

# Miscibility of poly(chloromethyl methacrylate) with various polymethacrylates

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The miscibility behaviour of poly(chloromethyl methacrylate) (PCMMA) with various polymethacrylates was examined by differential scanning calorimetry and for lower critical solution temperature behaviour. PCMMA is miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PnPMA), poly(isopropyl methacrylate) (PiPMA) and poly(tetrahydrofurfuryl methacrylate) (PTHFMA), but is immiscible with poly(*n*-butyl methacrylate) (PnBMA). Blends of PCMMA with PMMA and PTHFMA degrade before phase separation could be induced by heating. The cloud point for other miscible blends decreases in the order PEMA > PnPMA  $\approx$  PiPMA. Except for PTHFMA, the trend is consistent with the general observations that the miscibility of a polymethacrylate with other polymers decreases with increasing size of the pendant group. The miscibility behaviour of PCMMA with polymethacrylates is similar to that of poly(vinyl chloride).

(Keywords: poly(chloromethyl methacrylate); polymer blends; miscibility; lower critical solution temperature)

## INTRODUCTION

Two dissimilar polymers are likely to be miscible with each other if there are some specific interactions between them<sup>1</sup>. Therefore, the incorporation of functional groups into a polymer can often change its miscibility behaviour. For example, chlorinated polymer often shows a wider range of miscibility than the corresponding non-chlorinated polymer. While polyethylene is practically immiscible with other organic polymers, chlorinated polyethylene is miscible with polyesters<sup>2-5</sup>, polymethacrylates<sup>6</sup> and ethylene/vinyl acetate copolymer<sup>7-9</sup>. Likewise, poly(methyl methacrylate) (PMMA) is immiscible with poly(propylene oxide) but is miscible with polyepichlorohydrin<sup>10</sup>.

PMMA is miscible with a large variety of polymers including poly(vinyl chloride) (PVC)<sup>11-14</sup>, poly(ethylene oxide)<sup>15-18</sup>, poly(vinylidene fluoride) (PVDF)<sup>19-22</sup>, styrene/acrylonitrile copolymers (SAN)<sup>23-25</sup> and  $\alpha$ -methylstyrene/acrylonitrile copolymers ( $\alpha$ MSAN)<sup>26,27</sup>. However, PMMA is immiscible with other polymethacrylates such as poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PnPMA) and poly(*n*-butyl methacrylate) (PnBMA)<sup>28</sup>. It is of interest to study how the miscibility behaviour of PMMA is affected by the

incorporation of chlorine atoms into its pendant methyl groups. We have recently reported that poly(chloromethyl methacrylate) (PCMMA) is miscible with bisphenol-A polycarbonate<sup>29</sup> and  $\alpha$ MSAN<sup>30</sup>. In the present study, we examine the miscibility of PCMMA with various polymethacrylates. It will be shown that the miscibility behaviour of PCMMA is similar to that of PVC in forming miscible blends with several polymethacrylates.

## EXPERIMENTAL

### Materials

Chloromethyl methacrylate (CMMA) was prepared following the procedure reported by Ueda *et al.*<sup>31</sup>. CMMA was polymerized in 2-butanone at reflux temperature for 24 h using 0.25% by weight of azobisisobutyronitrile as initiator. The polymer was obtained by precipitation of the solution in excess methanol. The number-average molecular weight of PCMMA was 58 000 from intrinsic viscosity measurements using the appropriate Mark-Houwink equation<sup>31</sup>. The main characteristics of various polymethacrylates used in this study are given in Table 1.

Table 1 Characteristics of polymethacrylates

Polymer	Abbreviation	Source	Molecular weight	$T_g^a$ (°C)
Poly(methyl methacrylate)	PMMA	Du Pont (Elvacite 2010)	$\bar{M}_w = 120\,000$	100
Poly(ethyl methacrylate)	PEMA	Du Pont (Elvacite 2042)	$\bar{M}_w = 310\,000$	65
Poly( <i>n</i> -propyl methacrylate)	PnPMA	Scientific Polymer Products	$\bar{M}_w = 175\,000$	45
Poly(isopropyl methacrylate)	PiPMA	Scientific Polymer Products	<sup>-b</sup>	82
Poly( <i>n</i> -butyl methacrylate)	PnBMA	Du Pont (Elvacite 2044)	$\bar{M}_w = 288\,000$	20
Poly(tetrahydrofurfuryl methacrylate)	PTHFMA	Scientific Polymer Products	$\bar{M}_w = 240\,000$	57
Poly(chloromethyl methacrylate)	PCMMA	This laboratory	$\bar{M}_n = 58\,000$	87

<sup>a</sup>  $T_g$  of quenched polymer

<sup>b</sup>  $[\eta] = 0.33 \text{ dl g}^{-1}$  in 2-butanone at 30°C

### Polymer blends

Blends of PCMMA with various polymethacrylates were prepared by solution casting from tetrahydrofuran (THF). Solvent was allowed to evaporate slowly over a period of 1–2 days at room temperature. The cast films were then dried *in vacuo* at 110°C for 3 days.

### $T_g$ measurements

The glass transition temperatures ( $T_g$ ) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C min<sup>-1</sup>. The value  $T_g$  was taken as the initial onset of the change of slope in the d.s.c. 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) behaviour. The film was sandwiched between two microscope cover-glasses and heated in a Fisher-Johns melting-point apparatus at a heating rate of about 10°C min<sup>-1</sup>. 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 a LCST. The temperature at which the film first showed cloudiness was taken as the cloud point.

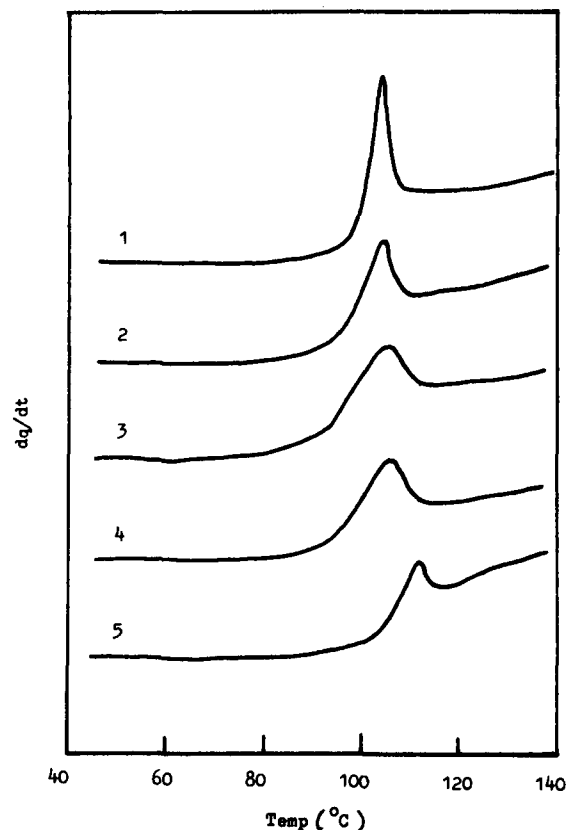


Figure 1 D.s.c. curves for annealed PCMMA/PMMA blends: (1) 100% PCMMA; (2) 75% PCMMA; (3) 50% PCMMA; (4) 25% PCMMA; and (5) 100% PMMA

## RESULTS

### PCMMA/PMMA blends

All the PCMMA/PMMA blends were transparent. The glass transition temperatures of PCMMA and PMMA are quite close to each other. D.s.c. measurement of  $T_g$  to ascertain miscibility of a blend is not normally used if the difference in  $T_g$  values of the component polymers is less than 20°C. It has been reported recently that for a blend of two polymers with similar  $T_g$  values, the enthalpy recovery of an annealed blend can be used to ascertain its miscibility<sup>32,33</sup>. Annealing of a polymer below its  $T_g$  results in a decrease in enthalpy, which is recovered during heating. The enthalpy recovery is manifested as an endothermic peak in a d.s.c. scan. An annealed immiscible PVC/PiPMA blend in which the difference in  $T_g$  values of the two component polymers is 2.5°C shows two distinct endothermic peaks<sup>32</sup>. To study the enthalpy recovery of PCMMA/PMMA blends, each blend was first heated to 150°C and kept at that temperature for 5 min to erase its thermal history. The sample was then rapidly cooled to -78°C in an acetone-dry ice bath followed by annealing at 70°C for 10 days. Each annealed blend showed one endothermic peak when scanned through the glass transition, as shown in Figure 1. It is concluded that PCMMA is miscible with PMMA. All the PCMMA/PMMA blends remained transparent upon heating to 280°C, where discoloration began to develop. This shows that the blends degrade before phase separation could be induced by heating.

### PCMMA/PEMA blends

All the PCMMA/PEMA blends were transparent. In this case, the  $T_g$  values of the two polymers were sufficiently far apart to allow the use of  $T_g$  measurements to ascertain miscibility. Each blend has a single  $T_g$ , indicating that PCMMA is miscible with PEMA. The

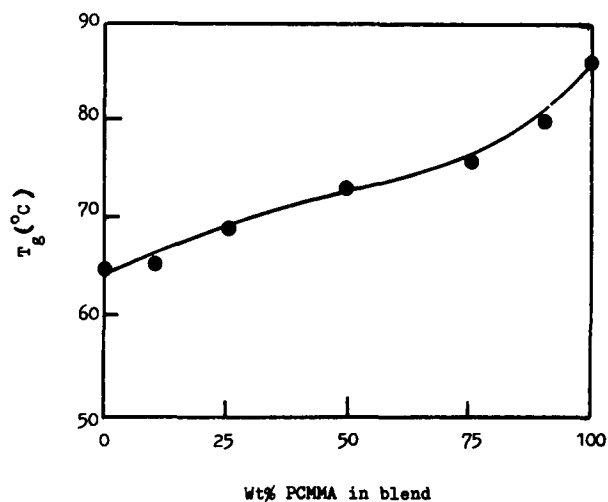


Figure 2  $T_g$ -composition curve for PCMMA/PEMA blends

$T_g$ -composition curve for PCMMA/PEMA blends is shown in Figure 2. A PCMMA/PEMA blend containing 10% by weight of PCMMA remained transparent up to 280°C. Blends containing 25, 50, 75 and 90% by weight of PCMMA turned cloudy when heated to 230–260°C, showing LCST behaviour. The cloud-point curve is shown in Figure 3.

### PCMMA/PnPMA blends

PCMMA was also found to be miscible with PnPMA as each of the blends was transparent and had a single  $T_g$ . The  $T_g$ -composition curve is shown in Figure 4. All PCMMA/PnPMA blends showed LCST behaviour and the cloud-point curve is shown in Figure 3.

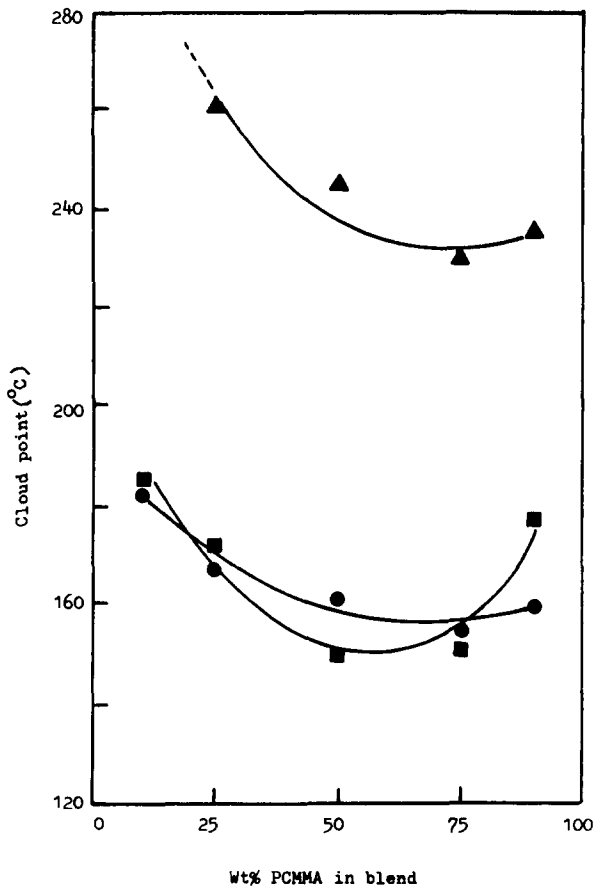


Figure 3 Cloud-point curves for: (▲) PCMMA/PEMA blends; (■) PCMMA/PnPMA blends; and (●) PCMMA/PiPMA blends

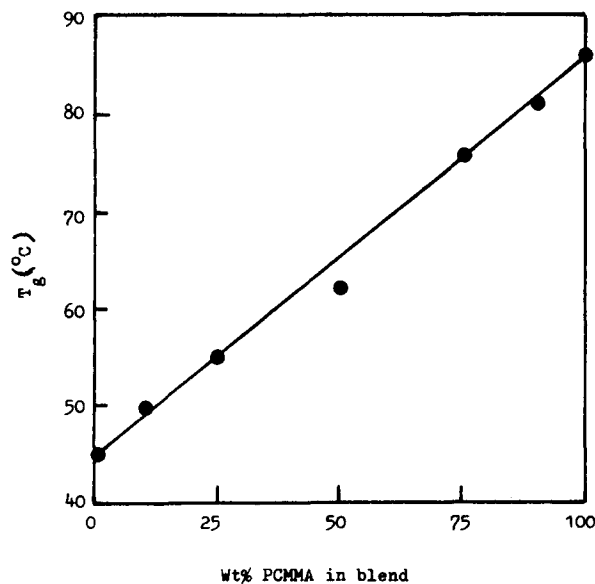


Figure 4  $T_g$ -composition curve for PCMMA/PnPMA blends

*PCMMA/PiPMA blends*

All the blends were transparent and showed LCST behaviour. The cloud-point curve is shown in Figure 3. Since the  $T_g$  values of the two polymers are close to each other, d.s.c. measurements were made on annealed samples. As shown in Figure 3, the cloud points are quite low. As such, the blends were initially kept at 125°C for 5 min before quenching and subsequently annealed at 70°C for 10 days. Each annealed blend showed one

enthalpy recovery peak, as shown in Figure 5. It is concluded that PCMMA is also miscible with PiPMA.

*PCMMA/PTHFMA blends*

All the blends were transparent and remained so upon heating to 280°C where discoloration began to develop. Each blend has a single composition-dependent  $T_g$ , as shown in Figure 6. These results lead to the conclusion that PCMMA is miscible with PTHFMA.

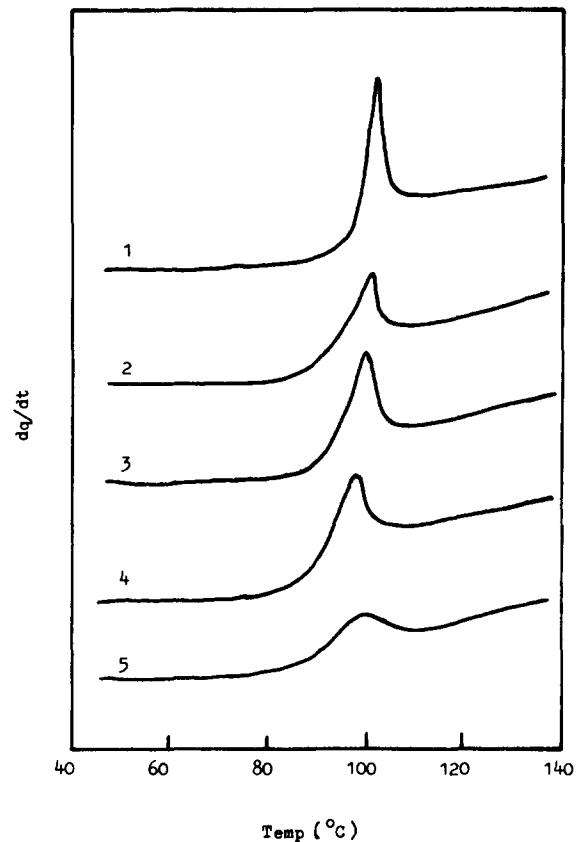


Figure 5 D.s.c. curves for annealed PCMMA/PiPMA blends: (1) 100% PCMMA; (2) 75% PCMMA; (3) 50% PCMMA; (4) 25% PCMMA; and (5) 100% PiPMA

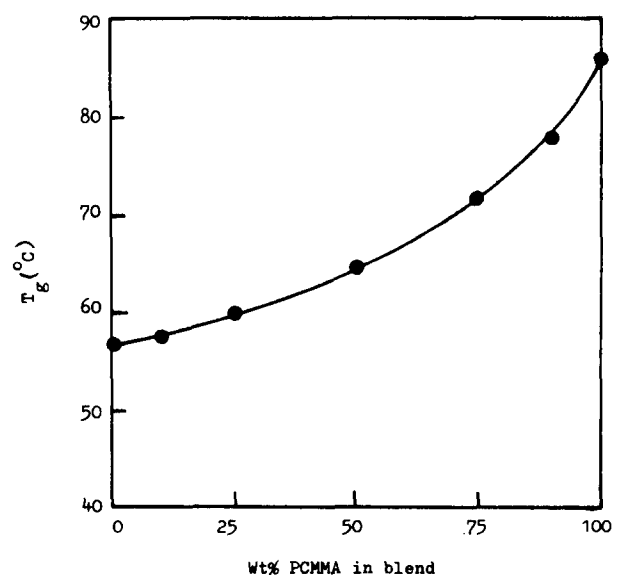


Figure 6  $T_g$ -composition curve for PCMMA/PTHFMA blends

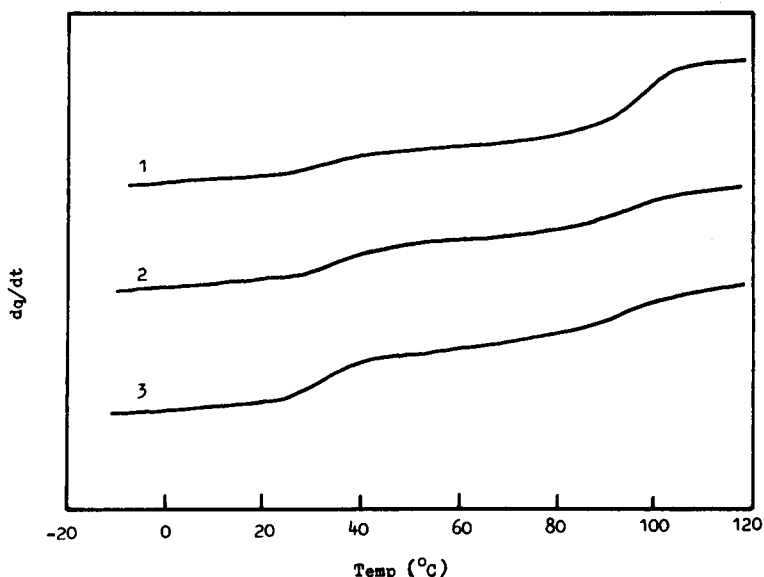


Figure 7 D.s.c. curves for PCMMA/PnBMA blends: (1) 75% PCMMA; (2) 50% PCMMA; and (3) 25% PCMMA

#### PCMMA/PnBMA blends

The blends were opaque. Each of the blends showed two  $T_g$  values, as shown in Figure 7. These results show that PCMMA is immiscible with PnBMA.

#### DISCUSSION

The present study shows that PCMMA is miscible with PMMA, PEMA, PnPMA, PiPMA and PTHFMA. Further information on the miscibility behaviour can be obtained from their  $LCST$  behaviour. According to the free-volume theory<sup>34,35</sup>, a miscible blend undergoes phase separation at a temperature where the unfavourable free-volume effect outweighs the favourable interactional (enthalpic) effect. The free-volume effect depends on the difference in free volumes or thermal expansion coefficients of the component polymers. The thermal expansion coefficients for PMMA, PEMA, PnPMA, PiPMA and PnBMA are  $6.1 \times 10^{-4}$ ,  $6.1 \times 10^{-4}$ ,  $6.3 \times 10^{-4}$ ,  $6.5 \times 10^{-4}$  and  $6.3 \times 10^{-4} \text{ K}^{-1}$ , respectively<sup>36</sup>. It is reasonable to assume that the free-volume effects are similar throughout this series of blends. The cloud-point value can then be taken to indicate the intensity of enthalpic interaction in a blend. The present results then indicate that PCMMA interacts most intensely with PMMA and PTHFMA, as these blends degrade before phase separation occurs. The intensity of interaction between a polymethacrylate with PCMMA decreases in the order  $\text{PMMA} \approx \text{PTHFMA} > \text{PEMA} > \text{PnPMA} \approx \text{PiPMA} > \text{PnBMA}$ . With the exception of PTHFMA, the interaction becomes weaker as the pendant alkyl group of the polymethacrylate becomes bigger. Such a trend has been observed for blends of polymethacrylates with SAN<sup>24</sup>,  $\alpha$ MSAN<sup>26</sup> and polyepichlorohydrin<sup>10</sup>. The good miscibility of PTHFMA, which has a big pendant group, appears to be exceptional. We have previously reported that the miscibility behaviour of PTHFMA is similar to that of PMMA in forming miscible blends with PVC<sup>37</sup>, SAN<sup>37</sup>,  $\alpha$ MSAN<sup>37</sup> and poly(vinylphenol)<sup>38</sup>. The good miscibility of PTHFMA could be due to the presence of two interacting moieties: the carbonyl group and the ether oxygen in the tetrahydrofuran ring.

That PCMMA but not PMMA forms miscible blends with other polymethacrylates indicates the importance of chlorine in achieving miscibility. Although it is not the aim of this study to elucidate the nature of interactions in the blends, it is worth while to consider the possible roles of chlorine. Since the miscibility behaviour of PCMMA is similar to that of PVC, it is informative to review the interactions in PVC-containing blends. For PVC/polycaprolactone blends, it has been established by Fourier-transform infra-red (FTi.r.) spectroscopy that a hydrogen-bonding type of interaction exists between the  $\alpha$ -hydrogen of PVC and the carbonyl group of polycaprolactone, but a possible dipole-dipole interaction involving the C-Cl bond is not ruled out<sup>39</sup>. Recently, Vorenkamp and Challa<sup>40</sup> studied the effect of chlorination of PVC on miscibility with PMMA. From the heats of mixing of low-molecular-weight analogues and FTi.r., it was concluded that the interaction is best described as a Lewis acid-base type interaction between the hydrogen of the CHCl group and the carbonyl group. It remains to be seen whether a similar interaction involving the hydrogen of the  $\text{CH}_2\text{Cl}$  group in PCMMA also exists in those miscible blends containing PCMMA.

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