Macromolecules **2008**, *41*, 7469−7477

Layered Structure Formation in the Reaction-Induced Phase Separation of Epoxy/Polyimide Blends

Fenghua Chen,[†] Tongchen Sun,[†,‡] Song Hong,[†,‡] Kun Meng,[†] and Charles C. Han*[,†]

State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China, and Graduate School of Chinese Academy of Sciences, Beijing 100190, China

Received March 22, 2008; Revised Manuscript Received September 1, 2008

ABSTRACT: A fluorinated polyimide was employed to investigate reaction-induced phase separation of epoxy/polyimide blends. Three distinct morphological structures were obtained. Among these, an unusual three-layered structure was observed in a certain polyimide concentration range. The polyimide-rich phase was mainly localized in the middle layer and the outer layers were epoxy-rich. The thickness of the outer layers (10−30 μm) was much larger than the characteristic length of the bicontinuous domains in the middle layer. In the lower polyimide concentration range, polyimide-rich particles formed in the epoxy-rich matrix as aggregates without further coalescence. At higher polyimide concentrations, polyimide-rich phase formed continuous domains while epoxy-rich phase formed connected nonspherical particles. Evolution of the layered structure was elucidated from scanning electron micrographs. No layer existed in the sample before phase separation began. The reaction conversion of epoxy was very low when layers started to form. During that period, the outer layers thickened rapidly. The mechanism of this unusual layered structure formation was discussed based on the characteristics of this epoxy/polyimide system. Also a refractive index cross-over was observed which was caused by the gradual increase of the refractive index of epoxy during the isothermal curing process.

Introduction

Epoxies are widely used as thermoset resins in the aerospace and electronic applications due to their excellent thermal and dimensional stabilities, high modulus, and good solvent resistance. However, epoxy resins are inherently brittle, which necessitates the toughening modification. Various materials have been used in the toughening of the epoxy resins.[1−20] Polyimides, which have high glass transition temperatures (T_g) and high thermal and mechanical stabilities, are useful tougheners for the epoxy resin.[13−16]

When a second polymer component is introduced into the epoxy resins, phase separation usually occurs during the curing reaction. Since morphology has a significant influence on the performance, structure evolution during reaction-induced phase separation is an important and active area of research.[21−23] Various morphologies have been observed for the epoxy/polyimide systems with different compositions: polyimide-rich particles dispersed in the epoxy-rich matrix when the initial polyimide (PI) concentration was less than 10 wt %; a continuous PI-rich phase when the initial concentration of PI was more than 30 wt %; and a bicontinuous structure in the intermediate concentration range.[21] Besides the above morphologies, i.e., dispersed and bicontinuous, Kim et al. observed a dual phase morphological structure where the former two kinds of morphologies coexisted.[22] With the change of the mixture components, e.g., with or without accelerator for the anhydride cured epoxy system, different morphological structures were obtained. These structures included spherical PI-rich particles with no accelerator, and large irregular-shaped PI-rich domains with the addition of accelerator, which resulted in a nearly cocontinuous structure.[23]

We studied the morphology of phase separated epoxy/PI system for wide concentration and curing temperature range by scanning electron microscopy and light scattering. We paid special attention to the unusual three-layered structure previously reported.[24] In this paper we studied the kinetics and mechanism of this unusual layered structure and the conditions of its formation. We believe this structure offers a special advantage in applications for the inter fiber lamella toughening for multilayered fiber composites.

Experimental Section

Materials. Diglycidyl ether of bisphenol A (DGEBA), with epoxide equivalent weight of 189 from Shell Chemical Co. (Epon 828), and 4,4′-diaminodiphenyl sulfone (DDS), of 97% purity from Sigmma-Aldrich Chem. Co. were both used as received. The polyimide was synthesized from 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 4,4′-methylene dianiline (MDA), with the procedure described in a previous paper,[24] and had a number average molecular weight $M_n = 2 \times 10^4$. T_g of the polyimide (6FDA-MDA) was about 270 °C, measured with a differential scanning calorimeter (Diamond DSC, Perkin-Elmer Co.). The chemical structures were schemetically shown in Figure 1.

Sample Preparation. A transparent homogeneous mixture of DGEBA, DDS and 6FDA-MDA was obtained by casting from a 10 wt % (total weight of solutes in the solution) tetrahydrofran (THF) solution. The mixing ratio of DGEBA:DDS was fixed at 1:0.27 by weight, which corresponded to 0.8 hydrogens of amino groups per glycidyl group.[25] The cast film was dried under reduced pressure at room temperature for 2 h. The mixture was then sandwiched between a glass slide and a cover glass with poly(tetrafluoroethylene) spacer of 100 μm in thickness.

Surface Modification of the Glasses. In addition to the as-received glasses, glasses modified with a silane agent were also used as the hydrophobic substrates. Clean slides were soaked in piranha solution (H_2SO_4:H_2O_2 = 3:1 by volume) at 85 °C for 1.5 h, washed and immersed in the 0.1 mol/L silane solution, which was prepared from trichloro(octadecyl)silane ($C_{18}H_{37}SiCl_3$) dissolved in hexane, at ambient temperature for 4 h. Afterward, the glasses were rinsed with hexane, acetone and deionized water in sequence and dried under a flow of ultrahigh purified nitrogen. The surface

---

* To whom correspondence should be addressed. Telephone: +86 10 82618089. Fax: +86 10 62521519. E-mail: c.c.han@iccas.ac.cn.
[†] Institute of Chemistry, Chinese Academy of Sciences.
[‡] Graduate School of Chinese Academy of Science.

10.1021/ma801213n CCC: $40.75

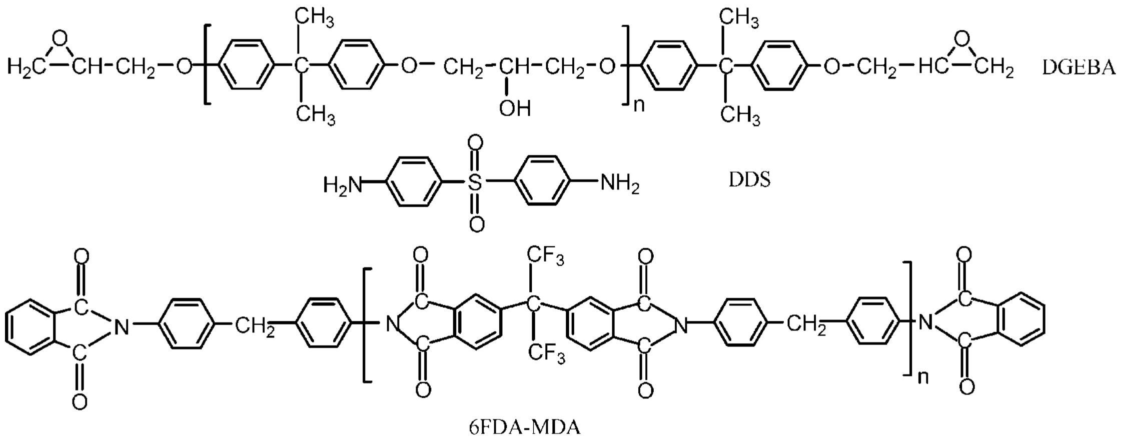
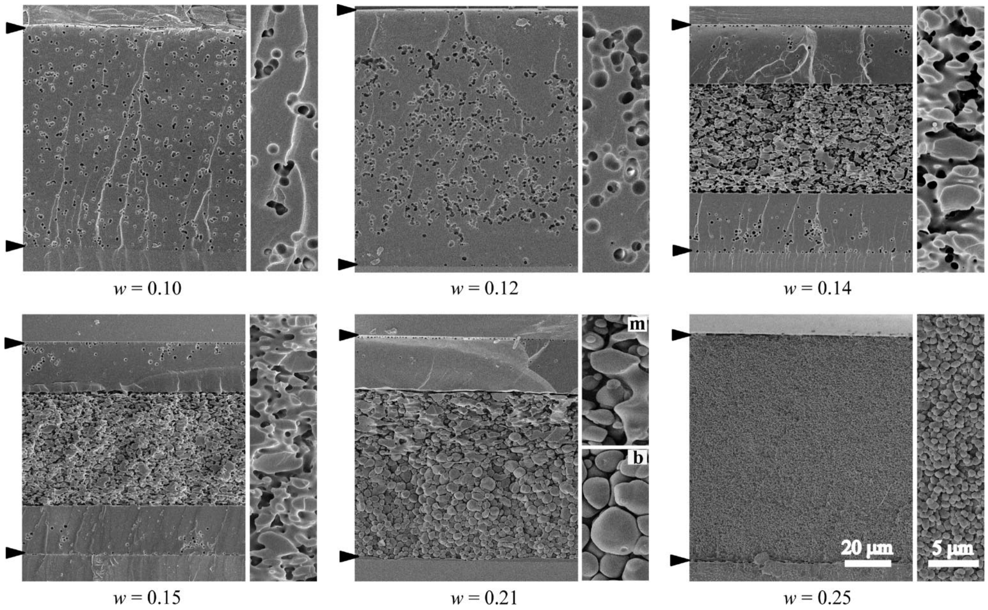


Figure 1. Schematic chemical structures of epoxy resin (DGEBA), 4,4′-diaminodiphenyl sulfone (DDS) and polyimide (6FDA-MDA).



$w = 0.10$ $w = 0.12$ $w = 0.14$

$w = 0.15$ $w = 0.21$ $w = 0.25$

Figure 2. Scanning electron micrographs of fractured surfaces of epoxy/PI blends with different PI weight fractions w. All samples were cured at 130 °C for 1440 min. Arrows indicate the location of the glass surfaces. The picture on the right in each panel is a higher magnification of the middle part. For $w = 0.21$, higher magnifications at two different locations, the middle (m) and the bottom (b) parts, are shown. THF etching removes the PI-rich domains, corresponding to the voids in the pictures.

characteristics were determined by sessile-drop contact-angle measurement with a homemade instrument. The water contact angle of the treated glasses was around 110°.

Measurements. Samples were cured in heating blocks controlled at the desired temperatures and then fractured with the glasses in liquid nitrogen. For most of the samples, the fractured surfaces were etched in THF at room temperature for 10 min. For samples cured at 115 °C for short times, with conversion of the epoxy being very low, the samples were peeled off from the substrates in liquid nitrogen and no etching treatment was followed. All the sample surfaces were coated with platinum and observed with a scanning electron microscope (SEM) (JEOL JSM 6700F).

For transmission electron microscopy observation, the sample peeled off from the glasses in liquid nitrogen was then microtomed in the cross direction from the middle part of the film, using a Leica EM UC6 ultramicrotome. The microtomed film, 100 nm thick, was observed with a transmission electron microscope (TEM) (JEOL JEM-2200FS).

A homemade time-resolved light scattering (TRLS) instrument with a temperature controlled hot chamber was used to monitor the reaction-induced phase separation. Wavelength of the incident laser beam was 532 nm. The samples were prepared using the same method as described above, while thickness of the sandwiched spacer was reduced to 50 μm. The sample was positioned with surface normal to the incident beam during the curing process and central part with morphology dimension commensurate with the q-range of our TRLS detection system (0.1 $\mu\text{m} < q^{-1} < 2.5\ \mu\text{m}$) was detected. Detector images were recorded every 20 s for the sample cured at 115 °C.

Reaction conversion of epoxy was determined by titration. Samples with PI weight fraction of $w = 0.15$ cured at 115 °C for different times were dissolved in chloroform or the mixture of chloroform with chlorobenzene (1:1 by volume) and then titrated with hydrogen bromide in glacial acetic acid. Crystal violet was added as indicator. The unreacted epoxide content was calculated according to the test method ASTM D1652.

Results and Discussion

Figure 2 shows scanning electron micrographs of fractured surfaces at different PI weight fractions and cured at 130 °C for 1440 min. PI-rich domains at the fractured surface were removed with THF, so that they correspond to voids in the pictures. The experiments were repeated to confirm the reproducibility of the structures.[24] SEM images in Figure 2 showed that several distinct morphologies were obtained, i.e. PI-rich particles in clusters formed in the low w range, an unusual layered structure formed in the relatively intermediate w range and PI-rich continuous structure formed in the higher w range. The unusual layered structure had not been reported by other researchers. In this work, we carried out a series of experiments to understand the layered structure formation.

The three-layered structure was observed in the PI weight fraction range of $0.14 \leq w < 0.21$. Boundaries between the layers were sharp and parallel to the film surfaces. The outer layers, with thickness ranged from 10 to 30 μm, were composed of mostly epoxy-rich phase with only a few PI-rich particles. Almost all of the PI-rich domains were localized in the middle region, where bicontinuous domains formed with a characteristic length much smaller than the thickness of the outer layers.

In the lower concentration range, e.g., $w = 0.10$, the PI-rich phase formed discrete spherical domains, i.e. particles, with a relatively narrow size distribution. Some PI-rich particles adhered together and formed aggregates (clusters) without further coalescence, which could be observed throughout the sample. Similar adhered-together particles have been shown in other epoxy/PI blends.[12,26] At $w = 0.12$, the PI-rich particles were aggregated and connected into larger clusters. Coalescence of the particles partly occurred but shape and size of each particle were still recognizable.

At higher concentrations, e.g. $w = 0.25$, PI-rich phase formed continuous domains extending over the whole film thickness, and the epoxy-rich phase presented as nonspherical particles. Similar morphological structure was observed at $w = 0.22$, 0.30, and 0.50. The typical size of epoxy-rich particles decreased with the increase of PI content, 1 μm at $w = 0.25$ and 0.30 while 0.2 μm at $w = 0.50$. The epoxy-rich particle morphology has been reported in other epoxy/PI blends at relatively high PI concentrations.[22]

Several morphological structures were observed at $w = 0.21$. Two layers were locally formed instead of three layers. An epoxy-rich layer was localized at the top of the sample. Two different domain structures formed in the lower layer. Bicontinuous domains formed next to the epoxy-rich layer and epoxy-rich particles formed in the region far from the epoxy-rich layer. Also, structures of epoxy-rich particles distributed from the top to the bottom of this sample and three layers including very thin outer epoxy-rich layers (several micrometerss) and epoxy-rich particles distributed in the thick middle layer were observed. In other repeated experiments carried out at $w = 0.21$, the two layer structure was observed all over the sample, with the epoxy-rich layer located on the bottom and bicontinuous domains in the phase separated layer similarly formed in the region next to the epoxy-rich layer.

Temperature influence on the morphological structures was studied and the results were shown in Figure 3. Three-layered structure was observed for all the temperatures investigated in the case of $w = 0.15$. Thickness of the middle layer decreased with the increase of temperature. Epoxy-rich particles with similar shape to that formed at $w = 0.25$ and $T = 130$ °C existed in the middle layer for $w = 0.15$ at higher temperatures. The higher the temperature was, the larger epoxy-rich particles coarsened in the middle layer. However, bicontinuous phase domains of the middle layer were always recognizable.

On the edge of the composition region where layered structure was observed, e.g., at $w = 0.14$, the three-layered structure again formed at 160 °C. However, PI-rich aggregated particles and three-layered structure with relatively thin middle layer coexisted at 180 °C. At 200 °C, PI-rich particles and a multilayered structure formed. These multi layers occurred unexpectedly. As shown in the SEM image, one layer was epoxy-rich with a few dispersed PI-rich particles, and next layer consisted of PI-rich continuous phase with epoxy-rich particles. The layers alternated and formed a five layered structure.

After the sample $w = 0.21$ was cured at 160 °C, three layers including thin outer epoxy-rich layers and a middle layer with epoxy-rich particles, resembling that observed at $T = 130$ °C, formed. This three-layered structure also consisted of a bicontinuous structure in the middle layer and epoxy-rich particles, with a much wider size distribution than that at lower temperatures, coexisting as the outside layers.

At 180 °C, the three-layered structure also formed, but the structures in the middle layer varied greatly. Some parts of the middle layer showed a bicontinuous structure; while other parts contained two distinct domains, i.e. bicontinuous structure in the region near the epoxy-rich layers and packed epoxy-rich particles in the middle.

At 200 °C, a two-layered structure similar to that obtained at 130 °C was observed. However, multi layers again formed, where the epoxy-rich layers were localized near to the surface and in the middle part of the sample film and epoxy-rich particles were packed in the PI-rich matrix in other layers.

In the lower PI concentration range, e.g. $w = 0.12$, clusters of PI-rich particles in epoxy-rich matrix were formed at all of the temperatures. With the increase of curing temperature, the average cluster size decreased, while the extent of coalescence of the particles increased. Similar phenomenon was observed at $w = 0.10$ (results were not shown).

In the case of $w = 0.25$, phase separated structure similar to that formed at $T = 130$ °C was observed at all temperatures. Average size of the packed epoxy-rich particles increased slightly with the increase of temperature. We believe that in most cases the epoxy-rich domains appeared as if they were discrete particles but actually they were gelled together because they always stayed together even after the samples were washed with THF and the PI-rich phase was removed. We think that, due to the high viscosity of PI, it was difficult for the epoxy-rich particles to coarsen even if they had some contact and connection among the domains. The hindered droplets coalescence observed in the polycarbonate/deuterated poly(methyl methacrylate) blends[27] might be similar to this phenomenon. However, the droplets in that work did not coalesce possibly due to a copolymer layer formation at the interface between the phase-separating blend components.

The appearance of three-layered structures had not been reported by other researchers. Therefore, we checked different methods of sample preparation for the study of phase separation kinetics. In this series, the samples were fixed at PI concentration $w = 0.15$ and cured at $T = 130$ °C for 1440 min. Both solution blending and melt-blending methods were carried out. In general, the solution blended (used in this report) and melt-blended samples formed similar phase structure including the layered structure. Only the solution blended samples were displayed in Figure 4.

We also conducted this experiment under different sample environments in order to check the reproducibility. First, the glass surface was chemically treated to be covered with hydrophobic $-SiC_{18}H_{37}$. Samples which were sandwiched between such hydrophobic glasses could be removed easily from the substrates after curing. Micrographs of the sample observed with SEM (Figure 4a) illustrated that recognizable three-layered structure also formed with two outer epoxy-rich layers and a middle layer composed of bicontinuous structure. Thus we can conclude that the epoxy-rich layers were not caused by the phase separation induced by the surface wetting layers. Although the thickness of the outer layers was a little asymmetrical (17 μm thickness of the top and 41 μm of the bottom layer) and phase domains in the middle layer was a little different from that observed at $w = 0.15$ in Figure 2. The continuity of the PI-rich phase or the epoxy-rich phase was noticeable, but the epoxy-rich phase seemed to be larger than that observed in Figure 2.

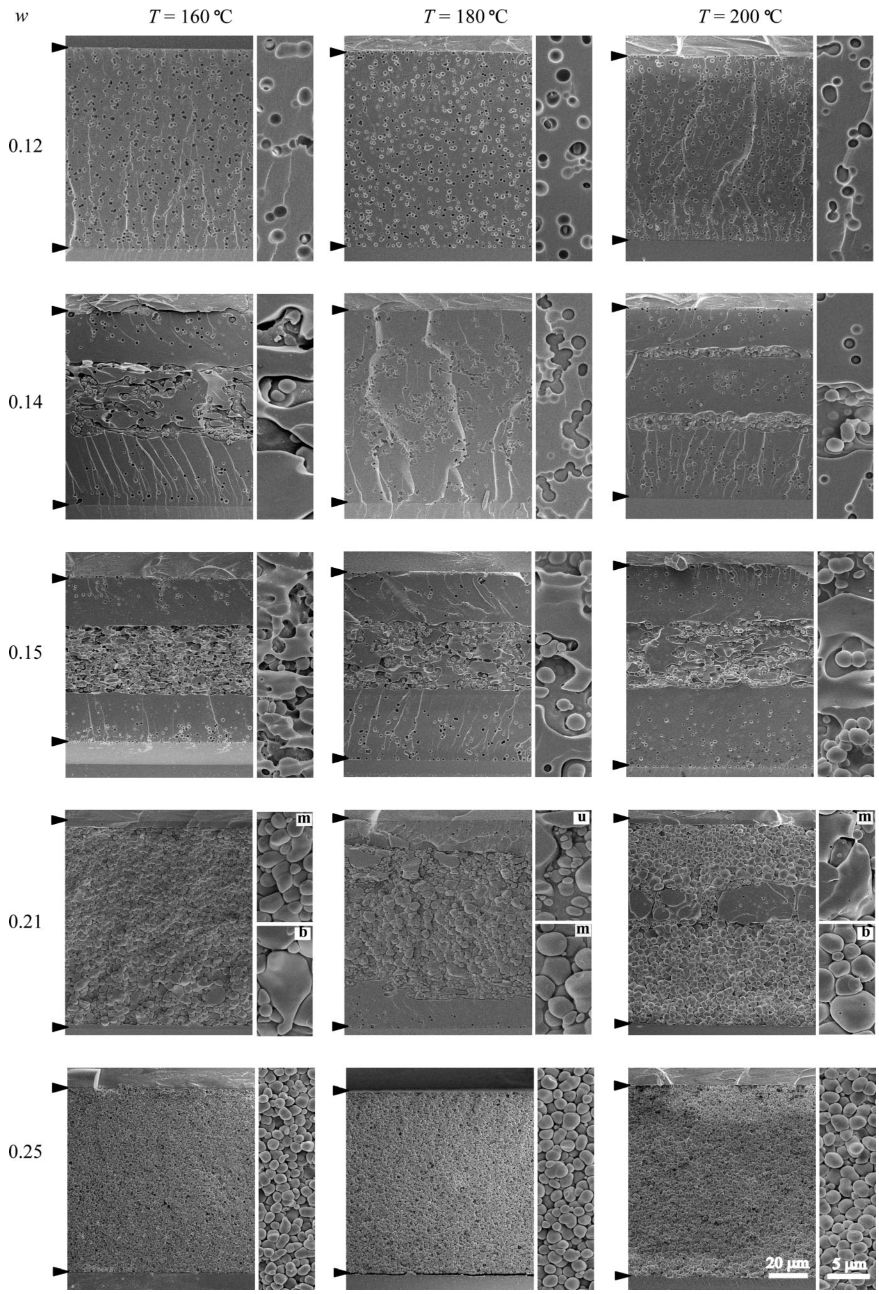
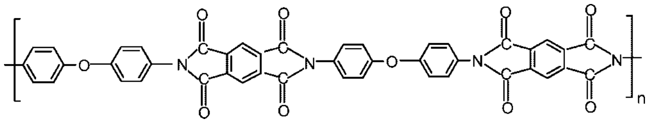


Figure 3. SEM micrographs of fractured and etched surfaces of epoxy/PI blends with different w, cured for 1440 min at different temperatures. Picture on the right in each panel is a higher magnification of the middle part. For $w = 0.21$, higher magnifications of two different locations, the upper (u) and the middle (m) parts or the middle and the bottom (b) parts, are shown.

Films made of polyimide, with a schematic structure shown below, were used as the substrates and again three layers were observed in the results as shown in Figure 4b. Thickness of the outer epoxy-rich layers ranged from 10 to 20 μm was a little smaller. And the phase domains in the middle layer were different from that observed in Figure 4a and Figure 2. The continuity and distribution of PI-rich phase were not uniform in the middle layer, leaving large epoxy-rich domains in some regions. When the sample was positioned with surface normal to the horizontal during the curing process, the three-layered structure also formed, with the whole structure resembling that observed in Figure 2. From these sets of experiments, it was certain that process conditions did not cause the layered structure; and we could essentially eliminate the surface wetting effect and the gravitational effect as the major physical drivers.



The in situ evolution of phase separation for sample $w = 0.15$ had been shown in the previous work.[24] Optical microscopy results showed that phase separated domains initially formed in the peripheral regions (near the surface) gradually disappeared during the phase separation process while images in the middle part always showed a phase separated structure, which might imply the formation of the layered structure. However, direct observation of layered structure formation in the surface normal direction was not available through the optical microscopic measurements. Here, the evolution of the layered structure was elucidated from the following experiments. Samples with $w = 0.15$ cured at 115 °C for different times were measured with SEM immediately after they were fractured in liquid nitrogen

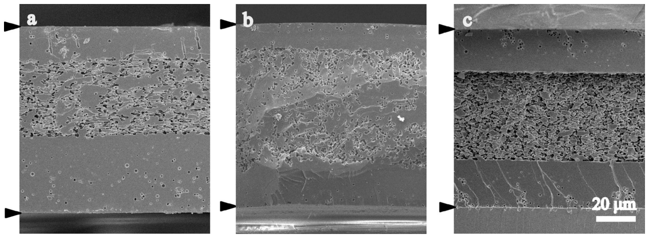


Figure 4. SEM micrographs of fractured and etched surfaces of sample $w = 0.15$ cured at 130 °C for 1440 min. Sample was sandwiched between hydrophobic glasses in the curing process (a), sample with polyimide film substrates (b), and sample being vertically held during the curing process (c).

and coated with platinum and the results were shown in Figure 5. At $t = 160$ min, phase separated domains were difficult to be discerned and it seemed homogeneous in most part of the sample film; however, three layers occurred in some region, although the outer layers were very thin. After $t = 160$ min, three layers were observed in the whole sample film; boundaries between the layers became clear and sharp quickly; phase separated domains gradually became clear in the middle layer and no phase separated domains were observed on the outside. The fractured and etched surface at $t = 1440$ min showed that a classical bicontinuous structure formed in the middle layer and only a very small amount of PI-rich particles existed in the outer epoxy-rich layers.

The relative thickness of the middle layer over the whole sample film was obtained from the SEM images, as shown in Figure 5b. Relative thickness of the middle layer decreased rapidly in the first tens of minutes after the layered structure occurred, from about 93% at $t = 160$ min to 67% at $t = 200$ min. This observation confirmed that the layer formation and development was realized by the asymmetric phase separation (viscosity and molecular weight asymmetry), which was caused by the low molecular weight of epoxy oligomers at the beginning of phase separation. After a long period, e. g. 1440 or 2880 min, the middle layer was around 50% or a little thicker.

Information of the reaction-induced phase separation at the initial stage was also studied by time resolved light scattering (TRLS) measurements as shown in Figure 6. Although signal of the scattered pattern was very weak at the beginning, a maximum in the scattering intensity (I_m) could be clearly identified in Figure 6b. Phase separation had already reached micrometer scale ($q_m \sim 0.002$ nm^{-1}, or $2\pi/q_m \sim 3$ μm) at about $t = 183$ min. While q_m, the scattering vector corresponding to the maximum intensity I_m, did not seem to have changed before $t = 188$ min, or the change was not observed due to the low scattered light intensity. The observed time dependence of the light scattering profiles, $I(q)_t$ showed a characteristic phenomenon of spinodal decomposition, i.e. bicontinuous structure might be formed at the beginning of phase separation. Afterward, the scattering intensity became stronger; correspondingly, I_m gradually increased and q_m gradually decreased until around $t = 285$ min, which indicated the process of phase separation and coarsening of phase structure. From 285 to 340 min, both I_m and q_m did not obviously change. TRLS observation for time longer than 340 min, the scattered light exhibited a period where the intensity gradually decreased and then increased again before q_m was finally frozen at about 1300 min, as shown in Figure 6, parts d and e. This decreasing and then increasing in the scattering intensity together with the loss of optical microscopic images[24] in the middle of this curing induced phase separation was a phenomenon caused by a refractive index cross-over of the two phase separated phases.[25] We will show more definitive data and discussion on this issue in a future paper.

After the sample $w = 0.15$ was cured at 115 °C for different times, the reaction conversion of epoxy was measured with titration method and the results were shown in Figure 7. At $t = 160$ min, only 2.8% of the total epoxide groups had reacted. Most of the epoxy in the sample was present as monomer, which acted as low viscosity liquid. Even after the sample had been cured for 200 min, conversion was still lower than 15%, and it reached about 50% at $t = 480$ min. The conversion gradually increased and reached 80.7% at $t = 720$ min. After that, the increment of conversion became smaller and smaller. If we use the usual conversion of 60% as the gel point,[10,11] the epoxy/PI system behaved fluid-like even after it was cured for $t = 400$ min at $T = 115$ °C. Since spinodal like phase separation definitely started (from TRLS) at 183 min, this viscosity and molecular asymmetry was definitely important to our layered structure formation.

Figure 8 shows transmission electron micrographs of the samples $w = 0.12$ and 0.25 cured at 130 °C for 1440 min. The samples were not stained. At $w = 0.12$, the microtomed specimen showed black particles embeded in a white matrix. On the contrary, the continuous phase in black was found for the case of $w = 0.25$. Morphologies obtained at the same conditions have been described according to the scanning electron micrographs in Figure 2, i.e., PI-rich particles at $w = 0.12$ and PI-rich continuous domains at $w = 0.25$. We could confirm that the natural contrast between the components resulted in the black image for the PI-rich phase during the TEM observation. It was interesting that although PI at $w = 0.25$ was still the minority component, it formed the continuous phase (although the epoxy-rich phase might be also continuous) with a sponge-like phase structure. However, this phase structure typifies an asymmetric phase separation.

Samples with $w = 0.15$ cured at 115 °C for different times were also studied with TEM. The central part of the microtomed film was observed. At $t = 150$ min, small PI-concentrated domains (black) formed. Although it was difficult to distinguish whether the PI-concentrated domains were connected, connection of the domains became obvious later. The domain size was growing with the proceeding of reaction and phase separation. At $t = 240$ min, size of the PI-concentrated domains was much larger than that of the initial ones, and bicontinuous phase-separated structure was clearly recognizable. These TEM images showed that phase separation might have started before $t = 150$ min. However, the phase separated domains were not clearly observed because they were small and the contrast was very low. At $t = 150$ min, a few hundred nanometer sized domains were observed by TEM. These domains quickly coarsened to about micrometer size as shown in Figure 9b to 9d, which were consistent with the TRLS results in Figure 6.

A three-layered structure has been observed by H. Tanaka in the poly(vinyl methyl ether)/water mixtures where the components had different affinity with the glass.[28,29] Each layer had a thickness of tens of micrometers. Besides the influence of surface effect on the outer-layer formation, hydrodynamic flow was speculated to be an important factor for the thickening of outer layers. The outer layers once formed were destroyed again with the coarsening of phase-separated domains.

In thin film polymer blends of deuterated poly(methyl methacrylate) and poly(styrene-*ran*-acrylonitrile), Wang and Composto[30] reported that the wetting layers in a trilayered structure were thickened by hydrodynamic flow-driven wetting in the early stage of phase separation. However, such interpretations could not explain the phenomenon in our present case exactly, since those surface effects were short ranged and the surface layers were wetting/adsorption induced. Also there were some investigations on the layer formation before phase separation started in colloid systems near the critical region. However, the mechanism of this pretransition wetting phenomenon is still an open question.[31]

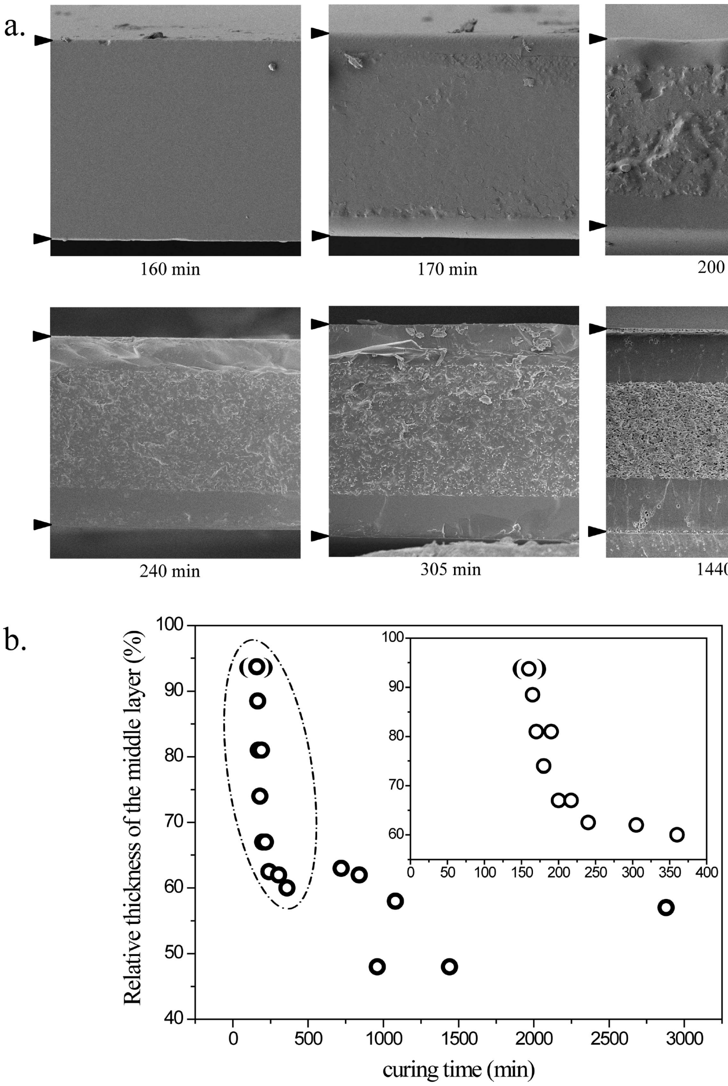


Figure 5. Sample $w = 0.15$ being cured at 115 °C for different times: scanning electron micrographs of the fractured surfaces (a), the relative thickness of the middle layer over the whole sample film (b), where the parentheses "()" mean that layer structure did not always occur at $t = 160$ min. Magnification of the circled part of the data in the left is shown in the upper right panel.

The three-layered structure, with very thick outer layers and a small scale bicontinuous structure in the middle layer, is quite different from reports in the literature. The experimental results showed that surface effect did not play an important role for the layered structure formation. When hydrophobic glasses or polyimide film were used as the substrate, recognizable three-layered structure still formed at the same curing conditions, although thickness of the outer layers and phase separated structure in the middle layer varied slightly.

In order to understand the process of phase separation, we should first clarify the characteristics of the present system: the polyimide 6FDA-MDA is a rigid polymer with a high glass transition temperature $T_g \sim 270$ °C. Once phase separated, the PI-concentrated phase will behave like an amorphous solid (glass) at the curing temperatures (lower than 270 °C). Besides, stepwise polymerization takes place in this system and molecular weight of epoxy gradually increases with the proceeding of curing reaction. Thus the coexistence curve is shifting with the reaction and phase separation is followed. It is assumed that the DGEBA/6FDA-MDA blends show an upper critical solution temperature behavior.[22] Since the epoxy monomer has a much lower molecular weight than the PI, the initial coexistence curve is quite asymmetrical, with the critical concentration w_c located at a low PI concentration. As the reaction proceeds, the molecular weight of epoxy is increasing, and the critical temperature T_{crit} moves to higher temperature, while w_c shifts to higher w. At the same time the coexistence curve becomes less asymmetrical. Thus the coexistent concentration of PI-concentrated phase rapidly shifts toward higher w. These shifts of the phase diagrams are schematically illustrated in Figure 10.

TRLS and morphological study of the sample at $w = 0.15$ cured for different times presented a key to the understanding of the layer formation process. A bicontinuous structure forms at the beginning of phase separation (at about 150 min of curing time) and grows with time. Φ_0 in Figure 10 is assumed to be the concentration of the initially homogeneous system, with A and B as the coexistent concentrations at the beginning of phase separation. As phase separation proceeds, A shifts to C and E in sequence, while B correspondingly shifts to D and F, with much larger change in scales. Since EO/OF $\ll$ CO/OD $<$ AO/OB, the volume fraction of the PI-concentrated phase will continuously decrease after the initial phase separation. In the case of viscoelastic phase separation in liquid mixtures, continuous domains of the minor component with higher viscoelasticity once formed would be elongated and shrunk to lower the volume fraction.[32,33] However, because of the elasticity (or the rigidity) of the entangled PI-rich network structure (which is gradually approaching the glass transition temperature of PI), this PI-rich phase can not maintain its total dimensions during the volume

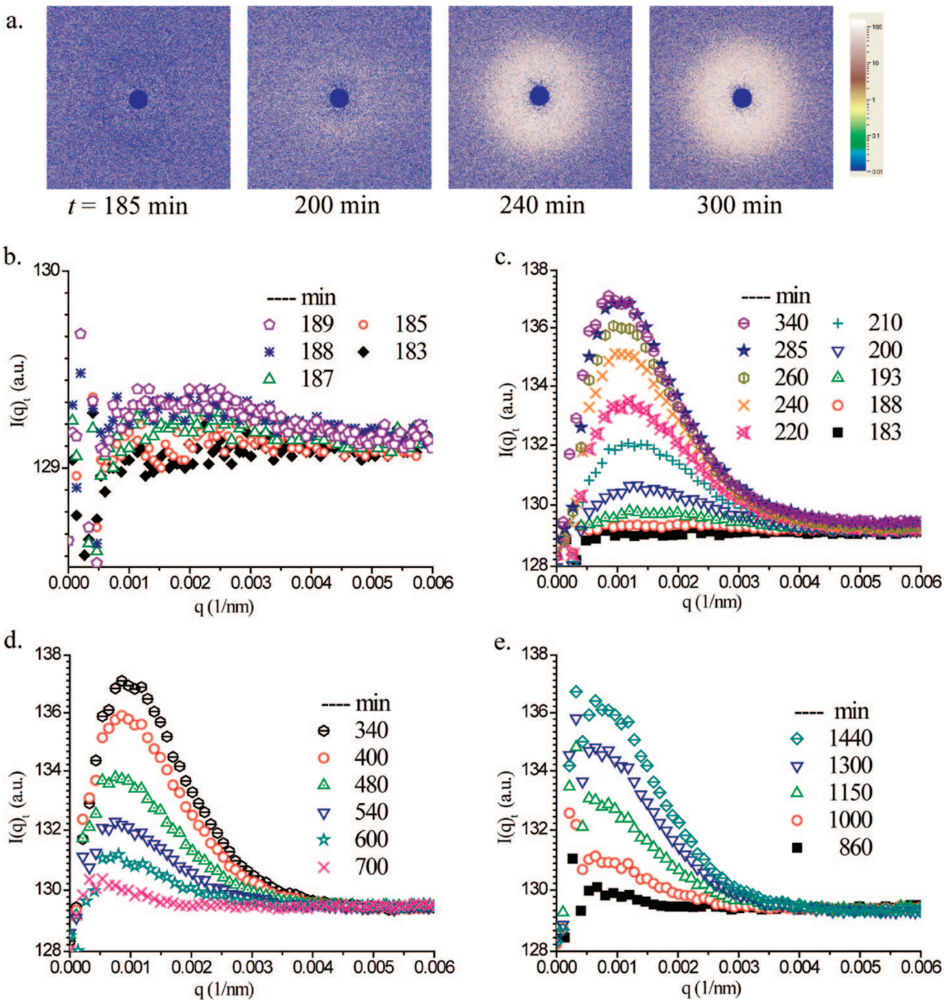


Figure 6. Time-resolved light scattering pattern (a) and circular averaged intensity profiles (b−e) of the sample *w* = 0.15 cured at 115 °C (a.u.: arbitrary unit).

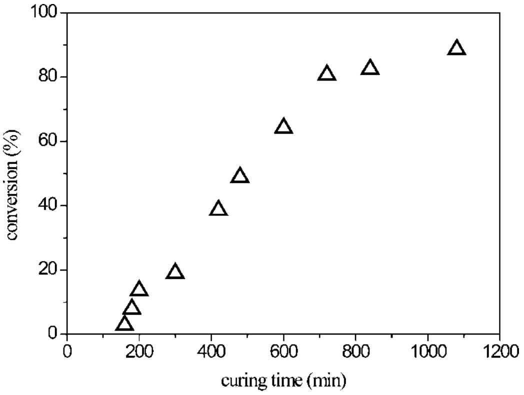
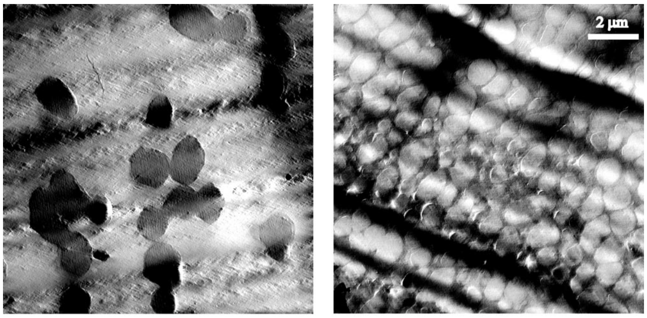


Figure 7. Reaction conversion of epoxy for the sample *w* = 0.15 cured at 115 °C for different times.

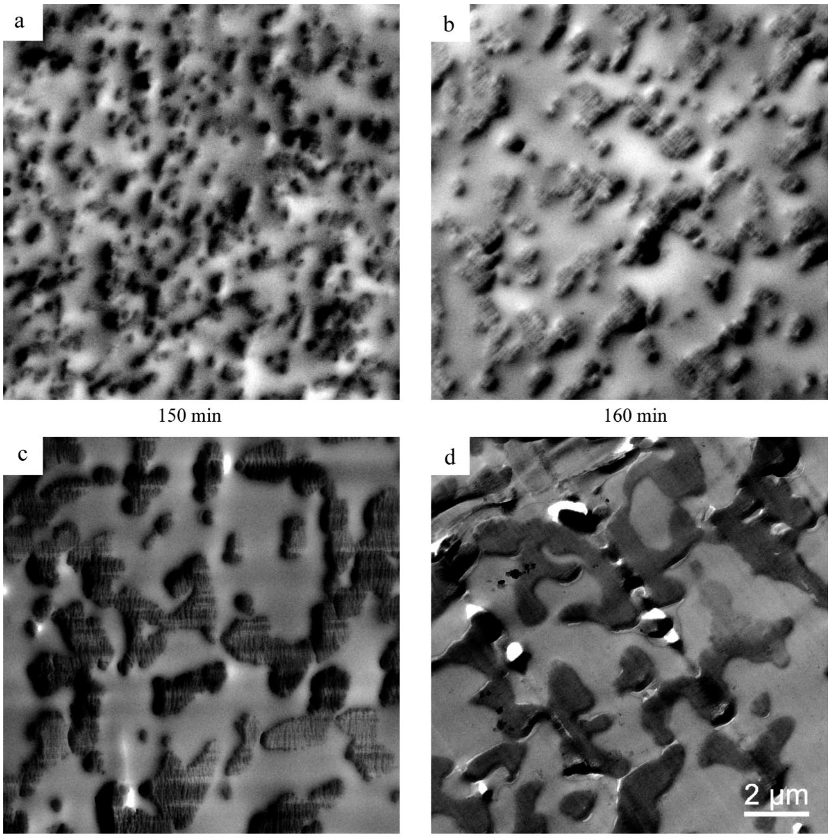


w = 0.12 *w* = 0.25

Figure 8. Transmission electron micrographs of microtomed films cured at 130 °C for 1440 min.

change. It can only shrink to its centroid to lower the volume fraction. Since there is no special physical or chemical bonding between the PI and the substrate,[34] the PI-concentrated domains, which gradually become solid-like (become glassy), have lower affinity with the substrate compared with the epoxy-rich phase and can be easily detached from the glass surface. Therefore, the continuous PI-concentrated domains will shrink toward the central part of the sample. At the same time, epoxy-oligomer-rich phase will be squeezed out toward the surface, forming the layered structure. During this period, the reaction conversion of epoxy is very low and most of the epoxy component existed as monomer or small oligomers. The fluidity of the epoxy component allows the PI-concentrated domain to coarsen and shrink quickly. It should be noted that this process is definitely accompanied by a long-range hydrodynamic flow process. The viscosity of epoxy-rich phase increases with the curing process. Before epoxy is cross-linked, the PI-rich domains are mainly localized in the middle part of the sample film. The rigidity of the PI-rich domains prevents its complete coalescence and shape change. Therefore, bicontinuous phase structure is observed in the middle layer.

In the range of lower *w*, discrete PI-concentrated particles quickly form as phase separation occurs. The particles collide with each other in the fluid matrix and sometimes adhere



150 min 160 min

200 min 240 min

Figure 9. Transmission electron micrographs of microtomed films of sample $w = 0.15$ cured at 115 °C for short times.

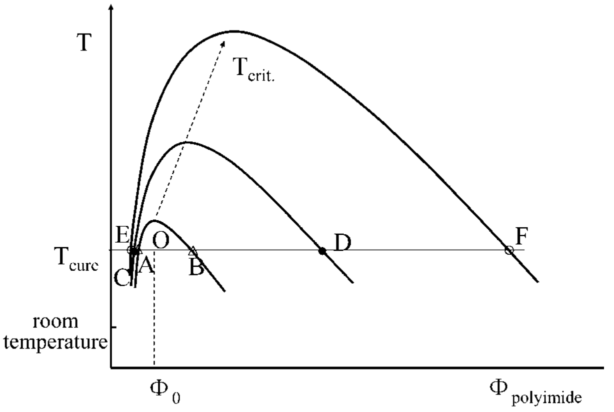


Figure 10. Schematic description of the shift of phase diagram in the system of DGEBA/DDS/6FDA-MDA during curing reaction.

together but they do not coalesce into a larger particle because of their low fluidity. When *w* was higher, PI-rich phase also shrink to decrease its volume fraction. However, it has a high enough volume fraction so that the asymmetrically phase separated epoxy-rich droplet phase can not flow out but locally concentrate and remain as droplets. Thus further shrinkage of PI-rich phase is prevented by the epoxy-rich droplets, and the hydrodynamic flowing to form a layered structure is suppressed. Finally, the PI-rich phase can maintain as continuous phase in the whole sample and epoxy-rich phase form particles with connections.

It is known that temperature influences both the reaction rate and phase separation rate. However, the curing temperatures used were always lower than the T_g of PI, therefore, the overall structure formed at any *w* did not change drastically at different curing temperatures (in Figures 2 and 3). At higher temperatures, fluidity of epoxy-oligomer-rich phase was extended before gelation set in, therefore, shrinkage of the PI continuous phase could proceed further, resulting in a thinner middle layer for $w = 0.15$. Also the multilayers could form at 200 °C for $w = 0.14$ and $w = 0.21$ as the indication of the strong influence of temperature on the interplay of reaction and phase separation.

Conclusion

A fluorinated polyimide 6FDA-MDA was employed to investigate the reaction-induced phase separation of epoxy/PI blends. Three distinct morphological structures were obtained. In the lower PI concentration range, aggregated PI-rich particles were formed in the epoxy-rich matrix. At higher *w*, PI-rich phase formed continuous domains while epoxy-rich particles were connected in the matrix. In the intermediate *w* range, a three-layered structure formed spontaneously. PI-rich phase mainly localized in the middle layer and the outer layers were mostly epoxy-rich phase. Thickness of the outer layers was much larger than the characteristic length of the bicontinuous domains in the middle layer.

The rigidity and high glass transition temperature behavior of PI, which contrasted with the high fluidity and low molecular weight of epoxy at the beginning of phase separation, were significant factors for this layered structure formation. Shrinkage of the entangled PI-rich network toward its coexistent composition and volume could be the essential cause of the layered structure formation.

Light scattering and optical microscopy revealed that there was also a refractive index cross-over between the PI-rich and epoxy-rich phases during the curing process. This phenomenon has generated some confusion and difficulty in the understanding and interpretation of such reaction-induced phase separation mechanism.

Further experiments and theoretical discussion are needed in order to understand the mechanism more quantitatively. Also aggregation of the PI-rich particles obtained at low PI contents and temperature dependence of the morphological structures are worth of further investigation. The formation of this layered structure offers a special advantage in the application for the interfiber lamella toughening of multilayered fiber composites.

Acknowledgment. This work has been financially supported by the ministry of Science and Technology of China (Grant 2003CB615600). The authors thank Dr. Xiaojuan Zhao, Dr. Jingang Liu and Prof. Shiyong Yang for the polyimide they kindly offered. The authors thank Prof. Mamoru Okada for his prominent contribution to the mechanism of the layer and aggregate formation.

References and Notes

(1) Inoue, T. *Prog. Polym. Sci.* **1995**, *20*, 19–153.
(2) Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. *Adv. Polym. Sci.* **1997**, *128*, 95.
(3) Varley, R. J.; Hodgkin, J. H.; Hawthorne, D. G.; Simon, G. P.; McCulloch, D. *Polymer* **2000**, *41*, 3425.
(4) Francis, B.; Poel, G. V.; Posada, F.; Groeninckx, G.; Rao, V. L.; Ramaswamy, R.; Thomas, S. *Polymer* **2003**, *44*, 3687.
(5) Venderbosch, R. W.; Meijer, H. E. H.; Lemstra, P. J. *Polymer* **1994**, *35*, 4349.
(6) Ishii, Y.; Ryan, A. J. *Macromolecules* **2000**, *33*, 158.
(7) Hedrick, J. L.; Yilgor, I.; Wilkes, G. L.; McGrath, J. E. *Polym. Bull.* **1985**, *13*, 201.
(8) Swier, S.; Assche, G. V.; Vuchelen, W.; Mele, B. V. *Macromolecules* **2005**, *38*, 2281.
(9) Alig, I.; Ruellmann, M.; Holst, M.; Xu, J. *Macromol. Symp.* **2003**, *198*, 245.
(10) Giannotti, M. I.; Foresti, M. L.; Mondragon, I.; Galante, M. J.; Oyanguren, P. A. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3953.
(11) Park, S.; Lee, H.; Han, M.; Hong, S. *J. Colloid Interface Sci.* **2004**, *270*, 288.
(12) Hay, J. N.; Woodfine, B.; Davies, M. *High Perform. Polym.* **1996**, *8*, 35.
(13) Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, *30*, 213.
(14) Hourston, D. J.; Lane, J. M. *Polymer* **1992**, *33*, 1379.
(15) Kimoto, M.; Mizutani, K. *J. Mater. Sci.* **1997**, *32*, 2479.
(16) Iijima, T.; Hamakawa, S.; Tomoi, M. *Polym. Int.* **2001**, *50*, 1214.
(17) Agag, T.; Takeichi, T. *Polymer* **1999**, *40*, 6557.
(18) Gaw, K. O.; Kakimoto, M. *Adv. Polym. Sci.* **1999**, *140*, 107.
(19) Su, C. C.; Woo, E. M. *Polymer* **1995**, *36*, 2883.
(20) Biolley, N.; Pascal, T.; Sillion, B. *Polymer* **1994**, *35*, 558.
(21) Bonnet, A.; Pascault, J. P.; Sautereau, H.; Camberlin, Y. *Macromolecules* **1999**, *32*, 8524.
(22) Park, J. W.; Kim, S. C. *Polym. Adv. Technol.* **1996**, *7*, 209.
(23) Gan, W. J.; Yu, Y. F.; Wang, M. H.; Tao, Q. S.; Li, S. J. *Macromolecules* **2003**, *36*, 7746.
(24) Chen, F.; Wang, X.; Zhao, X.; Liu, J.; Yang, S.; Han, C. C. *Macromol. Rapid Commun.* **2008**, *29*, 74.
(25) Kim, B. S.; Chiba, T.; Inoue, T. *Polymer* **1995**, *36*, 67.
(26) Girard-Reydet, E.; Vicard, V.; Pascault, J. P.; Sautereau, H. *J. Appl. Polym. Sci.* **1997**, *65*, 2433.
(27) Karim, A.; Douglas, J. F.; Satija, S. K.; Han, C. C.; Goyette, R. J. *Macromolecules* **1999**, *32*, 1119.
(28) Tanaka, H. *Phys. Rev. Lett.* **1993**, *70*, 53.
(29) Tanaka, H. *Phys. Rev. E* **1995**, *51*, 1313.
(30) Wang, H.; Composto, R. J. *J. Chem. Phys.* **2000**, *113*, 10386.
(31) Gruell, H.; Woermann, D. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 814.
(32) Wang, X.; Okada, M.; Han, C. C. *Macromolecules* **2006**, *39*, 5127.
(33) Tanaka, H. *Phys. Rev. Lett.* **1993**, *71*, 3158.

(34) Cured sample film easily peeled off from glass substrates where polyimide-rich phase formed continuous domains and existed near to the substrate, e.g., at $w = 0.25$. However, such a case seldom happened when the epoxy-rich phase was near to the glasses at lower polyimide concentrations.

MA801213N