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Interactions in blends of bisphenol-A polycarbonate and poly(styrene-*co*-methacrylic acid)

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Abstract

Interactions in bisphenol-A polycarbonate/poly(styrene-*co*-methacrylic acid) (PC/P(S-MAA)) blends, which show UCST phase transition and Miscibility Valley phenomena in temperature-copolymer composition plane, were investigated by Fourier transform infrared (FT-IR) spectroscopy. It was found that methacrylic acid (MAA) units in poly(styrene-*co*-methacrylic acid) (P(S-MAA)) formed associated dimers at low temperature and the dimer dissociated with elevating temperature. Since the temperature dissociating associated dimer of MAA units was corresponding to phase transition temperature in PC/P(S-MAA) blends, the UCST phase behavior would be caused by association–dissociation in MAA units. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blend; Interactions; UCST

1. Introduction

It has been well known that phase behaviors in dissimilar polymer pairs are strongly affected by intermolecular interactions [1–3]. Hence, a lot of studies on polymer blends have focused on the relationship between miscibility or phase separation and intermolecular interactions [1–3]. In our previous studies, we have studied phase behavior and intermolecular interactions in polymer blends containing polar groups [4–10]. Among them, it was suggested that associative interactions between identical components induced phase separation in polymer blends [10].

In our previous studies, we found UCST phase transition in blends of bisphenol-A polycarbonate (PC) and poly (styrene-*co*-methacrylic acid) (P(S-MAA)) [11]. In addition, we also found that the plots of the phase transition temperature at critical composition of the blends show concave curve against copolymer composition of P(S-MAA) [11]. This concave curve of UCST against copolymer composition was named as *Miscibility Valley*. Both the UCST phase transition and Miscibility Valley phenomena are also found in blends of polybutadiene and hydrogenated terpene resin [12]. The UCST phase behavior and Miscibility Valley phenomena in the both systems have been explained on the basis of lattice theory for miscibility in polymer blends containing random copolymers [13,14]. However, because PC/P(S-MAA) blends contain polar groups, such as methacrylic acid (MAA) units, discussion on specific interaction is needed to elucidate of the miscibility in the PC/P(S-MAA) blends.

It has been well-known that the carboxylic acids in P(S-MAA) form associated dimers [10,15–17]. Since the associations between identical components may cause phase separation [10], it is considered that the dimerizations of MAA units in P(S-MAA) concern with the phase behavior in PC/P(S-MAA) blends. Then, in this study, we investigate the relation between association of MAA units and phase behavior in PC/P(S-MAA) blends.

2. Experiments

Materials. PC and P(S-*co*-MAA) were supplied from Mitsubishi Kasei Co., Ltd. and Dainippon Ink Co., Ltd., respectively. Molecular characteristics of the polymers were listed in Table 1. Before using the polymers, they were reprecipitated using THF as a good solvent and methanol as a poor solvent.

Blend preparation. PC and P(S-MAA), weighted to desired composition, were dissolved in THF at a concentration about 5 wt%. The solution was stirred until it became clear. Then, the solvent was evaporated on glass plates.

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Table 1
Molecular characteristics of samples

Sample	MAA content (wt%)	T_g (°C)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_z \times 10^{-4}$
PC		154			2.4
M-4	4	119	28	11	
M-6	6	124	30	12	
M-10	10	132	30	12	
M-15	15	143	31	12	
M-23	23	157	21	8.8	

Resulting film specimens were dried at 90°C for 3 days and around T_g for 1 h in reduced pressure.

Measurements. Infrared spectroscopy was performed using a JEOL JIR-100 Fourier transform infrared (FT-IR) spectrometer. The film samples were annealed at desired temperature, quenched in liquid N_2 and then measured. All the measurements were carried at a resolution of 1 cm^{-1} and scan times of 100.

3. Results and discussion

Fig. 1 shows schematic representations of association of MAA units in P(S-MAA). MAA units take both associated dimer and free states. In general, infrared absorptions of carbonyl stretching bands of associated dimers and free states in MAA units appear at 1750 and 1700 cm^{-1}, respectively [10,15–17]. Hence, we would know state of the association of MAA units in PC/P(S-MAA) blends by analyzing the FT-IR spectra of carbonyl stretching bands at 1750 and 1700 cm^{-1}. Then, we focus on these peaks as an index for association of MAA units.

Fig. 2 shows FT-IR spectra attributed to the carbonyl stretching bands for P(S-MAA)M-15. As mentioned above, the absorbance peaks centered at 1700 and 1745 cm^{-1} are attributed to the carbonyl groups of associated dimer and free state of MAA units, respectively. The carbonyl groups of associated dimer and free state are denoted as $C{=}O_b$ and $C{=}O_f$, respectively. Since intensity of the peak of $C{=}O_b$ is much stronger than that of $C{=}O_f$, it is obvious that most MAA units form associated dimer and a part of MAA units takes free state in only P(S-MAA). This result is closely corresponding to the FT-IR analyses for poly(ethylene-*co*-methacrylic acid) or poly(styrene-*co*-acrylic acid) [3,15–17]. If the states of the associations of MAA units in P(S-MAA) relate strongly to the phase behavior in PC/P(S-MAA) blends, it is expected that the FT-IR spectra of the carbonyl stretching bands is drastically changed around phase transition temperature of PC/P(S-MAA) blends.

Fig. 3 shows FT-IR spectra around 1750 cm^{-1} for PC/P(S-MAA)M-15 8/2 (w/w) blends annealed at 150, 180, 200 and 220°C. Intensive peak centered at 1775 cm^{-1} is attributed to carbonyl stretching band of carbonate bonds

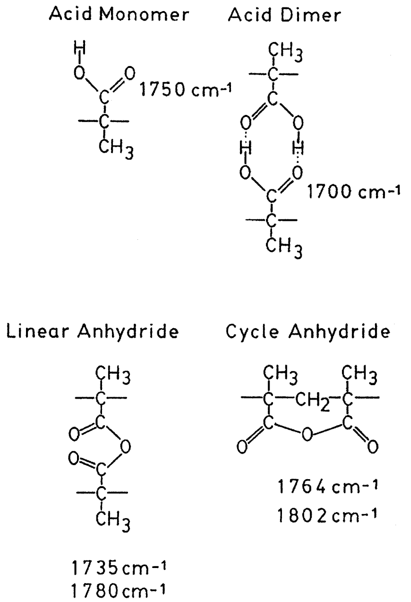

Fig. 1. Schematic diagram showing the carboxylic acid monomer and dimer.

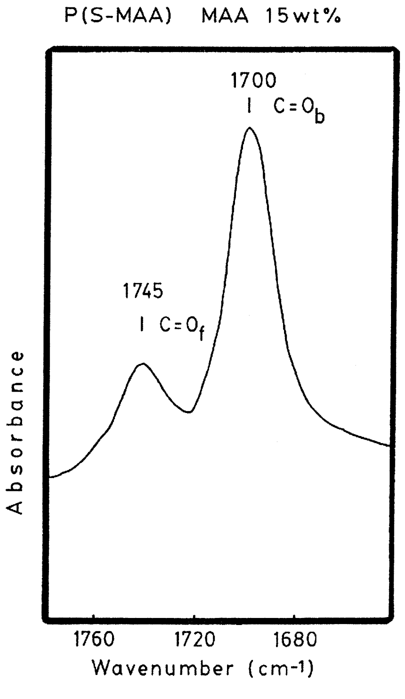

Fig. 2. FT-IR spectra attributed to carbonyl stretching band in P(S-MAA).

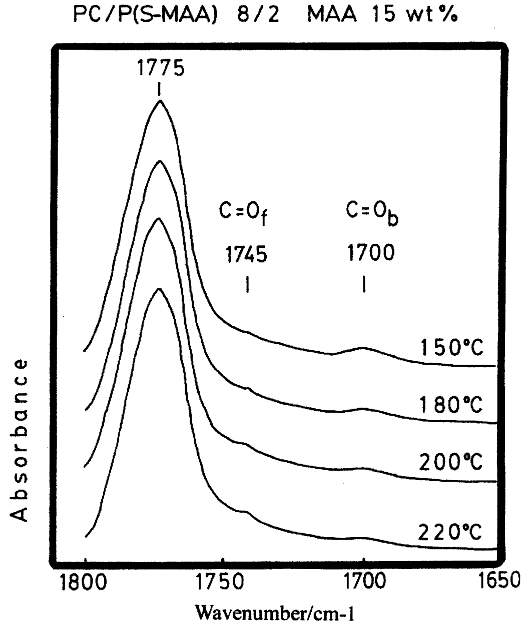

Fig. 3. FT-IR spectra of PC/P(S-MAA)M15 8/2 blend annealed at 150, 180, 200 and 220°C for 2 h.

of PC. The peak at 1775 cm^{-1} is invariant with variation of annealing temperature. Therefore, it is considered that there is no specific interaction between PC and P(S-MAA). On the other hand, intensity of the peak of $\mathrm{C{=}O_b}$ at 1700 cm^{-1} is decreased with elevating annealing temperature. In addition, shoulder at 1745 cm^{-1} which is assigned to $\mathrm{C{=}O_f}$ is appeared with elevating annealing temperature. This result suggests that population of the $\mathrm{C{=}O_f}$ is increasing and that of the $\mathrm{C{=}O_b}$ is decreasing with elevating temperature in PC/P(S-MAA) blends. However, because the intensity of the peak at 1775 cm^{-1} is much too strong in comparison with that of the carbonyl stretching bands of MAA units, detection of peak of $\mathrm{C{=}O_f}$ is too difficult. Then, states of associations of MAA units in PC/P(S-MAA) blends are discussed by absorbance ratio of the peak of $\mathrm{C{=}O_b}$ at 1700 cm^{-1} to invariant peak of 1775 cm^{-1}.

Fig. 4 shows plots of the absorbance ratio of the peak at 1700 cm^{-1} to that of 1775 cm^{-1} in PC/P(S-MAA) 8/2 (w/w) blends against annealing temperature. The absorbance ratio of each blend is drastically decreased with elevating annealing temperature. Especially, in PC/P(S-MAA)M-15 8/2 blend, the absorbance ratio is changed discontinuously at certain temperature. This suggests that associated dimers tend to dissociate with elevating temperature. Hence, it is considered that the temperature drastically decreasing the absorbance ratio is regarded as dissociating temperature of associated dimer of MAA units. If the dimerization–dissociation of MAA units concern with UCST phase behavior in PC/P(S-MAA) blends, it is considered that the temperatures dissociating the associated dimers of MAA units in PC/P(S-MAA) blends are closely corresponding to the phase transition temperature in PC/P(S-MAA) blends obtained in our previous study [11].

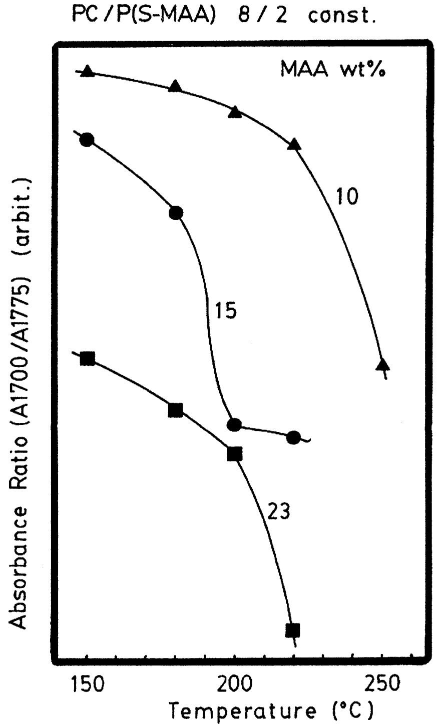

Fig. 4. Temperature dependence of FT-IR absorbance ratio of $\mathrm{C{=}O_b}$ stretching band to peak at 1775 cm^{-1}(A1700/A1775) in PC/P(S-MAA) 8/2 blends.

Fig. 5 shows plots of dissociating temperature of associated dimers of MAA units in PC/P(S-MAA) (w/w) 8/2 blends against MAA contents in P(S-MAA). In this figure, closed circles are the dissociating temperature of MAA dimers obtained by FT-IR and solid line is phase boundary curve against copolymer composition, so-called as Miscibility Valley, obtained in our previous study [11].

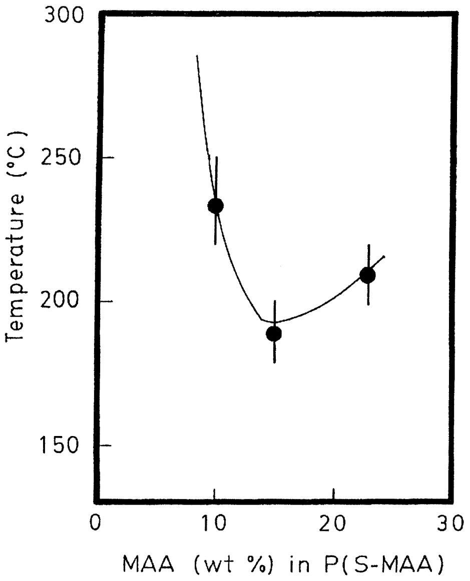

Fig. 5. Miscibility valley for PC/P(S-MAA) 8/2 blends. ●: FT-IR, solid line: previous study [11].

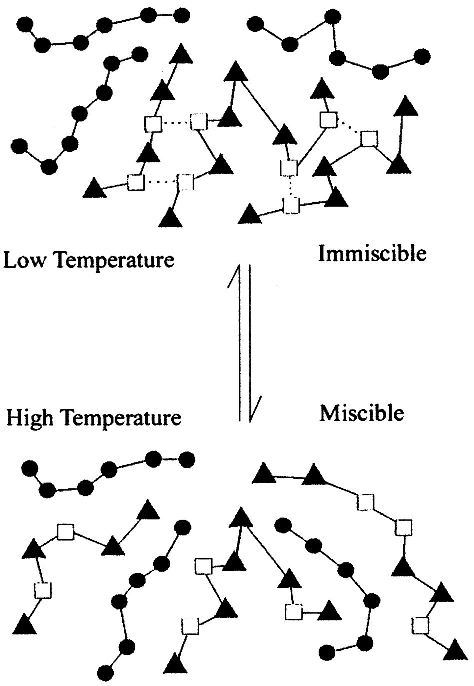

Fig. 6. Schematic representation of UCST behavior of PC/P(S-MAA) blends.

Hence, at higher temperature than the Miscibility Valley curve, PC/P(S-MAA) 8/2 blends are miscible. The dissociating temperatures of MAA dimers in the PC/P(S-MAA) blends are closely corresponding to the curve of Miscibility Valley. Therefore, it is suggested that the phase separations in PC/P(S-MAA) blends are caused due to the formation of associated dimers of MAA units.

Fig. 6 indicates schematic representations variation of association and state of mixture in PC/P(S-MAA) blends with variation of temperature. In this figure, circles, triangles and squares indicate PC units, PS units and MAA units, respectively. At relatively low temperature, since the MAA units form associated dimers, PC/P(S-MAA) blends show phase separation. On the other hand, at relatively high temperature, associated dimers of MAA units are dissociated. Hence, at the high temperature region, PC/P(S-MAA) blends take miscible state. However, for the miscibility in PC/P(S-MAA) blends, it is considered that repulsive interactions between MAA and PS of P(S-MAA) also have significant effects on the miscibility in the PC/P(S-MAA) blends [11–14]. Therefore, it is important for explanation of miscibility in the PC/P(S-MAA) blends to discuss interaction parameter, χ, taking account of intramolecular repulsive interactions. In our previous study [11], we calculated χ between PC and P(S-MAA) and found that the χ showed minimum value at 15 wt% of MAA content in P(S-MAA). Therefore, PC/P(S-MAA)-15 blends show the widest miscible region [11].

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