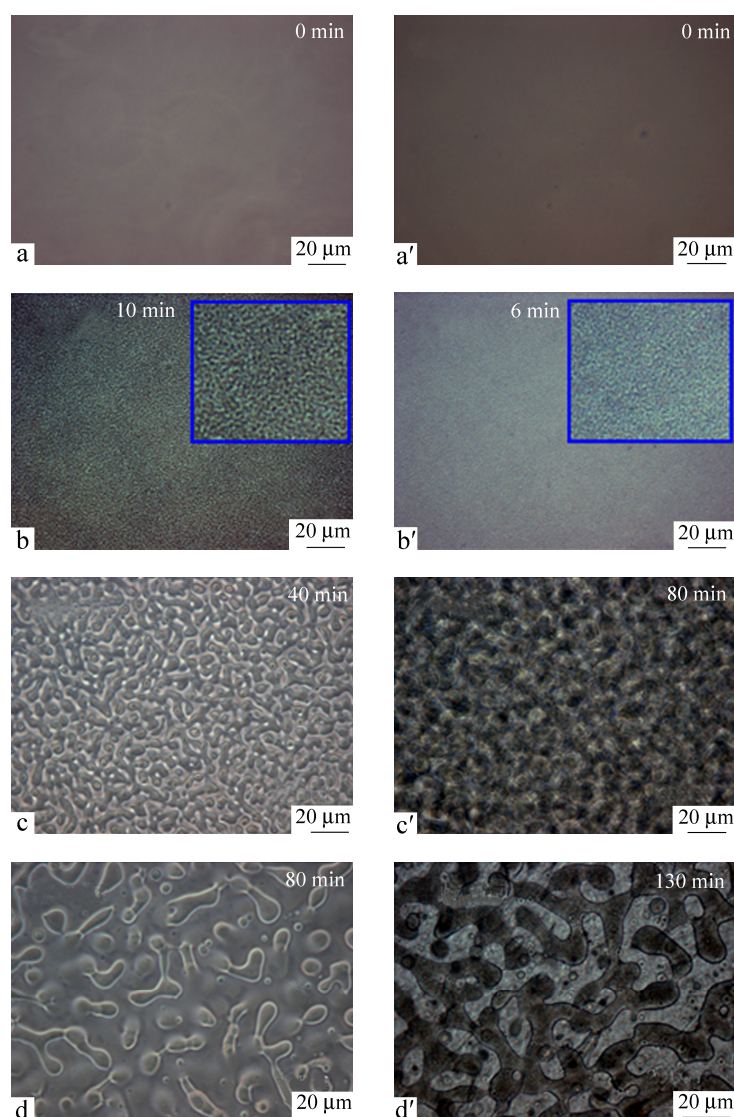


Fig. 7 The phase morphology of PMMA/SMA 80/20-SC (a, b, c, d) and 80/20-MM (a', b', c', d') blends subjected to isothermal phase separation at 230 °C for various time (The inlays of (b) and (b') present the partial enlargement of the phase morphology.)

Cao *et al.*^[55] predicted that the intermediate stage of SD was prolonged with enhanced entanglement effects. The slow down of the phase separation dynamics in the later stage of SD was also observed in binary liquid polymer mixtures^[56]. Hence, the result of entanglement effects on phase morphology evolution presented here is conceivable. In the latest interesting finding reported by Nurkhamidah *et al.*^[57], even the formation of phase separation morphology in UCST-type blend system could be very different resulting from entanglement density difference.

CONCLUSIONS

In summary, by means of preparing the polymer blends with different degrees of chain entanglements, the effects of chain entanglement on thermodynamics and kinetics of liquid-liquid phase separation were demonstrated in detail. The thermodynamics of phase separation could be influenced by chain entanglement, resulting in the lower critical concentration fluctuations and wavelength in melt-mixed blends, subsequently the cloud point is lower and delay time is shorter. However, the phase separation rate of melt-mixed samples is slower than that of solution-cast blends. Lower equilibrium SD temperature thermodynamically is not equivalent to faster kinetics of phase separation in the same composition polymer blends with different condensed structure. The kinetics is strongly dependent on diffusion dominated by segmental dynamics confined by chain entanglement.

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