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Phase behavior of blends of high temperature copolycarbonates with styrene/acrylonitrile copolymers

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Abstract

The phase behavior of blends of copolycarbonates containing 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexanone and bisphenol-A repeat units with styrene/acrylonitrile copolymers (SAN) was examined by differential scanning calorimetry or time resolved light scattering. No combination of the copolycarbonates or SAN materials proved to be miscible. Some of the blends studied become cloudy upon heating, which is explained by index of refraction changes with temperature rather than a lower critical solution temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Light scattering; Lower critical solution temperature

1. Introduction

Callaghan et al. reported that while the interaction between bisphenol-A polycarbonate (BPA-PC), and styrene/acrylonitrile copolymers (SAN) is unfavorable for miscibility, there is an optimal (or minimum) interaction energy density at about 25% by weight acrylonitrile in the SAN which places the blends on the verge of being miscible [1]. This near miscibility is partly responsible for the commercial success of blends of BPA-PC with ABS (i.e. rubber modified SAN) materials. Recently, a series of copolycarbonate materials based on varying ratios of bisphenol-A and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexanone (TMC) (Fig. 1) have been commercialized primarily to provide higher heat resistance, relative to BPA-PC, which is demanded by some applications; note that the glass transition temperature of the TMC-PC homopolymer is 240 versus 149 °C for the BPA-PC homopolymer.

One could envision some interest in blends of these new high heat resistant copolycarbonates with ABS materials; therefore, it would then be useful to know the state of miscibility, or the interactions, of these copolycarbonates with SAN copolymers. Given the near miscibility of BPA-PC with some SANs [1] and the well-known opportunities for favorable interactions in copolymer–copolymer blends [2], it would not be surprising to find that some of these commercial copolycarbonates are miscible with SAN copolymers over some region of acrylonitrile content. Indeed, Okamoto et al. have reported some intriguing evidence for miscibility of one of these copolycarbonates with a particular SAN copolymer [3]. They suggested that the blend shows lower critical solution temperature (LCST) behavior and reported time resolved light scattering results that suggest phase demixing by spinodal decomposition as a proposed phase boundary is crossed during temperature jump experiments.

Based on the reasoning outlined above and motivation from the observations of Okamoto et al., a study was initiated to broadly explore the phase behavior of copolycarbonate/SAN blends over the full range of compositions for each copolymer. The Okamoto et al. work provided reason to believe that the copolymer–copolymer composition map would contain some region of miscibility [3]. If this were the case, then it should be possible to obtain information about interactions between repeat unit pairs by analysis of the experimentally determined boundary between the regions of miscibility and immiscibility as described in the recent literature on other systems [2]. However, to our surprise, no region of miscibility could be found which left us with the responsibility of how to rationalize our findings with the observations reported by Okamoto et al. Thus, this paper describes in detail our experimental investigations of the phase behavior of the copolycarbonate/SAN blends and what we believe is an explanation for the observations by Okamoto et al.

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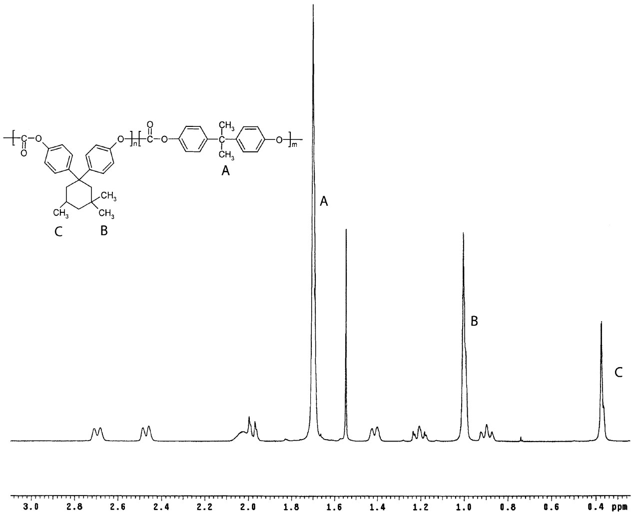

Fig. 1. Structure and nuclear magnetic resonance spectra of a TMC-PC copolycarbonate.

2. Experimental

2.1. Materials and characterization

The polymers used in this study, shown in Table 1, were used as received except for the TMC-PC homopolymer, which was precipitated in methanol three times from a dichloromethane solution to remove residual monomer.

The compositions of the copolycarbonates were characterized by ^{1}H NMR at 500 MHz. Deuterated chloroform was used as the solvent, which contained tetramethylsilane for establishing the shift reference. The ^{1}H NMR spectra for the commercial copolycarbonate designated here as PCTMC40 is shown in Fig. 1. The composition of each copolymer was determined by comparing the area of the methyl hydrogen shifts A–C. The resulting compositions are given in Table 1. Molecular weight information was obtained by gel permeation chromatography. Cross-linked polystyrene was used as the fixed phase and tetrahydrofuran was the carrier phase. The column was calibrated with polystyrene standards. Index of refraction values were estimated by group contribution methods when experimental data were not available [4]. Calorimetric information was obtained with a Perkin Elmer DSC7, where scans and calibrations were performed at 20 °C/min. Glass transition temperatures are defined here as the onset of the transition. Equation of state properties of the copolymers were determined with a Gnomix mercury dilatometer. The resulting data were fitted to the Sanchez–Lacombe equation of state to extract the corresponding characteristic parameters P^*, T^* and ρ^* shown in Table 2 [5,6].

2.2. Sample preparation and miscibility evaluation

All polymer blends were prepared by solution casting 7 wt% solutions of polymer in dichloromethane onto glass slides at room temperature. Cast blends were dried in a vacuum oven for 2 days during which the temperature was slowly raised to 210 °C where the temperature was maintained for 12 h.

Miscibility was assessed by observing glass transition behavior and the amount of scattered light. The latter employed a polarized 632 nm He–Ne laser light source which was directed through a sample on a glass slide. The scattered light was focused with a set of adjustable lenses and detected by a 512 pixel photodiode array. The angle corresponding to each pixel was determined with a diffraction grating with known line widths. Temperature ramp experiments were performed with a FP 80 HT Mettler hot stage, while temperature jump experiments were performed using a heated brass block. We did not preheat the samples during temperature jump experiments. Our light scattering apparatus is described in greater detail elsewhere [7].

3. Assessment of equilibrium blend phase behavior

The TMC-PC copolycarbonates and the TMC-PC homopolymer were blended with the various SANs listed in Table

Table 1
Polymers used in this study

Polymer	Source	Commercial description	Composition (wt%)	M_w	M_n
PCTMC11	Bayer	Apec 9330	11.1% TMC[a]	52,100	21,900
PCTMC30	Bayer	Apec 9340	30.2% TMC[a]	57,500	23,200
PCTMC40	Bayer	Apec 9358	38.9% TMC[a]	61,800	27,600
PCTMC64	Bayer	Apec 9371	64.2% TMC[a]	65,600	23,900
TMC-PC	Bayer	–	Homopolymer	218,700	91,000
PS800	Pressure Chem.	–	Homopolymer	800	620
PS2000	Pressure Chem.	–	Homopolymer	2000	1,900
SAN6.3	Dow Chemical Co.	–	6.3% AN	343,000	121,000
SAN16	Dow Chemical Co.	–	15.9% AN	173,900	–
SAN25	Dow Chemical Co.	Tyrill	25% AN	166,800	77,200
SAN33	Monsanto Co.	–	33% AN	146,000	68,000
SAN40	Asahi Chemical	–	40% AN	122,000	61,000

[a] Determined here by ^{1}H NMR.

Table 2
Polymer properties and Sanchez–Lacombe lattice fluid characteristic parameters

Polymer	Glass transition (°C)	Density (g/cc) (30 °C)	P^* (MPa)	T^* (K)	ρ^* (cc/g)	Range (°C)	Refractive index (25 °C)
PCTMC11	156	1.180	471.9	793	1.2510	237–293	1.582[a]
PCTMC30	167	1.169	443.2	787	1.2452	241–296	1.576[a]
PCTMC40	180	1.161	432.5	791	1.2295	230–287	1.573[a]
PCTMC64	203	1.137	488.0	770	1.2436	245–299	1.565[a]
TMC-PC	237	1.110	397.0	820	1.1905	253–297	1.554[b]
SAN6.3	104	1.057[b]	–	–	–	–	1.586[b]
SAN16	105	1.070[b]	–	–	–	–	1.579[b]
SAN25	107	1.082[b]	–	–	–	–	1.572[b]
SAN33	112	1.093[b]	–	–	–	–	1.567[b]
SAN40	113	1.102[b]	–	–	–	–	1.560[b]

[a] Calculated from regression of data in product literature.

[b] Calculated.

1 in equal weight proportions. The blends prepared are indicated by the various points on the two dimensional compositional map (% AN in SAN versus % TMC in copolycarbonate) shown in Fig. 2. All of these blends exhibited two glass transitions suggesting immiscible behavior. However, several of the blends appeared transparent or were only slightly hazy as shown in Fig. 2. The parallel lines in Fig. 2 define a region where the blend components differ in index of refraction by 0.01 or less; which is generally regarded as the critical difference necessary for assessing miscibility based on visual observation of blends [8]. The triangle in the middle of Fig. 2 represents the blend used by Okamoto et al. based on the content of AN in the SAN and the glass transition of the TMC-PC copolycarbonate which they reported [3]. Fig. 3 shows the DSC scans for selected blend compositions that lie within the two solid lines in Fig. 2. Several of these blends were transparent. All of these scans show evidence of two glass transition temperatures.

The two glass transitions observed are definitive evidence of immiscibility; therefore, the observed transparency at room temperature is a result of the two components having nearly equal refractive indices. However, Okamoto et al. measured the scattered light for their blend during several temperature jump experiments and fit the resulting scattered light intensity versus time data to the Cahn–Hillard diffusion model in the classical method used to estimate a spinodal temperature [3,9,10]. Since their blend was melt mixed at 290 °C and their estimate of a spinodal temperature was 223 °C, they explained their observations in terms of an LCST phase boundary greatly perturbed by shear within the extruder. Examples of the effects of shear on phase boundaries can be found in the literature; however, lowering the spinodal temperature by 67 °C seems rather extraordinary compared to prior literature reports [11–14].

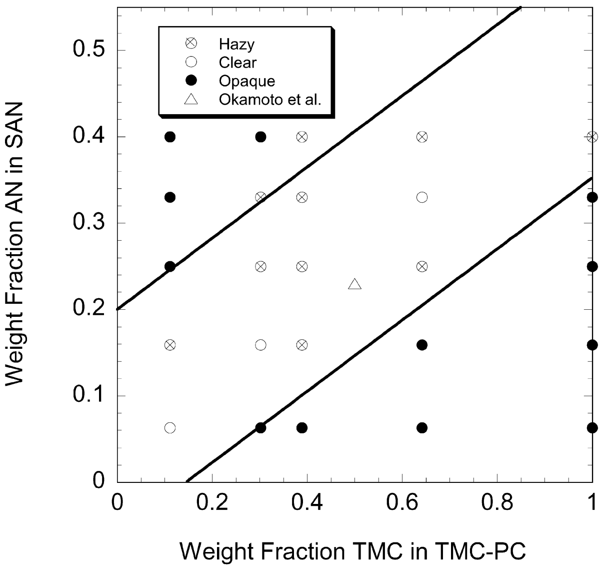

Fig. 2. Optical appearances of TMC-PC copolycarbonate/SAN blends.

Since blend systems with LCST-type phase diagrams are more likely to show miscibility at a given temperature at the extreme compositions, blends of PCTMC40/SAN25 and PCTMC64/SAN25 were prepared in weight fractions ranging from 10 to 90 wt%. However, none of these blends showed a single glass transition temperature.

Monodisperse polystyrenes of varying molecular weight were blended with TMC-PC and the copolycarbonates. Observed changes in miscibility as the polystyrene molecular weight and the TMC-PC copolycarbonate composition vary would allow some insight about the interaction energies for the TMC-PC/PS and TMC-PC/BPA-PC pairs through the Flory–Huggins and mean field theories [15–18]. This information coupled with the existing understanding of BPA-PC/SAN blend interactions would be useful in understanding the interactions of any TMC-PC copolycarbonates with SAN copolymers [1,19]. Monodisperse polystyrene with a molecular weight of 800 was found to be miscible with all of the TMC-PC copolycarbonates and TMC-PC while polystyrene with a molecular weight of 2000 was found to be immiscible with all of the TMC-PC copolycarbonates and TMC-PC. These observations qualitatively rule out the possibility of a favorable interaction between the TMC-PC and polystyrene such as that observed between tetramethyl polycarbonate and polystyrene [20].

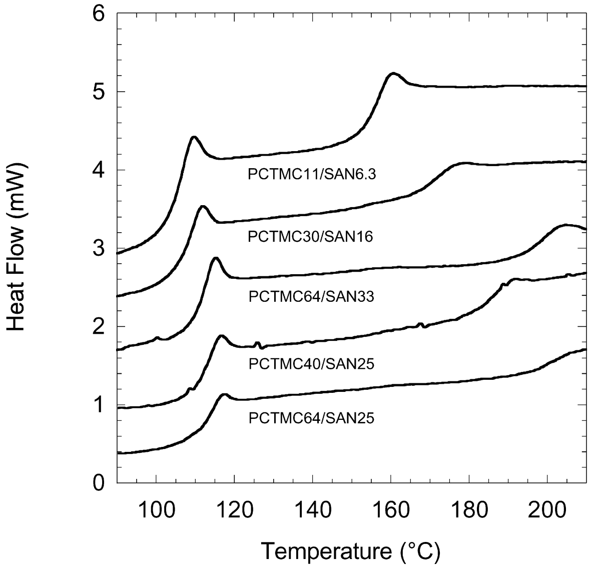

Fig. 3. DSC scans for TMC-PC polycarbonate/SAN blends.

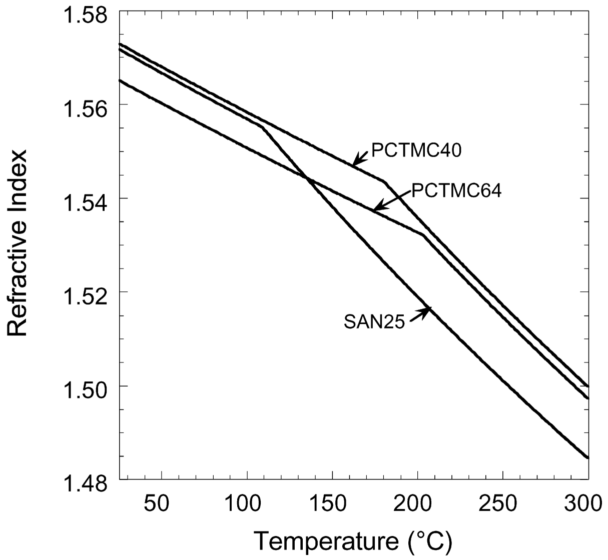

Fig. 5. Index of refraction as a function of temperature for selected polymers calculated using a group contribution method for volume versus temperature data and the Lorentz–Lorenz equation.

The high concentration of end groups in these very low molecular weight polystyrenes can obscure the detailed interpretations of such results [21].

4. Time resolved light scattering analysis

To determine if the clear to cloudy transitions reported by Okamoto et al. could also be observed using the current blends, the light scattered from the PCTMC40/SAN25 and PCTMC64/SAN25 blends was measured as a function of temperature. While these blends are initially hazy, they do become cloudy upon heating. An example of a temperature jump experiment using these blends is shown in Fig. 4. While these data appear similar to those collected during spinodal decomposition, the change in scattered light intensity with time is related to the change in the temperature of the specimen with time and not a phase separation.

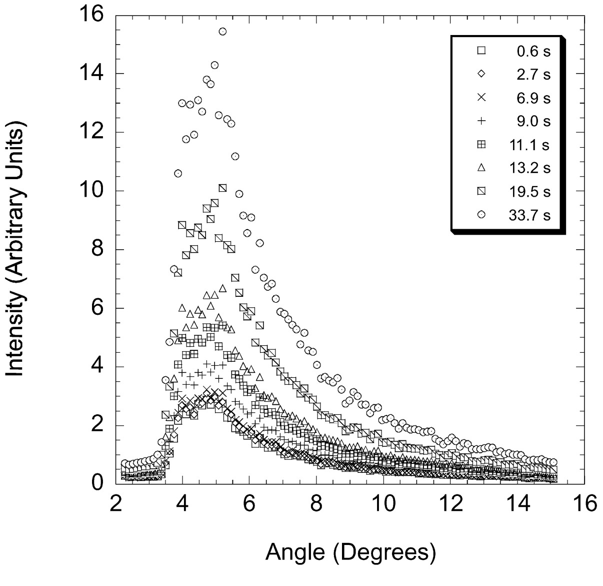

Fig. 4. Changes in scattered light intensity as a function of scattering angle and time during a temperature jump experiment for a PCTMC40/SAN25 blend.

A clear to cloudy transition in a two-phase mixture can occur in the absence of any change in phase structure. This phenomenon has caused confusion about blend phase behavior in other systems [22,23]. For a given morphology, the scattered light intensity is proportional to the square of the difference in indices of refraction between the phases. As the density of a material changes, so does the electron cloud density, and the associated index of refraction. Since the thermal expansion coefficient of a polymer in the melt state is approximately twice that of the glassy state in most cases, the refractive index difference between two polymers will change significantly as a function of temperature in the temperature interval between their respective glass transitions [4].

At 25 °C, the index of refraction for SAN25 is below that of the PCTMC40 and above that of PCTMC64 as shown in Table 2. The relationships between index of refraction and temperature were calculated using the Lorentz–Lorenz equation and thermal expansion information estimated through group contribution methods [4,24,25]. Fig. 5 shows how the refractive indices of the two TMC-PC copolymers and SAN25 change as a function of temperature. We propose that the clear to cloudy transitions observed with these blends are due to how the difference in the refractive indices of these polymers changes with temperature. If this is the case, then measured scattered light intensity should be directly correlated to the refractive index difference between the phases. Fig. 6 shows the intensity of scattered light, which was determined by summing

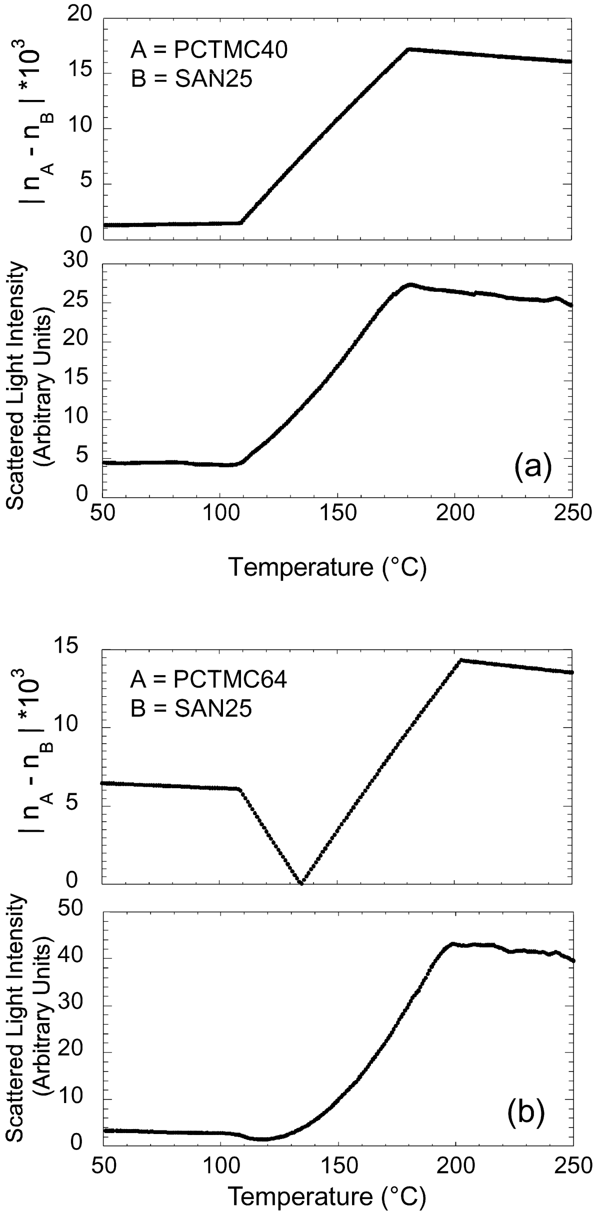

Fig. 6. Scattered light intensity and index of refraction difference for (a) PCTMC40/SAN25 and (b) PCTMC64/SAN25 as a function of temperature. Scans were performed at 2 °C/min.

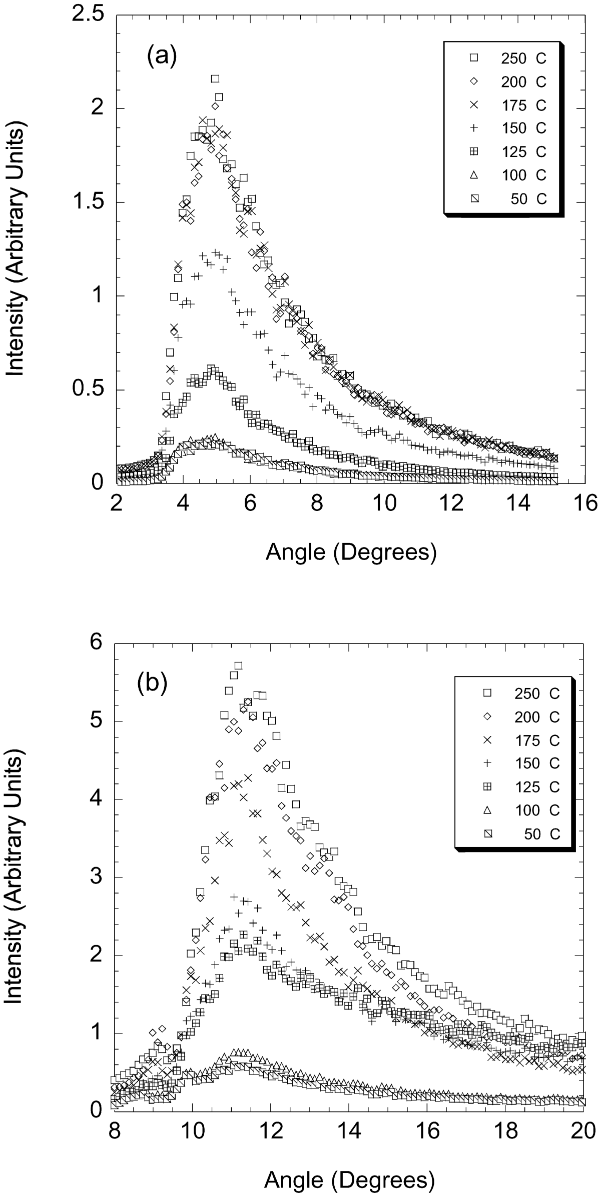

Fig. 7. Scattered light intensity profiles for (a) PCTMC40/SAN25 and (b) PCTMC64/SAN25 blends measured at the indicated fixed temperatures.

the light intensity over several fixed angles of scattering light, while the temperature was increased 2 °C/min. One can see that the intensity of scattered light directly parallels the index of refraction difference calculated for these materials. Scattering profiles were also obtained during constant temperature conditions to confirm that the changes in scattered light intensity are not time dependant. The resulting scattering patterns for the PCTMC40/SAN25 and PCTMC64/SAN25 blends are shown in Fig. 7. Identical curves were obtained by either increasing or decreasing the temperature between isothermal data collections. If one of the samples is held at 300 °C for several minutes and then rapidly quenched by liquid nitrogen, the sample then produces the same lower intensity scattering pattern observed before this thermal treatment. The rapid cooling caused by a quench in liquid nitrogen would prevent a change in morphology from occurring, leaving changes in scattering intensity to be explained by refractive index changes.

While it is apparent that the transparent to opaque transitions noted in the copolycarbonate blends are due to index of refraction changes, one is left with explaining the changes in scattered light intensity with time during a temperature jump experiment reported by Okamoto et al. [3]. The forgoing evidence suggests that any time dependent changes in scattered light intensity during a temperature jump experiment are related to the kinetics of heat transfer for

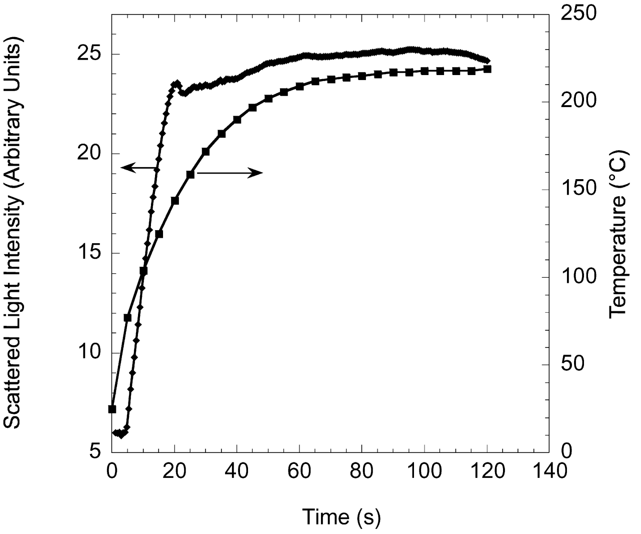

Fig. 8. Temperature and scattered light intensity versus time for a PCTMC40/SAN25 blend during a temperature jump experiment.

the blends studied here. To determine if the heat transfer effects occur on the same time scale as the changes in scattered light intensity, a thermocouple was embedded in PCTMC64 on a glass slide and the temperature was recorded versus time during a temperature jump. Fig. 8 shows the measured temperature versus time relation during the jump along with the scattered light intensity for PCTMC40/SAN25 as a function of time. The lower part of Fig. 9 is a plot of the scattered light intensity versus the temperature implied by the temperature versus time data shown in Fig. 8. The upper part of Fig. 9 gives the index of refraction difference for the PCTMC40/SAN25 blend as a function of temperature. While the two plots in Fig. 9 do not correlate as well as those shown for the temperature ramp experiments in Fig. 6, it is apparent that the temperature change during a temperature jump experiment occurs on the same time scale as the observed changes in scattered light intensity. An increase in scattered light intensity may be evident sooner than indicated by the measured temperature because the latter does not fully reflect the gradient of temperature within the sample during the temperature jump. The scattered light intensity is a summation through the thickness of the sample and will be influenced by the temperature gradients. In addition, the thermal mass of the thermocouple may result in some time lag between the actual and the indicated temperature when attempting to measure rapid changes in temperature in a poor heat conductor.

Okamoto et al. [3] analyzed their light scattering results using the Cahn–Hillard diffusion model for spinodal decomposition [9,10]. The data obtained here during temperature jump experiments were analyzed similarly to demonstrate that one could mistakenly assign a LCST to a blend not actually undergoing phase separation provided the rate of heat transfer is not adequate to give a near

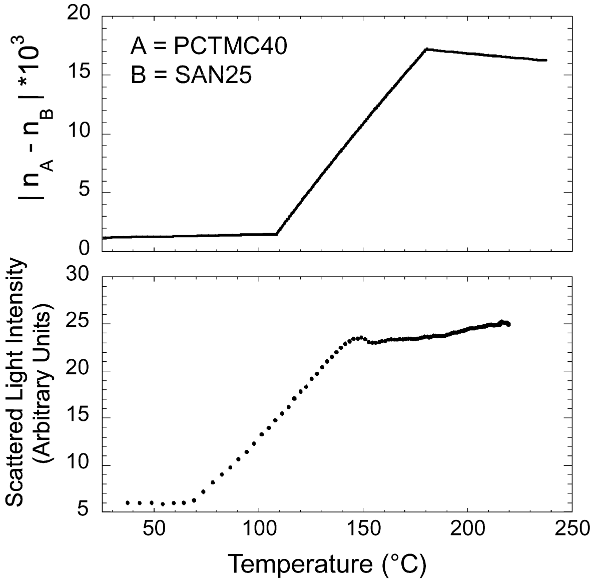

Fig. 9. Scattering light intensity and index of refraction difference versus temperature for a PCTMC40/SAN25 blend during the temperature jump experiment shown in Fig. 8.

instantaneous temperature change. The growth rate, $R(q)$, for a spinodal decomposition using the linearized Cahn–Hillard model is

$$R(q) = -Dq^2 - 2M\kappa q^2 \tag{1}$$

where D is the apparent diffusion coefficient, q is the wavevector, κ is the interfacial free energy density, and M is the mobility. A plot of $R(q)/q^2$ versus q^2 for a given temperature has an intercept of D. Fig. 10 shows this type of analysis for the current temperature jump experiments. The apparent diffusion coefficients are then plotted as a function of temperature and extrapolated to zero to determine the spinodal temperature. Fig. 11 shows the apparent diffusion coefficients for the PCTMC40/SAN25 and PCTMC64/SAN25 blends.

While the data obtained during a clear to opaque transition in the TMC-PC copolycarbonate blends seems to be described fairly well by the linearized diffusion model for spinodal decomposition, there are several observations that indicate that this is not an appropriate analysis. First, the apparent diffusion coefficient deduced is very large when compared to other blend systems. One might expect the kinetics of a TMC-PC copolycarbonate/SAN blend phase separation to be similar to that of tetramethyl polycarbonate/PS blends. Guo and Higgins have determined by light scattering analysis that the apparent diffusion coefficients for the TMPC/PS system are of the order of 10^{-15} cm^2/s within 10 °C of the spinodal temperature at 233 °C [26]. The apparent diffusion coefficients within 10 °C of the predicted zero apparent diffusion coefficient for the TMC-PC copolycarbonates/SAN25 blends (122–155 °C) deduced here are of the order of 10^{-11} cm^2/s. The apparent diffusion

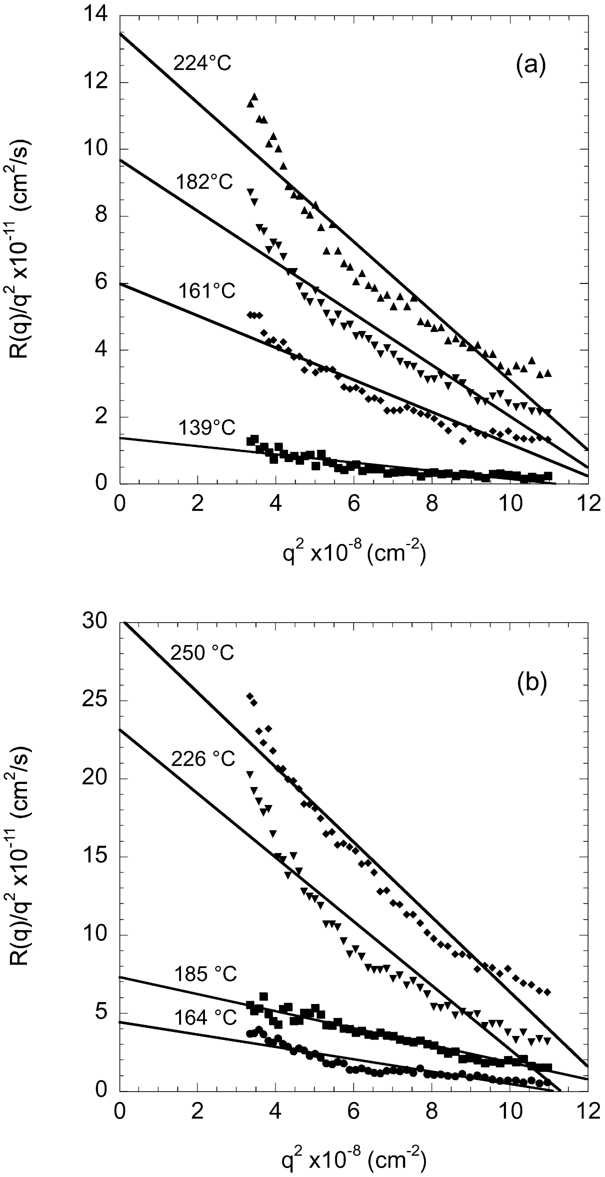

Fig. 10. Plots of R/q^2 versus q^2 for (a) PCTMC40/SAN25 and (b) PCTMC64/SAN25 blends obtained during temperature jump experiments.

coefficients reported by Okamoto et al. are also on the order of 10^{-11} cm^2/s [3]. Another fundamental problem associated with fitting the kinetic data to the Cahn–Hillard model arises from the fact that only a small range of wavevectors were used to determine $R(q)/q^2$ versus q^2 plots as in Fig. 12. The expanded region around these wavevectors identified in Fig. 12 as open circles shows that the relationship between $R(q)/q^2$ and q^2 is quite non-linear. This non-linearity is not consistent with the Cahn–Hillard diffusion model. Yet another discrepancy between the behavior expected during phase separation and that observed in this system is related to the shape of the curves of scattered light intensity versus wavevector. The angular position of the maximum in scattered light intensity in Figs. 4 and 7 is invariant with time. The latter stages of phase separation involve an increase in the size of the phase domains resulting in a shift of the peak position [27–29]. The invariant peak position, therefore, suggests that the phase morphology is not changing during the clear to opaque transition for the cast blends studied.

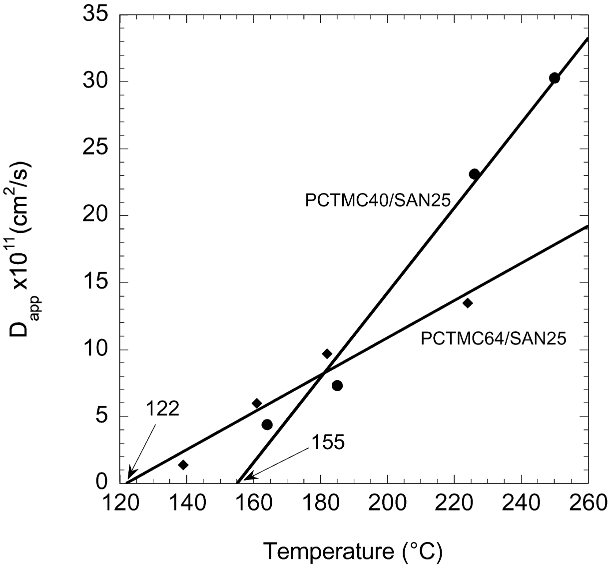

Fig. 11. Apparent diffusion coefficients for PCTMC40/SAN25 and PCTMC64/SAN25 blends. According to the classical Cahn–Hillard analysis, the intercepts would correspond to the spinodal temperatures if the blends were indeed undergoing phase separation.

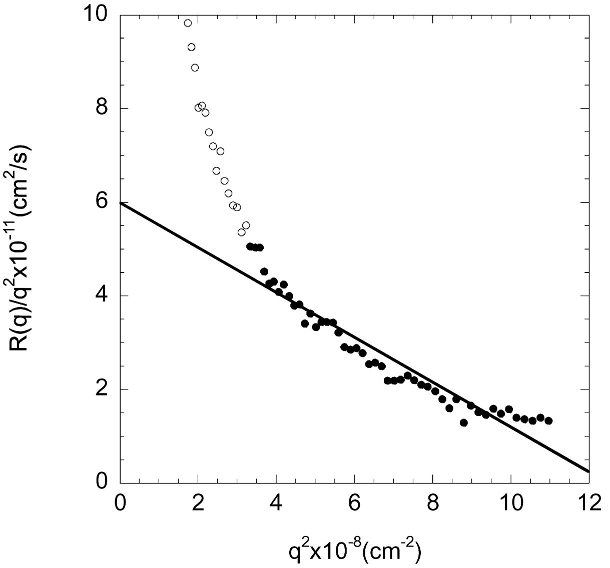

Fig. 12. R/q^2 versus q^2 curve expanded over a larger range of q^2 values for the PCTMC40/SAN25 temperature jump to 161 °C. The filled markers represent data used in Fig. 10(a); the open circles were disregarded in the regression shown in Fig. 10(a).

5. Conclusions

Despite a suggestion of miscibility between a TMC-PC copolycarbonate and a SAN copolymer, the range of TMC-PC copolycarbonates and the TMC-PC homopolymer were found to be immiscible with several SAN materials. Due to the temperature dependence of the refractive index difference between phases in these blends, a clear to cloudy transition occurs during heating even though no phase separation takes place. This assertion was proven through the analysis of glass transition behavior, the correlation between predicted refractive indices and scattered light, the kinetics of the changes in scattered light, scattered light peak position, and the angular dependence of the Cahn–Hillard growth factor. If the linearized Cahn–Hillard model is used to describe the changes during a temperature jump experiment, the corresponding analysis could lead one to assign a LCST to these blends even though no phase transition actually occurs.

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