

# Miscibility of Poly(tetrahydrofurfuryl methacrylate) and Poly(tetrahydropyranyl-2-methacrylate) with Some Chlorine-Containing Polymers

Y. F. CHONG and S. H. GOH\*

Department of Chemistry, National University of Singapore, Singapore 0511

## SYNOPSIS

The miscibility of poly(tetrahydrofurfuryl methacrylate) (PTHFMA) and poly(tetrahydropyranyl-2-methacrylate) (PThPMA) with some chlorine-containing polymers was studied by differential scanning calorimetry (DSC). PThPMA was found to be miscible with poly(vinyl chloride) (PVC), polyepichlorohydrin (PECH), and a vinylidene chloride/vinyl chloride copolymer [P(VDC/VC)] and only partially miscible with an epichlorohydrin/ethylene oxide copolymer [P(ECH/EO)]. PTHFMA was shown to be miscible with PECH and P(VDC/VC), but its miscibility with P(ECH/EO) is composition-dependent. Information about interactions between components in PTHFMA/P(VDC/VC) and PThPMA/P(VDC/VC) blends was estimated from melting-point depression. The interaction parameters  $B$  were found to be  $-1.7$  and  $-3.6$  J/cm<sup>3</sup> for PTHFMA/P(VDC/VC) and PThPMA/P(VDC/VC) blend systems, respectively. The miscibility behavior of PTHFMA and PThPMA is compared to that of poly(cyclohexyl methacrylate).

## INTRODUCTION

There have been many studies on the miscibility behavior of homologous polymethacrylates with other halogenated polymers such as poly(vinyl chloride) (PVC),<sup>1-3</sup> polyepichlorohydrin (PECH),<sup>4</sup> a copolymer of epichlorohydrin and ethylene oxide [P(ECH/EO)],<sup>4</sup> poly(vinylidene fluoride) (PVDF),<sup>5-18</sup> and a copolymer of vinylidene chloride and vinyl chloride [P(VDC/VC)].<sup>19</sup> In general, the miscibility decreases with increasing bulkiness of the alkyl pendent groups of the polymethacrylate. The presence of additional functional moieties like carbonyl, ether oxygen, and hydroxyl in the pendent groups of the polymethacrylate can have a significant effect on its miscibility behavior. For example, PVC is miscible with poly(acetonyl methacrylate) (PACMA)<sup>20</sup> and poly(tetrahydrofurfuryl methacrylate) (PTHFMA),<sup>21</sup> whereas it is immiscible with poly(isopropyl methacrylate) (PiPMA).<sup>22</sup> The

presence of additional carbonyl groups in PACMA and ether oxygen atoms in PTHFMA appears to be responsible for the miscibility.

Poly(cyclohexyl methacrylate) (PCHMA) is miscible with several chlorine-containing polymers including PVC,<sup>3</sup> PECH,<sup>4</sup> and also P(VDC/VC),<sup>19</sup> which contains 86.5% by weight of vinylidene chloride (VDC). However, there is no suitable explanation to account for its good miscibility. It is interesting to compare the miscibility behavior of PTHFMA and its isomer, poly(tetrahydropyranyl-2-methacrylate) (PThPMA), with that of PCHMA, and to study the influence of the ring sizes and extra functional moieties of the methacrylate pendent groups in achieving miscibility.

## EXPERIMENTAL

### Materials

Tetrahydropyranyl-2-methacrylate was obtained from Polysciences, Inc., and purified by fractional distillation at 83°C/2 mmHg. PThPMA was pre-

\* To whom correspondence should be addressed.

pared by solution polymerization in 2-butanone at reflux temperature for 6 h, using 0.25% by weight of azobisisobutyronitrile as initiator. The polymer was obtained by precipitation of the solution in excess of methanol. It was then dried *in vacuo* at 90°C for 48 h. The number-average ( $\bar{M}_n$ ) and weight-average ( $\bar{M}_w$ ) molecular weights (GPC, polystyrene standards) of PTHPMA are 44,000 and 65,000, respectively. PECH and P(ECH/EO) are commercial products of the B. F. Goodrich company sold under the trademark of Hydrin 100 and Hydrin 200, respectively. PVC with an  $\bar{M}_w$  of 58,000 was obtained from Diamond Shamrock Co. Inc. The copolymer P(VDC/VC) containing 88% by weight of vinylidene chloride is a commercial product of Polysciences, Inc.; its  $\bar{M}_n$  is 90,000. PTHFMA with an  $\bar{M}_n$  of 180,000 was obtained from Scientific Polymer Products.

### Polymer Blends

Blends of PTHFMA and PTHPMA with PVC, PECH, and P(VDC/VC) were prepared by solution casting from tetrahydrofuran (THF). To stabilize PVC against degradation during heating, a stabilizer (Advastab TM-181) was added in an amount of 5% by weight of PVC for each blend. Blends of P(ECH/EO) were cast from methylene chloride, which was reported a good solvent for P(ECH/EO)/polymethacrylate blends.<sup>4</sup> All cast films were then dried *in vacuo* at 90°C for at least 3 days.

### Calorimetric Measurements

The melting points ( $T_m$ ) of PTHFMA/P(VDC/VC) blends were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. Samples were first heated to 185°C and maintained at this temperature for 5 min before being cooled to room temperature to ensure all samples had the same thermal history. The samples were rescanned 24 h later. The peak of the melting endotherm was recorded as  $T_m$  of the sample. Duplicate runs were made for each blend sample to ensure the reproducibility of the  $T_m$  values. The glass transition temperatures ( $T_g$ 's) of all samples were measured with the Perkin-Elmer DSC-4 differential scanning calorimeter equipped with an INTRACOOLED II. For the crystalline blends of P(VDC/VC), a cyclic heating and cooling procedure between the limits of -30 and 185°C was used.  $T_g$  was taken as the initial onset of the change of slope in the DSC curve. The reported  $T_g$  is the average value based on the second and subsequent runs.

### Cloud-Point Measurements

All the miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior. The film was sandwiched between two microscopic cover glasses and heated in a Fisher-Johns melting-point apparatus with a heating rate of about 10°C/min. The optical appearance of the film was observed with a magnifying glass attached to the apparatus. A transparent film that turns cloudy upon heating indicates the existence of LCST. The temperature at which the film first showed cloudiness was taken as the cloud point.

## RESULTS

### PTHPMA/PVC Blends

PTHPMA was found to be miscible with PVC. The miscibility is ascertained on the basis of the transparency of the blends and the occurrence of a single  $T_g$  in each blend. The  $T_g$ -composition curve is shown in Figure 1. All the blends remained transparent when heated up to 250°C. Further heating led to discoloration caused by degradation of PVC. It is known that PTHFMA and PCHMA are miscible with PVC, and LCST behavior was not observed for all these blends.

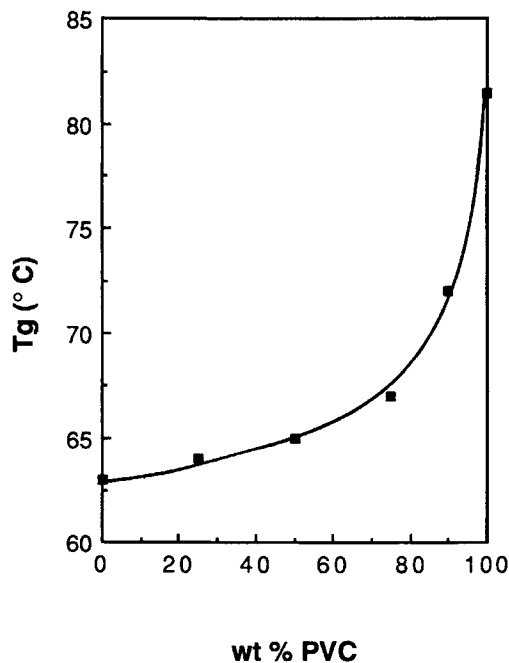
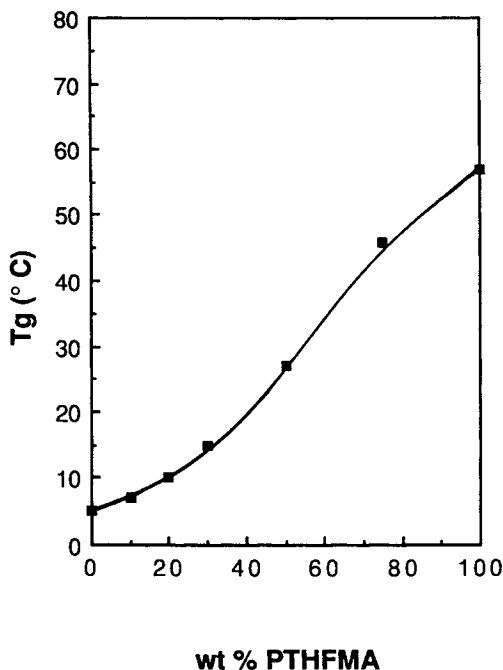


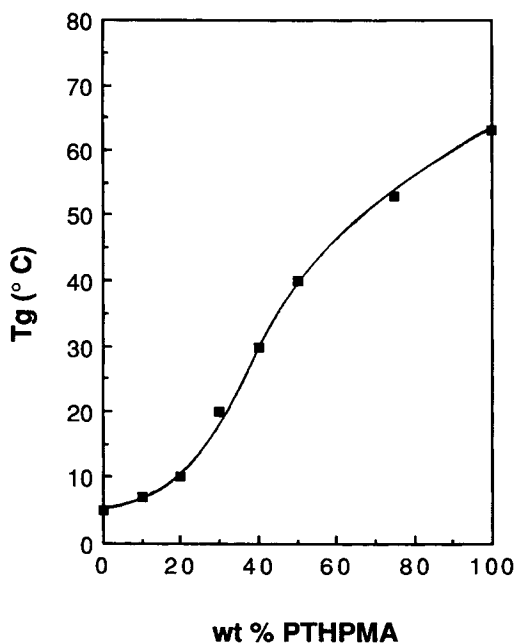
Figure 1  $T_g$ -composition curve for PTHPMA/PVC blends.



**Figure 2**  $T_g$ -composition curve for PTHFMA/P(VDC/VC) blends.

#### PTHFMA/P(VDC/VC) and PTHPMA/P(VDC/VC) Blends

The  $T_g$ -composition curves for blends of P(VDC/VC) with PTHFMA and PTHPMA are shown in Figures 2 and 3, respectively. The presence of a single



**Figure 3**  $T_g$ -composition curve for PTHPMA/P(VDC/VC) blends.

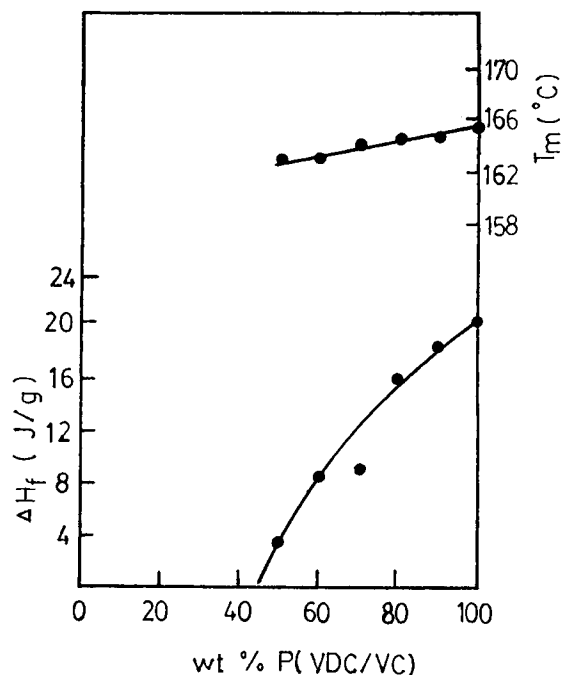
composition-dependent  $T_g$  in each blend indicates that the amorphous phase of P(VDC/VC) is completely miscible with PTHFMA as well as with PTHPMA. All these crystalline blends became transparent when heated above the melting point of P(VDC/VC) and did not undergo phase separation upon heating to 240°C. Beyond this temperature, severe decomposition of P(VDC/VC) occurs.

Since P(VDC/VC) is crystalline, it is of interest to study the melting behavior of P(VDC/VC) in the blends. The presence of PTHFMA and PTHPMA greatly depresses the crystallization of the P(VDC/VC) and also lowers its melting point as shown in Figures 4 and 5. It is obvious that PTHPMA suppresses the crystallization of P(VDC/VC) more than of PTHFMA. This may indicate a stronger interaction in PTHPMA/P(VDC/VC) blends than that in PTHFMA/P(VDC/VC) blends.

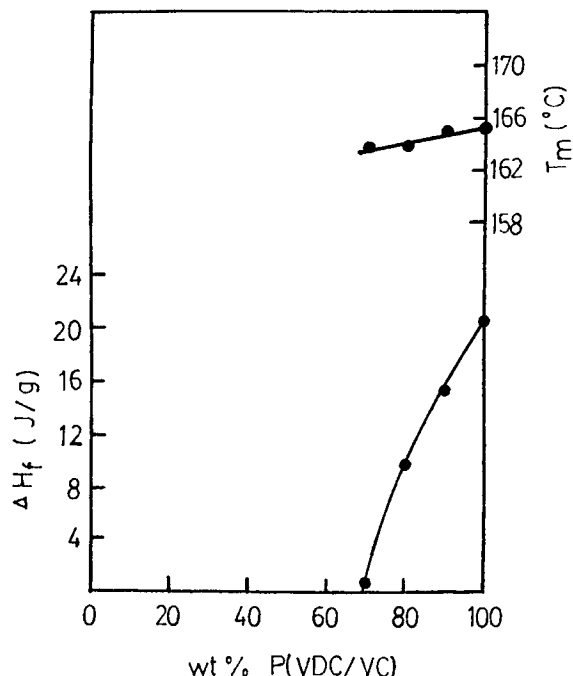
The intermolecular interaction parameter  $B$  for blends of PTHFMA and PTHPMA with P(VDC/VC) can be estimated from the melting-point depression of P(VDC/VC) in blends by using the equation<sup>5,11,23</sup>

$$T_m = T_m^0 + B(V_{2u}/\Delta H_{2u})T_m^0\phi_1^2$$

where  $T_m^0$  and  $T_m$  are the melting points of pure P(VDC/VC) and P(VDC/VC) in the blend, re-

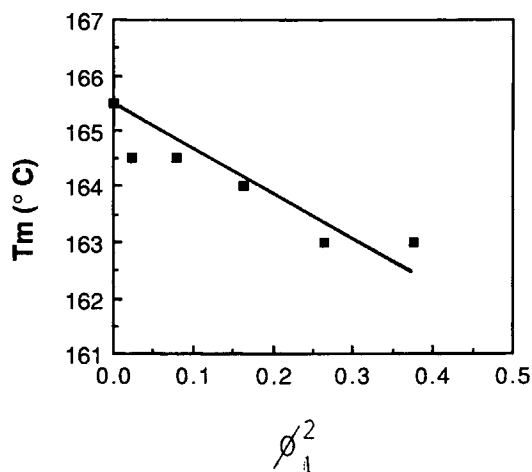


**Figure 4** Melting behavior for PTHFMA/P(VDC/VC) blends.

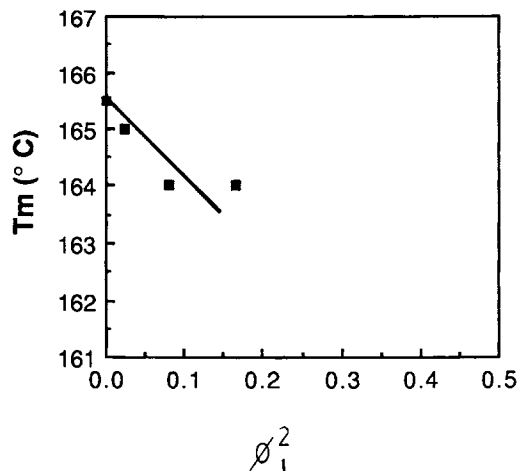


**Figure 5** Melting behavior for PTHPMA/P(VDC/VC) blends.

spectively;  $\Delta H_{2u}/V_{2u}$  is the heat of fusion per unit volume of repeating unit for P(VDC/VC) and its value is  $109.6 \text{ J/cm}^3$  (Ref. 24);  $\phi_1$  is the volume fraction of the noncrystallizable polymer in blends; and  $B$  is obtained from a plot of  $T_m$  against  $\phi_1^2$  as shown in Figures 6 and 7. The  $B$  values obtained are  $-1.7$  and  $-3.6 \text{ J/cm}^3$  for PTHFMA/P(VDC/VC) and PTHPMA/P(VDC/VC) blend systems, respectively. The results suggest that PTHPMA interacts more strongly with P(VDC/VC) than with



**Figure 6** Melting-point depression plot for PTHFMA/P(VDC/VC) blends.

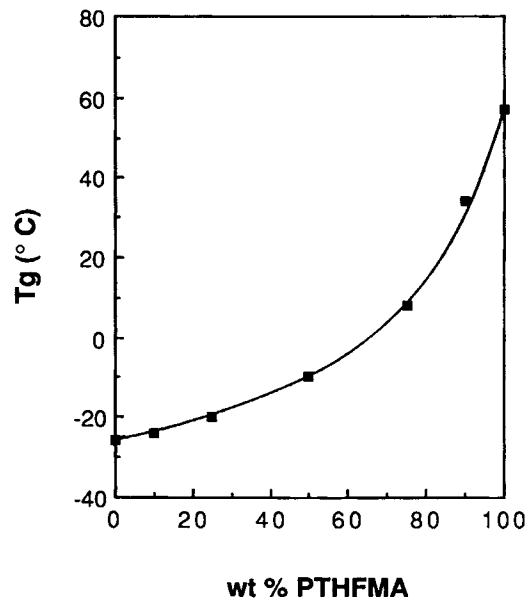


**Figure 7** Melting-point depression plot for PTHPMA/P(VDC/VC) blends.

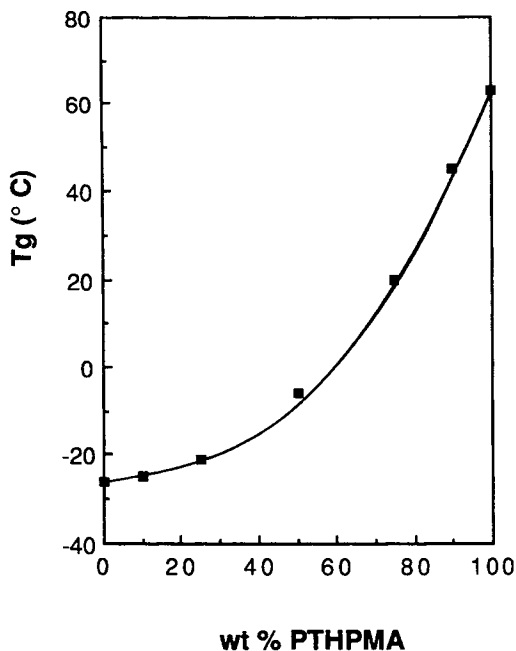
PTHFMA, despite of its bulkier tetrahydropyranyl pendent groups than those of PTHFMA.

#### PTHFMA/PECH and PTHPMA/PECH Blends

Blends of PECH with PTHFMA and PTHPMA were optically transparent at room temperature. DSC curves for both blend systems exhibit single composition-dependent  $T_g$ 's that are plotted against composition as shown in Figures 8 and 9. However, there was considerable broadening of the glass transitions at intermediate compositions for both blend

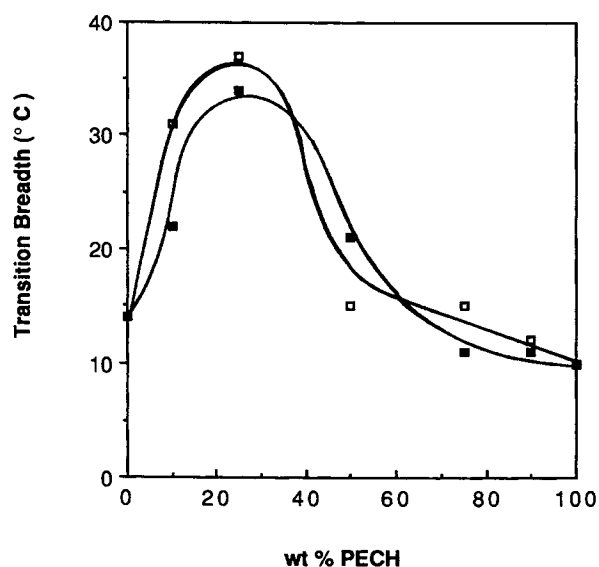


**Figure 8**  $T_g$ -composition curve for PTHFMA/PECH blends.



**Figure 9**  $T_g$ -composition curve for PTHPMA/PECH blends.

systems with maxima at about 25% by weight of PTHFMA or PTHPMA as shown in Figure 10. The definition of the transition breadth here is the difference between the onset and the completion temperatures of the glass transition in the second or subsequent runs. It has been suggested that the observed  $T_g$  broadening is due to the composition fluctuations and the breadth of the glass transition is

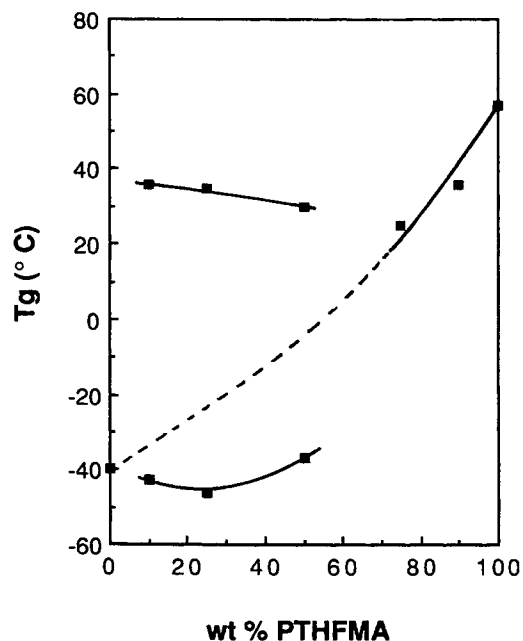


**Figure 10** Breadth of glass transitions for PTHFMA/PECH (□) and PTHPMA/PECH (■) blends.

associated with microheterogeneity.<sup>4,25</sup> This might imply a strong composition dependence of the interaction. However, the magnitude of fluctuations as well as transition breadth increase as the affinity of components in blend for each other decreases. Apparently, in general, PTHFMA/PECH blends have a greater transition breadth than do PTHPMA/PECH blends, especially for blends with higher contents of PTHFMA. This might be an indication of a stronger interaction in PTHPMA/PECH blends than that in PTHFMA/PECH blends. All transparent blends were examined for LCST behavior. However, they all remained clear upon heating to 280°C.

#### PTHFMA/P(ECH/EO) and PTHPMA/P(ECH/EO) Blends

Blends of P(ECH/EO) with 10, 25, and 50% by weight of PTHFMA were cloudy and remained so upon heating to 280°C. Each of these blends showed two  $T_g$ 's, indicating that it is an immiscible blend. However, blends containing 75 and 90% by weight of PTHFMA were transparent and did not undergo phase separation upon heating to 280°C. A single glass transition was observed in each of these blends. Hence, these two transparent blends are miscible blends. The  $T_g$ -composition curve for the PTHFMA/P(ECH/EO) blend system is shown in Figure 11.



**Figure 11**  $T_g$ -composition curve for PTHFMA/P(ECH/EO) blends.

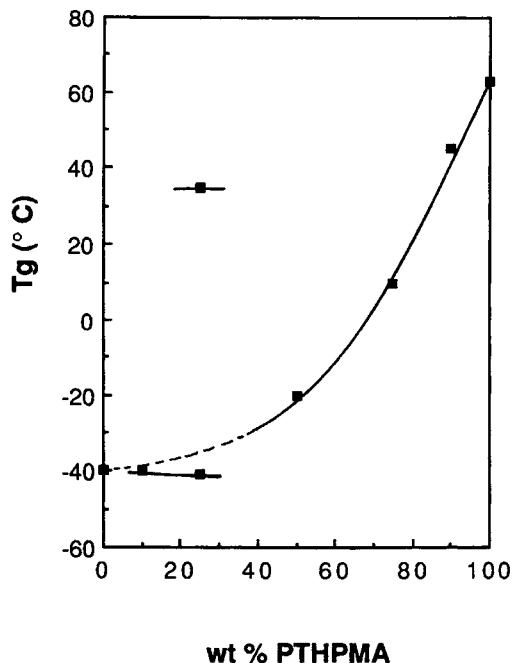


Figure 12  $T_g$ -composition curve for PTHPMA/P(ECH/EO) blends.

It is interesting to note that blends of P(ECH/EO) with PTHFMA and PTHPMA show similar miscibility behavior. Likewise, blends with 10 and 25% by weight of PTHPMA were cloudy and remained so upon heating. DSC measurement showed the existence of two  $T_g$ 's for the blend that contains 25% by weight of PTHPMA. The lower glass transition is sharp, and the  $T_g$  value is essentially the same as that of P(ECH/EO). On the other hand, the upper glass transition is broad and the  $T_g$  value is about 30°C lower than that of PTHPMA. The result indicates the presence of P(ECH/EO) in the PTHPMA-rich phase. For the blend containing 10% of by weight of PTHPMA, a sharp, lower glass transition was observed. However, the upper one was difficult to detect, possibly due to the broadness of the transition and the small amount of the PTHPMA-rich phase in the blend. For blends containing 50, 75, and 90% by weight of PTHPMA, only one  $T_g$  was observed in each of these blends, as shown in Figure 12. Furthermore, they are trans-

parent and remained so upon heating to 280°C. Hence, they are miscible blends. Obviously, the miscibility of PTHPMA/P(ECH/EO) blends is composition-dependent.

## SUMMARY AND DISCUSSION

Table I summarizes the miscibility behavior of PTHFMA, PTHPMA, and PCHMA with PVC, P(VDC/VC), PECH, and P(ECH/EO). It is evident that PTHFMA, PTHPMA, and PCHMA have a very similar miscibility behavior. Based on the interaction parameters estimated from the melting-point depression of P(VDC/VC), PTHPMA seems to show a better miscibility with P(VDC/VC) than does PTHFMA, despite the fact that PTHPMA has a bulkier pendent group than does PTHFMA. Furthermore, the transition breadths for PTHFMA/PECH blends are, in general, greater than that of the PTHPMA/PECH system. Since these two systems have the similar  $\Delta T_g$ , the difference in glass transitions of the components in blend, a broader transition breadth of PTHFMA/PECH system may indicate a weaker interaction in the blends than that in PTHPMA/PECH blends. It is interesting to note that PCHMA, which has a similarly bulky pendent group as PTHPMA, but without any other interacting functional moiety in its alkyl pendent groups, shows similar miscibility behavior as those of PTHPMA and PTHFMA. The latter two polymers both contain ether oxygen atoms in their pendent groups.

The present study agrees very well with the fact that blends with chlorine-containing polymers including PVC,<sup>1,7</sup> P(VDC/VC),<sup>19</sup> and PECH<sup>4</sup> show a stronger interaction for alkyl groups of intermediate size even though the miscibility of polymethacrylates with PVDF<sup>8,16,17</sup> decreases as the alkyl pendent groups get larger. Some recent papers<sup>3,26</sup> reported that if the cyclic pendent group of the polymethacrylate is aromatic, the miscibility of the polymethacrylate such as poly(benzyl methacrylate) decreases drastically. Hence, besides the ring sizes, structures, and interacting functional moieties of the methacrylate pendent groups, electronic effects and

Table I Miscibility Behavior of Blends

	PVC	P(VDC/VC)	PECH	P(ECH/EO)
PTHFMA	Miscible (Ref. 21)	Miscible	Miscible	Partially miscible
PTHPMA	Miscible	Miscible	Miscible	Partially miscible
PCHMA	Miscible (Ref. 3)	Miscible (Ref. 19)	Miscible (Ref. 4)	Not tested (Ref. 4)

the flexibility of the cyclic pendent groups may affect the miscibility behavior of polymethacrylates as well.

Financial support of this study by the National University of Singapore is gratefully acknowledged.

## REFERENCES

1. D. J. Walsh and J. G. McKeown, *Polymer*, **21**, 1330 (1980).
2. D. J. Walsh and J. G. McKeown, *Polymer*, **21**, 1335 (1980).
3. J. F. Parmer, L. C. Dickinson, J. C. W. Chien, and R. S. Porter, *Macromolecules*, **22**, 1078 (1989).
4. A. C. Fernandes, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **32**, 5481 (1986).
5. T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
6. T. T. Wang and T. Nishi, *Macromolecules*, **10**, 421 (1977).
7. E. Roerdink and G. Challa, *Polymer*, **19**, 173 (1978).
8. D. R. Paul, J. W. Barlow, R. E. Bernstein, and D. C. Wahrmund, *Polym. Eng. Sci.*, **18**, 1225 (1978).
9. B. S. Morra and R. S. Stein, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 2243 (1982).
10. B. S. Morra and R. S. Stein, *Polym. Eng. Sci.*, **24**, 311 (1984).
11. R. L. Imken, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **16**, 593 (1976).
12. T. K. Kwei, G. D. Patterson, and T. T. Wang, *Macromolecules*, **9**, 780 (1976).
13. M. Galin and L. Maslinko, *Eur. Polym. J.*, **23**, 923 (1987).
14. T. K. Kwei, G. D. Patterson, and T. T. Wang, *Macromolecules*, **9**, 603 (1976).
15. T. K. Kwei, H. L. Frisch, W. Radigan, and S. Vogel, *Macromolecules*, **10**, 157 (1977).
16. R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules*, **10**, 681 (1977).
17. D. C. Wahrmund, R. E. Bernstein, J. W. Barlow, and D. R. Paul, *Polym. Eng. Sci.*, **18**, 677 (1978).
18. Y. F. Chong, S. Y. Lee, and S. H. Goh, *Eur. Polym. J.*, **26**, 1145 (1990).
19. E. M. Woo, J. W. Barlow, and D. R. Paul, *J. Polym. Sci. Polym. Symp. Ed.*, **71**, 137 (1984).
20. Y. F. Chong, S. Y. Lee, and S. H. Goh, *Eur. Polym. J.*, **26**, 1207 (1990).
21. S. H. Goh and K. S. Siow, *J. Appl. Polym. Sci.*, **33**, 1849 (1987).
22. M. Bosma, G. ten Brinke, and T. S. Ellis, *Macromolecules*, **21**, 1465 (1988).
23. R. E. Bernstein, D. C. Wahrmund, J. W. Barlow, and D. R. Paul, *Polym. Eng. Sci.*, **18**, 1225 (1978).
24. R. A. Wessling and F. G. Edwards, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. Bikales, and N. G. Gaylord, Eds., Wiley, New York, 1971, Vol. 14, p. 540.
25. E. M. Woo, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 4243 (1985).
26. M. Nishimoto, H. Keskkula, and D. R. Paul, *Macromolecules*, **23**, 3633 (1990).

Received October 8, 1990

Accepted November 27, 1990