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Miscibility of polycarbonate with poly(methyl methacrylate-co-cyclohexyl methacrylate)

K. E. Min[1], D. H. Lee[1], and H. M. Jung[2]

[1]Department of Polymer Science, Kyungpook National University, Taegu 702-701, Korea
[2]New Material Department, Samlib Industrial Company, Taegu 702-803, Korea

SUMMARY

Miscibility of bisphenol-A polycarbonate, PC, with methyl methacrylate/cyclohexyl methacrylate, PMCHM, copolymers were examined by glass transition temperature and lower critical solution temperature, LCST, behavior.
PMCHM copolymers were found to be miscible with PC at levels of below 4% or less of CHM in weight. Relatively small amount of the comonomer markedly raised phase separation temperature on heating. This result can be rationalized by intramolecular repulsion effect reported earlier.

INTRODUCTION

It has been recently shown that the temperature at which a phase separates, i.e., cloud point, on heating because of LCST behavior can be elevated by incorporating relatively small amount of a suitable comonomer into one of the component polymer (1-3). This effect considered as a result of a strong interchain attraction such as hydrogen bonding introduced by addition of the comonomer or by a strong intrachain repulsion of the added comonomer with the original monomer unit. The latter promises to be of more potential use than former.

Investigation of recent literatures reveals a rapid growth in the number of pairs of polymers known to form miscible blends (4-6). Among others, it is interesting that the studies on a PC with commercial poly(methyl methacrylate), PMMA, system previously believed to be immiscible can form completely miscible blends at equilibrium (7-9). One of these results shows that phase separation temperature of these mixtures is not much above the glass transition, and special care has to be required even in solution prepared blends to prevent their phase separation (7). However, the reported results can mislead the phase behaviors of pure PC/PMMA blends system since the most of commercial acrylic polymers usually contain a small amount of comonomers, e.g. methyl or ethyl acrylate, to improve thermal stability and processability.

The purpose here is to examine how the temperature of phase separation of PC/PMMA blends can be raised by copolymerization of MMA with the intrarepulsive monomer like cyclohexyl methacrylate, CHM. And these were compared with previous results which seemed authors has left so-called 'comonomer effect' out of considerations.

MATERIAL AND PROCEDURES

The homopolymer and copolymers of MMA (Wako Chemical Co., Japan) and CHM (Polyscience Inc., USA) were synthesized in our laboratory by a typical suspension method at 80°C using benzoyl peroxide as initiator. The commercial samples of PC and PMMA were obtained through the courtesy of Dr. D. R. Paul of Univ. of Texas at Austin. The information about all of the polymers used in this study is listed in Table 1. Commercial PMMA was distinguished by adding suffix 'C' instead 'S' for synthesized product. The copolymers are identified by the appropriate acronym followed by a number that indicates the nominal weight % of comonomer determined by Perkin-Elmer Model 240 CHN analyzer.

Procedures of blends preparation were same as appeared in reference 7 for comparison. For instance, blends of each of copolymers were made with PC by dissolving both in tetrahydrofuran, THF, to obtain 5% total polymer by weight. One part of this solution was added to five parts heptane with vigorous agitation at room temperature to form a blend, and the precipitated blends were filtered and dried in a vacuum oven for three days at 70°C.

Table 1. Polymers used in this study

Acronym	Polymer	Copolymer* Composition (wt%)	Tg(°C)	MW Information	Source
PC	Polycarbonate	-	149	Mn= 13,300 Mw= 34,200	G. E. Lexan®101-131
PMMAC	Poly(methyl methacrylate)	-	106	Mn= 52,900 Mw=130,000 [η] = 0.50	Rohm & Haas Plexiglas® V-811
PMMAS	"	-	108	[η] = 0.78	Synthesized
PCHM	Poly(cyclohexyl methacrylate)	-	66	-	"
PMCHM1	Poly(cyclohexyl methacrylate-co-methyl methacrylate)	0.5% CHM	106	[η] = 0.78	"
PMCHM2	"	1.6% CHM	105	[η] = 1.03	"
PMCHM3	"	2.8% CHM	104	[η] = 1.03	"
PMCHM4	"	3.3% CHM	104	[η] = 1.00	"
PMCHM5	"	4.5% CHM	100	[η] = 0.90	"

*Determined by Elemental Analysis.
[η]: Intrinsic viscosity, at 25°C in methylene chloride.

Glass transition behavior was observed using Perkin-Elmer DSC-2 heating rate of 20°C/min. Sample was first heated from room temperature to 180°C immediately followed by rapid quenching to 30°C. The glass transition temperatures were defined as onset of the shift in heat capacities during the second heating. Phase separation temperature were estimated by using a technique described (2). At least three measurements per sample were performed, and the average value is reported. The reproducibility of this temperature from several determination was about ±3°C.

RESULTS AND DISCUSSION

The effect of polymer chemical structure and molecular mass on miscibility are very important because of their contribution to the free energy of mixing. The former effect become more significant if one of the blend components is copolymer. There are numerous case of miscibility involving copolymers when their corresponding homopolymers are not similarly miscible (4). The phase behavior of blends involving copolymers have been considered owing to the intermolecular specific interactions or by intrachain repulsive effects. We have already shown that significant elevation of PS/PVME blend cloud point by choosing appropriate styrenic copolymers and other similar cases (2,3).

The previous paper of Chiou et al.(7) shows that PC and PMMA can form completely miscible blends at equilibrium, however, used PMMA in that study is commercial product and it contains small amount of acrylic comonomer. So it can be assumed that the phase separation temperature of blends involving copolymer would basically different from that of PC/PMMA homopolymer blend. So we reexamined the phase behavior of PC/PMMA blends prepared by same procedures as reported except using PMMA homopolymer which prepared in our laboratory. Infrared

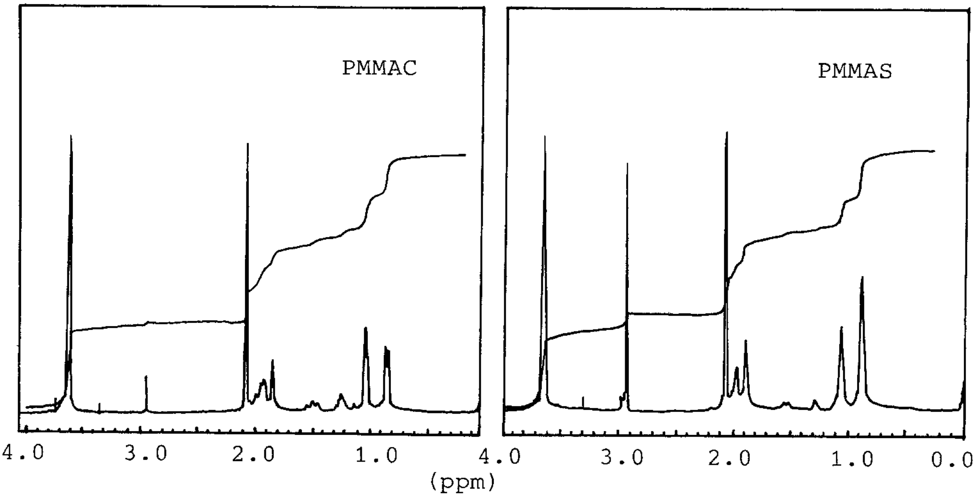

Figure 1. 500MHz proton NMR spectra of PMMAs in acetone-d6.

spectra of PMMAC and PMMAS which not shown here revealed unnoticeable difference except near by the region of 1450 cm^{-1},and 2800 to 3000 cm^{-1} which believed by owing to the addition of small amounts of acrylic comonomer. As it may seen in 500MHz proton NMR spectra of Fig.1, PMMAC also has discrepancy in stereoregularity to that of PMMAS but detail discussion was avoided since it is out of our present scope.

The second scan of DSC thermograms in Fig.2 shows that the 50% PC/PMMAS blend precipitated from THF solution by heptane exhibits a single Tg, however, clearly reveals some fluctuation in transition region, but not in PC/PMMAC blend. We concluded that small amount of comonomer in PMMAC is a reasonable factor affecting thermal behavior of this blend. Presumably, molecular mass of PMMA can be another factor since the intrinsic viscosity of PMMAS is slightly higher than that of PMMAC.

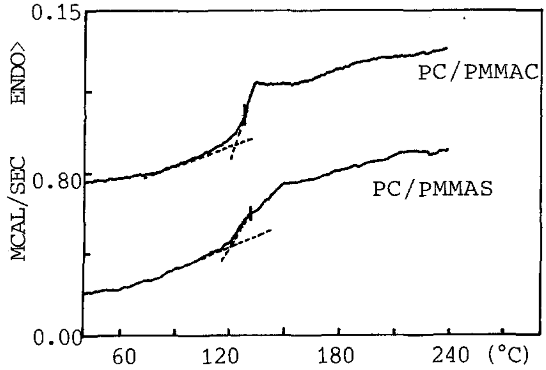

Figure 2. DSC thermogram of 50% PC blends precipitated from THF by heptane.

The solubility parameter of PCHM is similar or higher than that of polyethyl or methyl acrylate, and Tg of PCHM is much higher than those acrylate polymers. Therefore, we expected that CHM comonomer can be a most suitable component not only for increasing minimum cloud point of PC/acrylic copolymer blend but also a candidate for commercial PMMA as the thermal

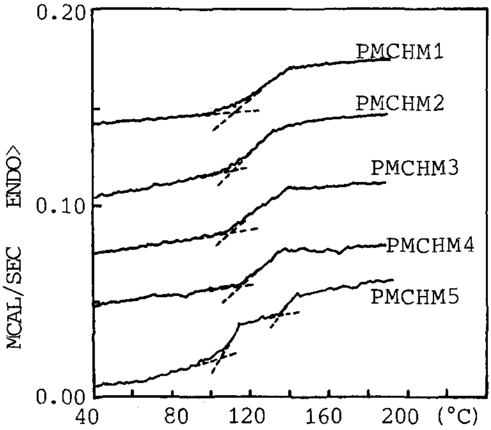

Figure 3. DSC thermogram for blends of PC with PMCHMs at 50 wt% PC.

stabilizer and processing aids. The DSC thermograms of 50% PC/PMCHM blends shown in Fig.3 exhibit single Tg's at the level of below 4% of CHM comonomer, however, PC is no longer miscible with containing beyond this level.

The PC/copolymer precipitates showing single glass transition temperature, originally in form of an opaque cluster of fibrils, as may seen in reported studies, turned into transparent films when heated and pressed on the hot stage at temperature just above their glass transition. However, precipitates of PC/copolymers having two Tg's, e.g., PMCHM5 never showed transparency on heating. On the other hand, the transparent film like 50% PC/PMCHM2 blend became transculent while further heating to the temperature higher than about 235°C.

The cloud point curves of PC with various PMCHM copolymers are shown in Fig.4, and the effect of comonomer content is more easily shown in Fig.5 by plotting a 50% PC versus the CHM content of the copolymer.

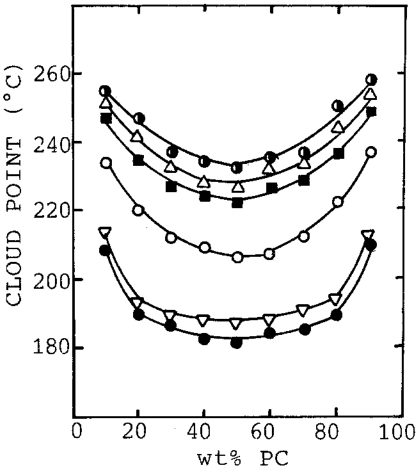

Figure 4. Cloud point curves for blends of PC with various PMCHM copolymers: (△) PMCHM1, (◑) PMCHM2, (■) PMCHM3, (○) PMCHM4, (▽) PMMAC, and (●) PMMAS.

As comonomer is incorporated, the cloud point first increases and then goes through a maximum. The pattern shown in Fig.5 has been observed for other homopolymer-copolymer systems

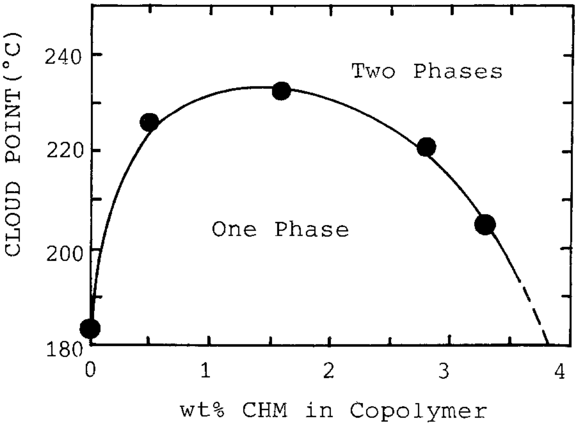

Figure 5. Effect of CHM content on cloud point for blends with PMCHM copolymer at 50wt% PC.

and the intramolecular repulsion effect reported earlier(2,10) can provide a rational explanation of this trends.

It should be note that the minimum cloud point has been raised to almost 50 degrees using only 2% comonomer in the copolymer. However, it is not still quite enough improvement to have a thermally stable PC/acrylic blends of any proportion can be prepared by melt processing methods, and further studies are required.

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