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Miscibility of copolycarbonate blends with poly(styrene-*co*-acrylonitrile) copolymer and their interaction energies

Y. Kim, J.E. Yoo, C.K. Kim*

Department of Chemical Engineering, Chung-Ang University, 221 Huksuk-Dong, Dongjak-Gu, Seoul 156-756, South Korea

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Abstract

The phase behavior of dimethyl polycarbonate-tetramethyl polycarbonate (DMPC–TMPC) blends with poly(styrene-*co*-acrylonitrile) copolymers (SAN) and the interaction energies of binary pairs involved in blend has been explored. DMPC–TMPC copolycarbonates containing 60 wt% TMPC or more were formed miscible blends with SAN containing limited amounts of AN. The miscibility of copolycarbonate with SAN decreases as the DMPC content increases. The miscible blends showed the LCST-type phase behavior or did not phase separate until thermal degradation. The binary interaction energies involved in the miscible blends were calculated from the phase boundaries using the lattice-fluid theory combined with binary interaction model. The phenyl ring substitution with methyl groups did not lead to interactions that are favorable for miscibility with polyacrylonitrile (PAN). The interaction energies of the polycarbonates blends with SAN copolymers as a function of AN content were obtained. It was revealed that the incline of the number of methyl groups on the phenyl rings of bisphenol-A unit acts favorably for the miscibility with SAN copolymer when SAN contains less than about 30 wt% AN and shifts the most favorable interaction to the low AN content.

Keywords: DMPC–TMPC copolycarbonates; SAN copolymers; Blends

1. Introduction

Successful design of polymer blend systems requires the ability to control or manipulate the phase behavior of the mixture. Since polymer–polymer interaction is an important element in predicting the thermodynamic phase behavior of polymer blends and some of their physical properties, the quantitative information about them is required in controlling morphology of polymer blend. For the purpose of obtaining information, to guide molecular structure design for useful blend, we have being explored how the molecular structure of a series of high performance polymers such as polycarbonates and polysulfones affects their interaction and miscibility with common polymers like polystyrene (PS), polymethyl methacrylate (PMMA), poly(styrene-*co*-acrylonitrile) (SAN), and poly(styrene-co-methylmethacrylate) (SMMA) [1–18]. Especially, in the previous researches, we have examined phase behavior of PC/SAN and TMPC (tetramethyl bisphenol-A polycarbonate)/SAN blends and their interaction energies as a function of acrylonitrile (AN) content of SAN copolymers [8,9]. It was revealed that PC blends with SAN were immiscible and their interaction energies were always positive regardless of AN content of SAN. However, TMPC blends with SAN copolymers were miscible and their interaction energies were negative when SAN copolymers contain less than 20 wt% AN [7]. We also examined dimethyl bisphenol-A polycarbonte (DMPC) blends with various copolymers containing styrene or methacrylate to produce miscible blends and to characterize interaction energies involved in them [18].

In this study, to understand how the methyl substitution on the phenyl ring of polycarbonate repeat unit affects miscibility with SAN copolymers, interaction energies between DMPC and SAN as a function of AN content of SAN copolymers were explored. Since DMPC did not form miscible blends with SAN copolymers, based on the miscibility of TMPC and SAN copolymers [8] DMPC–TMPC random copolycarbonates were prepared at various

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* Corresponding author. Tel.: +82-28205324; fax: +82-28243495.
E-mail address: ckkim@cau.ac.kr (C.K. Kim).

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compositions to produce miscible blends with SAN copolymers. Interaction energies of binary pairs involved in these blends were also extracted from the LCST-type phase boundaries of miscible blends using the lattice-fluid theory [19–23] combined with a binary interaction model [23–26].

2. Materials and procedures

DMPC, TMPC, and DMPC–TMPC copolycarbonates were synthesized in our laboratory. Bisphenol-A monomers were reacted with bis(trichloromethyl) carbonate, triphosgen, to produce the polycarbonates using an interfacial polymerization technique. Triethylamine was used as a phase transfer agent to transport salts from the aqueous phase into the organic phase where reaction with the soluble organic species occurs [10]. The resulting polycarbonates dissolved in methylene chloride, were precipitated with methanol. Some of the SAN copolymers were obtained from external sources while remainders were synthesized. The synthesis of SAN copolymer was performed in bulk at 70 °C with AIBN as an initiator and tri-dodecyl mercaptan as a chain transfer agent. Conversion for the synthesis of copolymers was kept about 10% to avoid composition drift. Molecular weight information of copolymers was obtained using GPC calibrated with polystyrene standards. The monomer content of the copolymers was determined by element analysis and ^{1}H NMR. Homopolymers and copolymers used in this study were listed in Table 1. The numerical part of the code for copolymers indicates the weight percent of tetramethylbisphenol-A or that of AN.

Blends were prepared via solution casting from methylene chloride. The casting solutions were dried at 35 °C for a day in an air circulating oven until most of the solvent had evaporated, and then the resulting films were further dried in a vacuum oven at 120 °C for a week. Glass transition temperature (T_g) of blend was determined using a differential scanning calorimeter (DSC, TA instrument, model DSC-2010). The first scan was run up to 180 °C to erase previous thermal history during sample preparation, then the sample was quenched to 25 °C to start the second scan. The onset of the transition in the heat capacity was defined as T_g.

The temperature at which phase separation caused by lower critical solution temperature (LCST), was measured by an annealing technique to access the closest true equilibrium temperature [8–17]. To observe approximate value of phase separation temperature, the specimen covered with a cover glass was mounted on a hot stage (Linkam THMS 600) equipped with a temperature controller (Limkam, TMS 92). The sample was heated rapidly to a temperature about 20 °C below the expected phase separation temperature and heated 2 °C/min. Changes in the image with temperature were observed as the specimens were heated at a rate of 2 °C/min. The temperature at which the image first started to change was taken as the approximate value of phase separation temperature. To determine the true equilibrium temperature, blend specimens were annealed in the hot stage at fixed temperatures in the vicinity of the expected phase boundary for 30 min. The image was observed to determine whether a change had occurred as a result of annealing or not. The temperature at which the image first started to change as a result of annealing was taken as the phase separation temperature.

Table 1
Polymers used in this study

Polymer	Copolymer composition[a]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]	Refractive index	Source
PS	–	192,400	2.16	1.593[c]	LG Chemical
SAN2	2% AN	213,000	1.72	1.591[c]	Asahi Chemical
SAN5.7	5.7% AN	210,000	1.92	1.588[c]	Asahi Chemical
SAN10	10% AN	215,000	2.03	1.583[d]	Synthesized
SAN15	15% AN	103,500	2.03	1.579[d]	Synthesized
SAN18	18% AN	13,500	1.95	1.577[d]	Synthesized
SAN20	20% AN	174,500	2.21	1.575[c]	Synthesized
SAN24	24% AN	153,000	1.83	1.572[c]	LG Chemical
DMPC	–	48,300	2.47	1.578[c]	Synthesized
TMPC	–	46,700	2.07	1.546[c]	Synthesized
DMPC–TMPC 41	41 wt% TMPC	40,500	2.05	1.565[d]	Synthesized
DMPC–TMPC 50	50 wt% TMPC	30,500	1.79	1.562[d]	Synthesized
DMPC–TMPC 60	60 wt% TMPC	23,400	1.69	1.559[d]	Synthesized
DMPC–TMPC 74	74 wt% TMPC	29,100	1.56	1.554[d]	Synthesized
DMPC–TMPC 83	83 wt% TMPC	28,400	1.64	1.551[d]	Synthesized

[a] Monomer content in copolymer was determined by elemental analysis.
[b] Molecular weights were determined by GPC using polystyrene standards.
[c] Data obtained from product literature.
[d] Obtained by group contribution method.

3. Results and discussion

3.1. Miscibility of blends

Blends of PC with PS and SAN are always immiscible [9, 13]. However, other studies [1–5,8] have shown that TMPC/PS blends and TMPC blends with styrene copolymers containing limited amounts of either MMA or AN exhibit one-phase behavior. The blends of DMPC–PS and DMPC–SAN were translucent and their thermograms reveal two T_g's regardless of blend compositions and AN content of SAN copolymers. Since DMPC–PS and DMPC–SAN blends were immscible, DMPC–TMPC copolymers were prepared at various compositions to obtain miscible blends with PS and SAN copolymers. Fig. 1 shows the selected DSC thermograms of PS blends with DMPC–TMPC copolymers containing various amount of TMPC. When the copolycarbonate contains 60% or more TMPC by weight, blends with PS exhibit a single glass transition that changes with blend composition as shown in Fig. 2 for DMPC–TMPC 60/PS blends. On ther other hand, blends of PS with copolycarbonates containing 50% TMPC or less were cloudy at the casting condition and exhibited two glass transitions that were distinctly separated.

When copolycarbonates contain 50 wt% TMPC or less, binary blends of DMPC–TMPC and SAN were not miscible regardless of blend compositions and the AN contents of SAN copolymers. However, copolycarbonates containing 60 wt% TMPC or more were formed miscible blends with SAN copolymers containing limited amounts of AN. Fig. 3 shows the selected DSC thermograms of DMPC–TMPC 60 blends with SAN copolymers containing various amount of AN. DMPC–TMPC 60 copolycarbonates were miscible with SAN copolymers containing 10 wt% AN or less regardless of blend compositions. DMPC–TMPC 74/SAN blends were also miscible when SAN copolymers contain 10 wt% AN or less, while DMPC–TMPC 83/SAN blends were miscible when SAN copolymers contain less than or equal to 15 wt% AN. Note that TMPC is miscible with SAN copolymers containing 18 wt% AN [8].

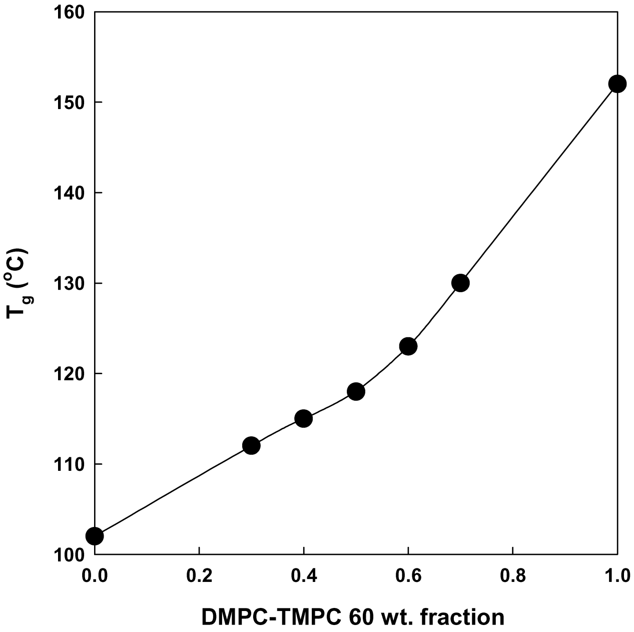

Fig. 2. T_g behavior of DMPC–TMPC 60/PS blends.

It may be difficult to detect phase separation by optical observation when each component of blend has similar refractive index. The difference in index of refraction by 0.01 or less is generally regarded as the critical difference necessary for assessing miscibility based on optical observation of blends [27]. It is known that PC blends with PS are not miscible but they are transparent because of the similarity of the refractive indices. Recently Haggard et al. reexamined phase behavior of blends containing SAN copolymers and copolycarbontes of 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexanone and bisphenol-A [27]. None of these blends were miscible. Some of the blends that

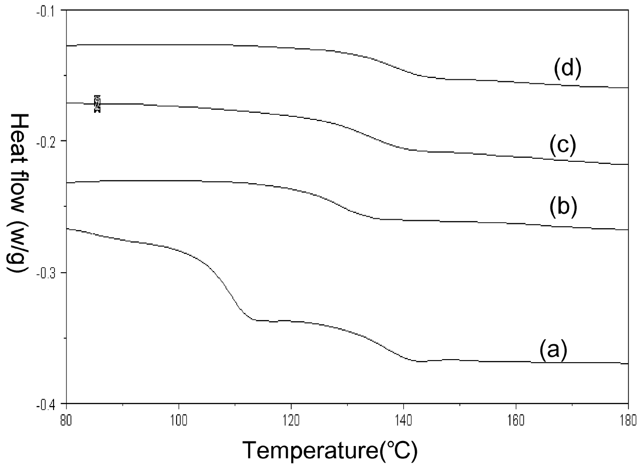

Fig. 1. The selected DSC thermograms of DMPC–TMPC/PS = 5/5 blends: (a) DMPC–TMPC 50/PS = 5/5; (b) DMPC–TMPC 60/PS = 5/5; (c) DMPC–TMPC 74/PS = 5/5; (d) DMPC–TMPC 83/PS = 5/5.

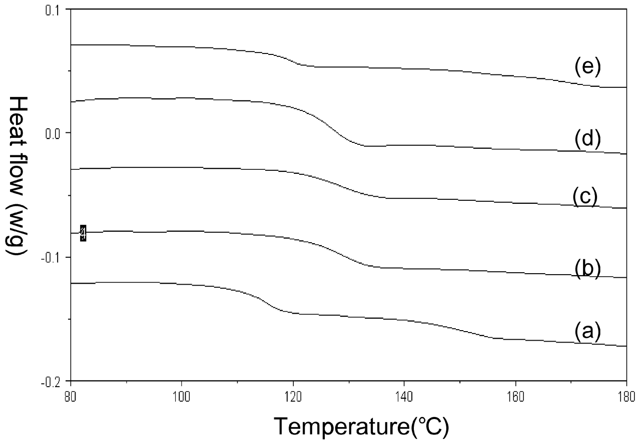

Fig. 3. The selected DSC thermograms of DMPC–TMPC 60 blends with PS or SAN copolymers: (a) DMPC–TMPC 60/SAN 15 = 5/5; (b) DMPC–TMPC 60/SAN 10 = 5/5; (c) DMPC–TMPC 60/SAN 5.7 = 5/5; (d) DMPC–TMPC 60/SAN 2 = 5/5; (e) DMPC–TMPC 60/PS = 5/5.

were transparent became cloudy upon heating not because of the LCST-type phase behavior but because of changes in refractive indices. Since optical observation often gives misleading result in judging the miscibility of blends, we examined refractive indices of polymers used here and then listed in Table 1. Among the miscible blends, DMPC–TMPC 60/SAN 10 blend exhibited the smallest difference in the refractive indices of components. The difference in the refractive indices of these two polymers (0.018) is larger than the critical difference. Note that DMPC/SAN 24 blend is still cloudy even though the difference in the refractive indices of these polymers is about 0.06. Because of these, it can be concluded that the transparent blends observed here are miscible.

To exhibit clearly the effects of copolymer composition on the miscibility of blends, the miscibility map for 50/50 blends as a function of AN content in SAN copolymer were shown in Fig. 4. The miscibility decreases as the DMPC content in copolycarbonate increases when the AN content of the SAN copolymer is held fixed. The addition of AN to styrene ultimately leads to immiscibility. To understand the changes in the miscibility with copolymer compositions, the phase separation temperatures of blends caused by the LCST-type phase behavior were examined.

3.2. LCST-type phase behavior

The temperature at which phase separation caused by LCST-type phase behavior was measured by an annealing technique to access the closest true equilibrium temperature [8–17]. For example DMPC–TMPC 60/SAN 10 = 5/5 blend was heated rapidly to a temperature about 200 °C and then heated at a rate of 2 °C/min. Changes in the image with temperature were observed as the specimens were heated at a rate of 2 °C/min. Changes in the image was observed at 230 °C. After determining the temperature at which phase separation occurred, blend specimens were annealed in the hot stage at a fixed temperature for 30 min. Fig. 5 shows image analyzer photography of DMPC–TMPC 60/SAN 10 = 5/5 annealed at 220 and 230 °C. Fig. 5(a) shows the image analyzer photography of blend after annealed at 220 °C and Fig. 5(b) shows the same blend after being annealed at 230 °C. The blend annealed at 220 °C was still clear and changes in the morphology of the blend were not observed while that annealed at 230 °C was opaque and changes in the morphology were observed. The presence of a separated phase structure implies that phase separation occurred by the LCST-type phase separation behavior. The phase boundary would appear to lie between 220 and 230 °C for this blend. By successively repeating annealing process within the determined temperature range, the location of the phase boundary was determined.

Fig. 6(a) shows the observed phase separation temperatures of miscible copolycarbonate/PS blends caused by LCST-type phase behavior. The effects of TMPC content were exhibited in Fig. 6(b) by plotting the phase separation temperature for a fixed PS content of blend (50 wt%) versus the TMPC content of the copolycarbonates. The miscibility of these copolycarbonates with PS decreases as the DMPC

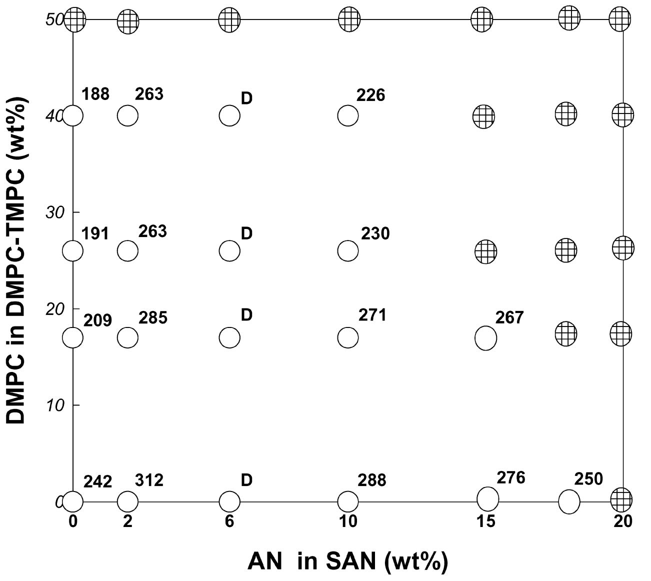

Fig. 4. Miscibility maps for 50/50 = DMPC–TMPC/SAN blends. Open circles indicate miscible blends while filled circles indicate immiscible blends. Numbers indicate phase separation temperatures of blends and 'D' means phase separation did not occurred until thermal degradation.

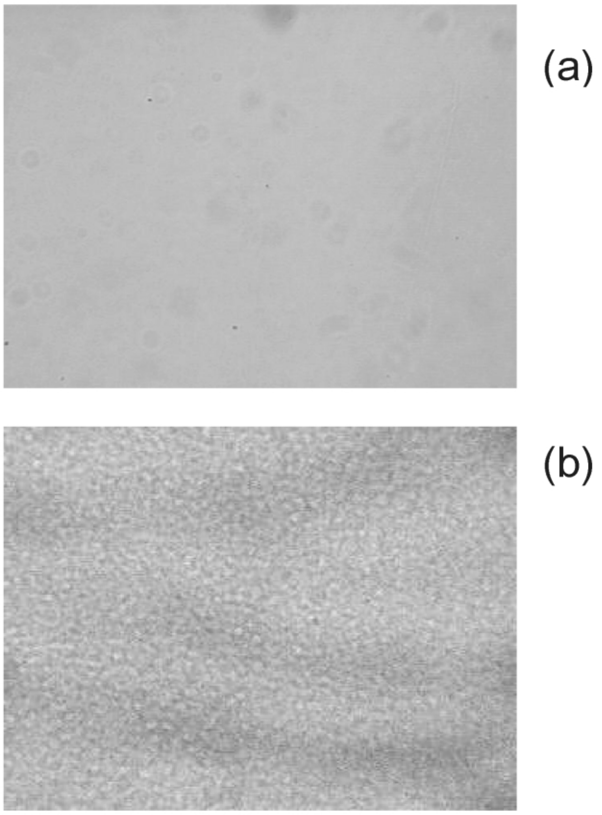

Fig. 5. The image analyzer photography of DMPC–TMPC 60/SAN 10 = 5/5 blend annealed at 220 and 230 °C, respectively: (a) annealed at 220 °C; (b) annealed at 230 °C.

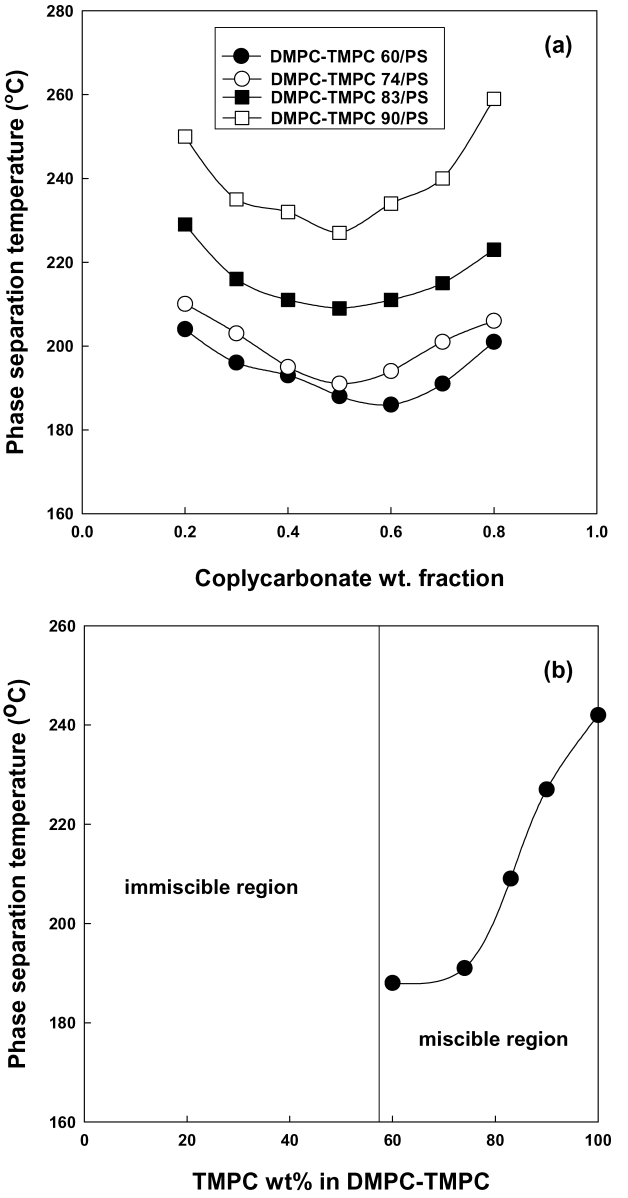

Fig. 6. (a) Phase separation temperatures of PS blends with various DMPC–TMPC copolycarbonates. (b) Effects of copolycarbonate composition on phase separation temperatures of 50/50 = DMPC–TMPC/PS blends.

content increases as expected. DMPC is miscible with TMPC but is immiscible with PS [3,5,10]. According to the binary interaction model [23–26], the unfavorable interaction of DMPC with PS and the favorable interaction of DMPC and TMPC both act against miscibility of the copolycarbonate with PS.

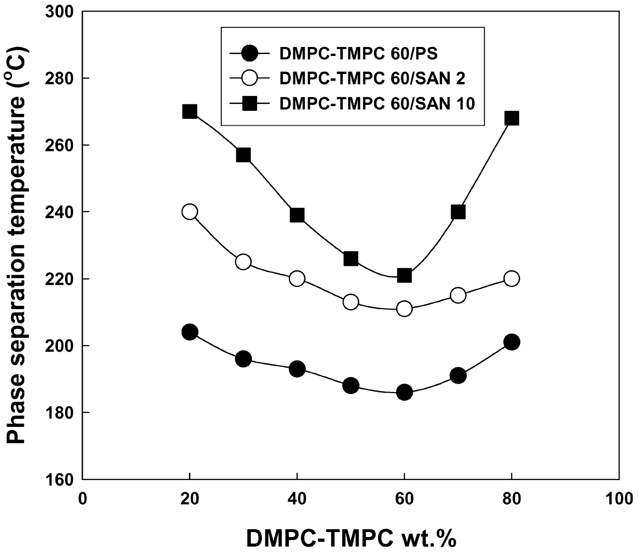

Fig. 7. Phase separation temperatures of DMPC–TMPC 60 blends with SAN copolymers.

Copolycarbonates containing 60 wt% TMPC or more were formed miscible blends with SAN copolymers containing limited amounts of AN. DMPC–TMPC 60 that was miscible with SAN copolymers containing 10 wt% AN or less exhibited LCST-type phase behavior as shown in Fig. 7. The phase separation curves are all very similar with which each shows a minimum at about 50 wt% DMPC–TMPC 60. Note that DMPC–TMPC 60 blends with SAN 5.7 copolymer did not phase separate on heating until thermal degradation temperature (~330 °C). These results indicate that addition of AN to the styrene initially increases miscibility with DMPC–TMPC but ultimately leads to immiscibility. DMPC–TMPC 74/SAN blends exhibited higher phase separation temperature than DMPC–TMPC 60/SAN blends when SAN copolymer contains the same amounts of AN (Fig. 8). It means that the decline of DMPC content in copolycarbonates is favorable for the miscibility with SAN. DMPC–TMPC 83 that was miscible with SAN copolymers containing less than or equal to 15 wt% AN also exhibited LCST-type phase behavior (Fig. 9). As shown in

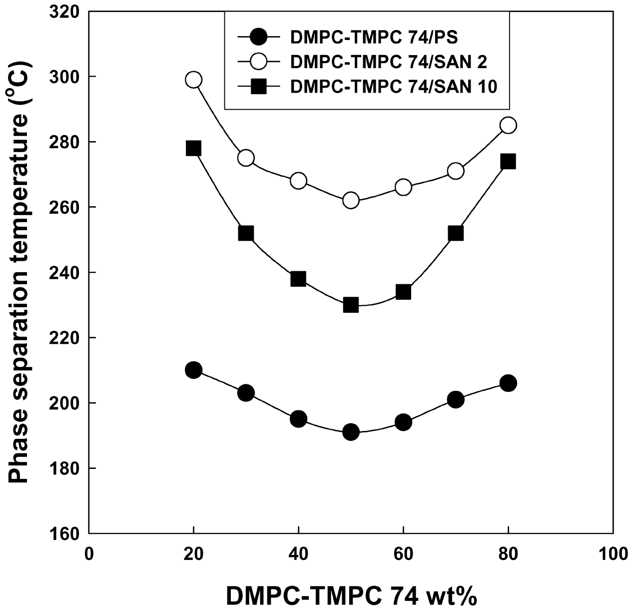

Fig. 8. Phase separation temperatures of DMPC–TMPC 74 blends with SAN copolymers.

Figs. 6–9, the decline of DMPC content in copolycarbonates broadens the miscible region of DMPC–TMPC/SAN blends and increases their phase separation temperatures. Note that TMPC is miscible with SAN copolymers containing 18 wt% or less AN [8]. To exhibit clearly the effects of copolymer composition on the phase behavior of blends, the miscibility map and experimentally determined temperatures at which 50/50 blends phase separate as a function of AN content in SAN copolymer were shown (see Fig. 4). The blend phase separation temperatures decreases as the DMPC content in copolycarbonate increases when the AN content of the SAN copolymer is held fixed. The addition of AN to styrene initially increases the phase separation temperatures but ultimately leads to immiscibility. To understand the phase behavior of blend, interaction energies of binary pairs involved in the blends were calculated from the phase separation temperatures using lattice-fluid theory [19–23] combined with binary interaction model [23–26].

3.3. Interaction energies

The detail background calculating the binary interaction energies involved in the miscible blends from the phase boundaries using the lattice-fluid theory combined with binary interaction model was described in the previous papers [7–23]. To extract information about interaction energy from the liquid–liquid phase boundaries shown in Figs. 6–9, it is assumed that to a good approximation these data correspond to the spinodal curve [7–15,20–23]. The morphology of blend observed at a reported phase separation temperature could be also characterized by a high level of phase interconnectivity in both the minor and major phase caused by spinodal decomposition [20–23].

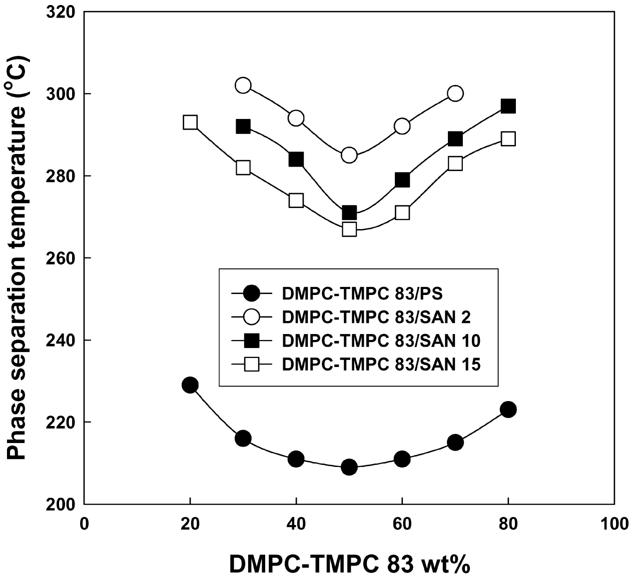

Fig. 9. Phase separation temperatures of DMPC–TMPC 83 blends with SAN copolymers.

According to the lattice fluid theory, the spinodal condition for a compressible mixture can be written

$$\frac{\mathrm{d}^2 g}{\mathrm{d}\phi^2} = g_{\phi\phi} - \frac{(g_{\tilde{\rho}\phi})^2}{g_{\tilde{\rho}\tilde{\rho}}} = 0 \tag{1}$$

where g is the free energy of mixing per unit volume and the subscripts ϕ and $\tilde{\rho}$ indicate partial derivatives with respect to ϕ (volume fraction) or $\tilde{\rho}$ (reduced density). In terms of the Sanchez–Lacombe theory, the indicated derivatives for binary mixture are given by [6]

$$g_{\phi\phi} = -2\tilde{\rho}\Delta P^*(i,j) + RT\left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*}\right) \tag{2}$$

$$g_{\tilde{\rho}\phi} = -(p_1^* - p_2^* - (1-2\phi_1)\Delta P^*(i,j)) + \frac{RT}{\tilde{\rho}} \times\left(\frac{1}{r_1 v_1^*} - \frac{1}{r_2 v_2^*}\right) - RT\left(\frac{1}{v_1^*} - \frac{1}{v_2^*}\right) \times\left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right) \tag{3}$$

$$g_{\tilde{\rho}\tilde{\rho}} = \frac{RT}{v^*}\left(\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1}{\tilde{\rho}^2}\left(1 - \frac{1}{r}\right)\right) \tag{4}$$

According to the binary interaction model, the interaction energy density between the pair of multicomponent polymers i and j, i.e. $\Delta P^*(i,j)$ can be expressed as

$$\Delta P^*(i,j) = \sum\sum_{k>l} \Delta P_{kl}^*(\phi_{ki} - \phi_{kj})(\phi_{lj} - \phi_{li}) \tag{5}$$

In the above, ΔP_{kl} is the binary interaction energy density between units k and l while ϕ_{ki} is the volume fraction of k unit in the polymer i. For a binary blend of copolymer i composed of units 1 and 2 with another copolymer j composed of units 3 and 4, the interaction energy density between polymer i and j is given by

$$\Delta P^*(i,j) = \Delta P_{13}^*\phi_1'\phi_3'' + \Delta P_{14}^*\phi_1'\phi_4'' + \Delta P_{23}^*\phi_{25}'\phi_3'' + \Delta P_{24}^*\phi_2'\phi_4'' - \Delta P_{12}^*\phi_1'\phi_2' - \Delta P_{34}^*\phi_3''\phi_4'' \tag{6}$$

where ϕ_k' and ϕ_k'' denote volume fraction of unit k in polymer i and j.

The characteristic parameters of each polymer evaluated from pressure-volume-temperature (PVT) data in the previous researches [7–9,18] were listed in Table 2. Fig. 10 shows $\Delta P^*(i,j)$ calculated from the experimental phase separation temperatures found for DMPC–TMPC 83 blends with PS using the theoretical spinodal condition, i.e. Eq. (1). The $\Delta P^*(i,j)$ values so obtained are essentially composition independent. This is also true for other blends not shown. As shown in Fig. 11, the calculated $\Delta P^*(i,j)$ for each DMPC–TMPC with PS is negative and monotonically increases with DMPC content. It means that DMPC units in copolycarbonates are unfavorable for miscibility with PS. According to the binary interaction model, the up-convex

Table 2
Characteristic properties of polymers

Polymers	T^* (K)	P^* (bar)	ρ^* (g cm^{-3})	References
PS	810	3725	1.0922	[7]
SAN2	803	3777	1.0935	[8]
SAN5.7	815	3792	1.0982	[8]
SAN10	819	3834	1.1028	[8]
SAN15	823	3893	1.1081	[8]
SAN20	828	3949	1.1135	[8]
SAN24	832	4001	1.1179	[8]
DMPC	781	4742	1.1830	[18]
TMPC	729	4395	1.1854	[7]

curvature stems from the favorable interaction between DMPC and TMPC. Using $\Delta P^*_{\mathrm{TMPC-S}} = -0.17$ cal/cm^3 obtained in the previous research [7] from the phase behavior of TMPC/PS blends, the interaction energy densities for the remaining monomer unit pairs in DMPC–TMPC/PS system were obtained by fitting the calculated values to Eq. (6) using linear regression. The calculated interaction energy densities for DMPC–PS and TMPC–TMPC pairs, i.e. $\Delta P^*_{\mathrm{DMPC-S}}$ and $\Delta P^*_{\mathrm{DMPC-TMPC}}$ were 0.30 cal/cm^3 and -0.09 cal/cm^3, respectively. Using the interaction energy densities obtained here and those determined previously [8,9], i.e. $\Delta P^*_{\mathrm{S-AN}} = 7.37$ cal/cm^3, $\Delta P^*_{\mathrm{TMPC-S}} = -0.17$ cal/cm^3, $\Delta P^*_{\mathrm{TMPC-AN}} = 5.92$ cal/cm^3, $\Delta P^*_{\mathrm{DMPC-S}} = 0.30$ cal/cm^3, and $\Delta P^*_{\mathrm{DMPC-TMPC}} = -0.09$ cal/cm^3, the interaction energy density for the remaining monomer unit pair for DMPC–TMPC/SAN system, i.e. $\Delta P^*_{\mathrm{DMPC-AN}}$ obtained in a similar fashion was 4.60 cal/cm^3

The interaction energy densities of the binary pairs involving in the various polycarbonates and SAN were listed in Table 3. To examine the reliability of the interaction energy densities obtained here, the spinodal curve calculated from the Eq. (1) and values listed in Table 3. Fig. 12 showed that experimental phase separation temperatures and the spinodal curve calculated from the Eq. (1) with a fixed value of $\Delta P^*_{\mathrm{DMPC-TMPC74-SAN10}} = -0.12$ cal/cm^3 for DMPC–TMPC 74/SAN 10 blends and with $\Delta P^*_{\mathrm{DMPC-TMPC83/PS}} = -0.07$ cal/cm^3 for DMPC–TMPC 83/PS. The curves agree with the experimentally determined phase separation temperatures.

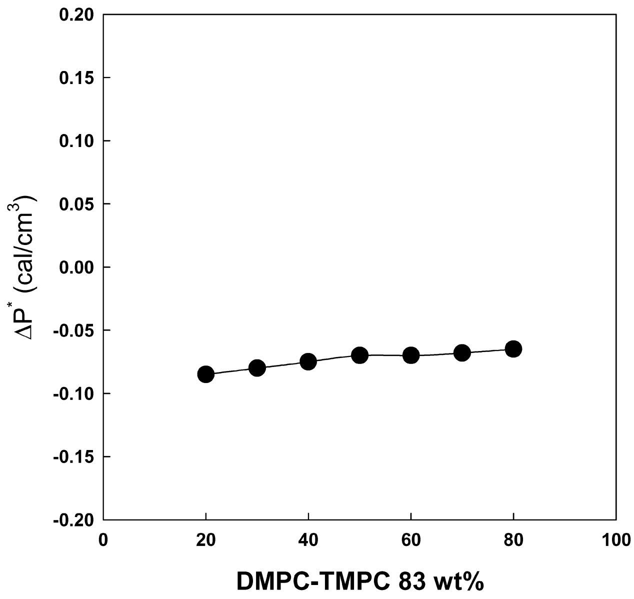

Fig. 10. Interaction energies for blends of DMPC–TMPC 83 with PS.

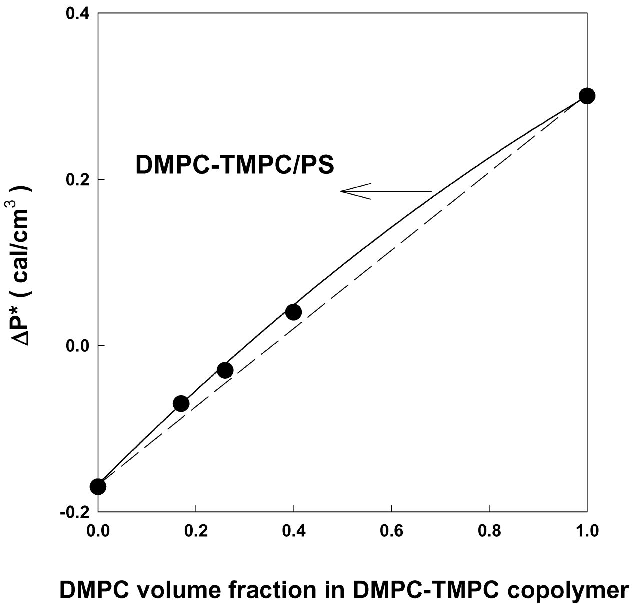

Fig. 11. Interaction energies for blends of DMPC–TMPC with PS. Note that solid line were obtained by fitting the interaction energies to Eq. (6) using linear regression.

It is known that the phenyl ring substitution with methyl groups leads to interactions that are favorable for miscibility with PS while it does not leads to interactions that are favorable for miscibility with PMMA [10]. As listed in Table 3, the addition of methyl groups on the ring of the bisphenol-A unit results in unfavorable interactions with polyacrylonitrile. It is interesting to examine the effects of phenyl ring substitutions with methyl groups on the miscibility with SAN copolymers. Fig. 13 shows interaction energy densities of the various polycarbonates blends with SAN copolymers as a function of AN content using the interaction energy densities of each pairs. These results also

Table 3
Interaction energies of various binary pairs

Interaction pairs	ΔP^* (cal/cm^3) (this study)	ΔP^* (cal/cm^3) (previous studies)	References
PC–S	–	0.43	[9,12]
DMPC–S	0.3	0.3	[16]
TMPC–S	–	−0.17	[7]
PC–AN	–	4.4	[9,12]
DMPC–AN	4.6	–	
TMPC–AN	–	5.92	[8]
PC–TMPC	–	−0.23	[9]
DMPC–TMPC	−0.09	–	

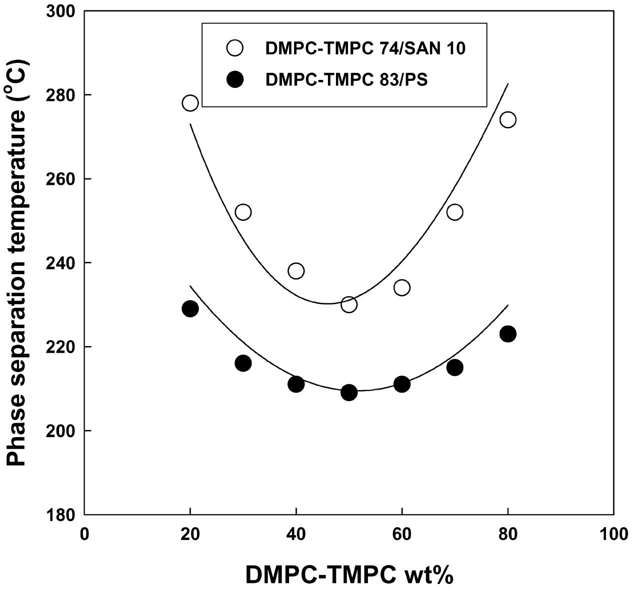

Fig. 12. Phase separation temperatures of the selected DMPC–TMPC/SAN and DMPC–TMPC/PS blends. Note that the spinodal curves were calculated from the Eq. (1) with a fixed value of $\Delta P^*_{\mathrm{DMPC-TMPC74/SAN10}} = -0.12\ \mathrm{cal/cm^3}$ for DMPC–TMPC 74/SAN 10 blends and with $\Delta P^*_{\mathrm{DMPC-TMPC83/PS}} = -0.07\ \mathrm{cal/cm^3}$ for DMPC–TMPC 83/PS.

confirm that high molecular weight blends of PC/SAN and DMPC/SAN are immiscible. However, the most favorable interaction occurs around 25 wt% AN for PC/SAN blends where $\Delta P^*_{\mathrm{PC-SAN}} = 0.04\ \mathrm{cal/cm^3}$ and around 19 wt% AN for DMPC/SAN blends, where $\Delta P^*_{\mathrm{DMPC-SAN}} = 0.02\ \mathrm{cal/cm^3}$. The interaction energy density for TMPC/SAN blends that are miscible when SAN copolymers contain less than 20 wt% AN exhibits a minimum value at around 9 wt% AN. These results indicate that by increasing number of methyl groups on the phenyl rings of bisphenol-A unit interaction energy with SAN copolymer becomes favorable when SAN contains less than about 30 wt% AN and minimum value of interaction energy shifts to the low AN content.

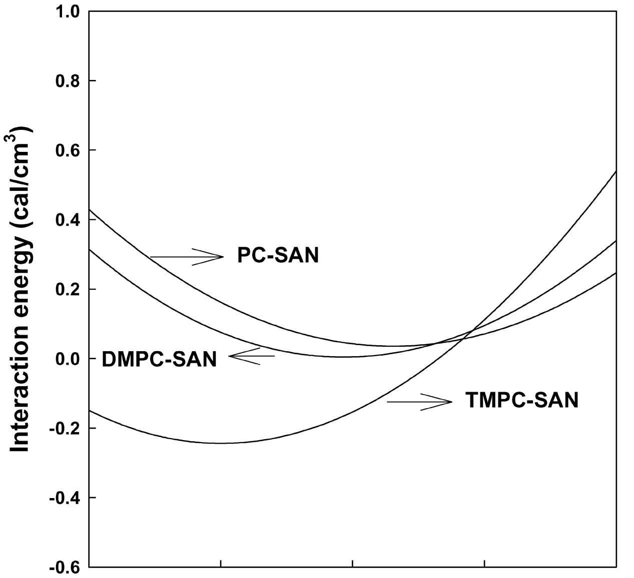

Fig. 13. Interaction energies of various polycarbonates as a function of AN content of SAN copolymers.

4. Summary

The phase behavior of DMPC–TMPC/SAN blends and interaction energies of binary pairs involved in blend has been explored to understand how the methyl substitution on the phenyl ring of polycarbonate repeat unit affects miscibility with SAN copolymers. Since DMPC does not form miscible blends with SAN copolymers regardless of AN content of SAN copolymer, based on the miscibility of TMPC and SAN copolymers DMPC–TMPC random copolycarbonates were prepared at various compositions to produce miscible blends with SAN copolymers. DMPC–TMPC copolycarbonates containing 60 wt% TMPC or more were formed miscible blends with SAN copolymers containing limited amounts of AN. The miscibility of copolycarbonate with SAN decreases as the DMPC content increases. The binary interaction energies involved in the miscible blends were calculated from the phase boundaries using the lattice-fluid theory combined with binary interaction model. From the interaction energies of binary pair, the interaction energy densities of the various polycarbonates blends with SAN copolymers as a function of AN content were obtained. It was revealed that by increasing number of methyl groups on the phenyl rings of bisphenol-A unit interaction energy with SAN copolymer becomes favorable when SAN contains less than about 30 wt% AN and minimum value of interaction energy shifts to the low AN content.

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