

# NOTE

## Plasticizer Effect on Miscibility of *isotactic* Poly(Methyl Methacrylate)-Poly(Vinyl Chloride) Blends

### INTRODUCTION

A polymer blend, showing one phase at equilibrium, has received considerable industrial and academic attention. However, with polymers, the thermodynamics of mixing do not usually promise mutual solubility and most binary polymer mixtures yield two distinctive phases. According to theories on polymer mixing, the free energy of mixing or thermodynamic interaction parameter between two polymers is the sum of the three contributions: the combinatorial entropy of mixing, the interactional or enthalpic, and the free volume contribution. It is accepted that the thermodynamic basis for mutual solubility in polymer blend is an exothermic heat of mixing, since the entropic contributions are so small.<sup>1,2</sup> In general, analysis of volume contributions on mixing by thermodynamic theories is mathematically complex and free volume effects are known to be unfavorable for polymer-polymer mixing.

In the literature, attention has been paid to the miscibility of the blend of PMMA with PVC. Walsh and McKeown<sup>3</sup> found that PVC and PMMA are miscible in all compositions when 2-butanone is used as a casting solvent, but the researchers were unsuccessful in preparing clear films from THF solution. Challa and his colleagues<sup>4,5</sup> reported that *s*-PMMA is partially miscible with PVC, whereas *i*-PMMA shows no miscibility, at all, and later the researchers concluded that PVC is more compatible with *s*-PMMA than with *i*-PMMA. Zhao and Prud'homme<sup>6</sup> investigated the influence of tacticity and molecular weight of PMMA on its miscibility with PVC, using the nonradiative energy transfer technique. They observed that a decrease in isotactic content and molecular weight of PMMA results in more random dispersion of the PVC chains, that is, it enhances the miscibility of PMMA with PVC. For this blend, two types of interactions have been mentioned: hydrogen bonding interactions, involving the carbonyl group of PMMA and the hydrogens of PVC, or a dipole-dipole interaction between the carbon and chlorine atom.<sup>7,8</sup>

The primary objective of this article is to examine the effect of plasticizer on miscibility of blends of *i*-PMMA with PVC. It is well known that the glass transition temperature,  $T_g$ , can be lowered by the addition of a compat-

ible plasticizer, and we expected the free volume of the polymer mixture can be manipulated by the incorporation of small amount of a plasticizer into certain polymers.

### EXPERIMENTAL

The information about polymers used in this study is listed in Table I. Atactic poly(methyl methacrylate), *a*-PMMA, and PVC were commercial products, supplied by Rohm and Haas Co. (Plexiglas 811) and Lucky Co. (LS100), respectively. The *i*-PMMA was prepared from the toluene medium by anionic polymerization at 0°C under nitrogen atmosphere, using phenylmagnesiumbromide as catalyst.<sup>9</sup> The polymerized product was purified by fractionation, using toluene as a solvent and methanol as a nonsolvent. A DSC and proton NMR analysis of the purified product showed that the isotacticity of PMMA was higher than 87%. Dimethyl phthalate (DMP, Junsei Chemical, Japan), diethyl phthalate (DEP, Hayashi Chemical, Japan), di-2-ethylhexyl phthalate (DOP, Janssen Chemica, Belgium), tricresyl phosphate (TCP, Junsei Chemical), and all chemicals were reagent grade and were used without further purification. Blends of *i*-PMMA/PVC and polymer/plasticizer mixtures were prepared by dissolving polymers in 2-butanone (MEK) in the desired proportions to a total solid content of 5% by weight. The solvent was evaporated at 50°C, and the resulting films were kept in a vacuum oven for 1 week at 70°C, and were then further vacuum dried for 5 h at 130°C just before thermal analysis.

Glass transition temperature was observed, using DuPont DSC-2000, at heating rate of 20°C/min. The polymer/plasticizer mixture was first heated from room temperature to 200°C, and blends of *i*-PMMA/PVC were heated to 150°C, immediately followed by rapid quenching to -20°C, using a mechanical cooler. The  $T_g$  was determined at the onset of the shift in heat flows during the second heating.

### RESULTS AND DISCUSSION

#### *a*-PMMA/DOP Mixture

The glass transition behavior of *a*-PMMA/DOP mixtures, prepared by *in situ* polymerization, has been studied ex-

**Table I** Polymers Used in This Study

Polymer Abbrev.	Isotacticity (%)	$T_g$ (°C)	$M_w$ Information	Source
<i>a</i> -PMMA	11	100.3	$M_n = 52,900$ $M_w = 105,400$	Rohm and Haas Plexiglas
<i>i</i> -PMMA	> 87	51.3	$[\eta] = 0.953^a$ $M_w = 425,500^a$	Synthesized
PVC	—	78.0	$M_n = 39,100^a$ $M_w = 134,600^a$	Lucky, Korea LS 100

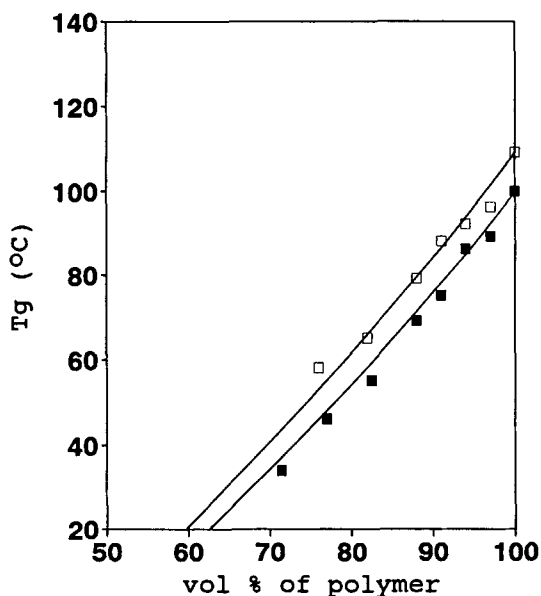
<sup>a</sup> Measured at 40°C in THF by GPC.

tensively by Kelly and Buche<sup>10</sup> and Kalachandra and Turner,<sup>11</sup> and studied this literature in order to evaluate the reliability of our techniques. The data for both *a*-PMMA samples are shown in Figure 1 and the physical values of the substances, used to calculate  $T_g$ s, are listed in Table II. Kalachandra and Turner's  $T_g$  behavior and calculated results, using eq. (1) suggested by Kelly and Buche, are reproduced also in Figure 1.

$$T_g = (V_1\Delta\alpha_1T_{g1} + V_2\Delta\alpha_2T_{g2}) / (V_1\alpha_1 + V_2\alpha_2) \quad (1)$$

where  $\Delta\alpha_i$  equals changes of volume expansion coefficient in glassy and rubbery state,  $V_i$  equals volume fraction of each component, and  $T_{gi}$  equals glass transition temperature of pure polymer or plasticizer.

Our data for *a*-PMMA (filled square) agree with Kelly's equation (solid line) well, but run parallel to data of



**Figure 1** Glass transition temperature for the atactic PMMA/DOP mixtures. Experimental data have been applied to the Kelly-Buche equation<sup>10</sup>; solid line, (□) data from Ref. 11, (■) our data.

Turner's (open square). We didn't expect the same results as Turner, since the *a*-PMMA used in our experiment was different. However, as shown in Figure 2, our data of changes in  $T_g$ , due to the addition of DOP, are almost identical with Turner's (open square), within experimental error. It should be noted that our sample was prepared by solution casting, that is, by a physical method, while Turner's PMMAs were prepared from a chemical method: *in situ* polymerization. This result reveals that the change in  $T_g$  of plasticized *a*-PMMA is not affected by the preparation method of the sample and is only a function of plasticizer content.

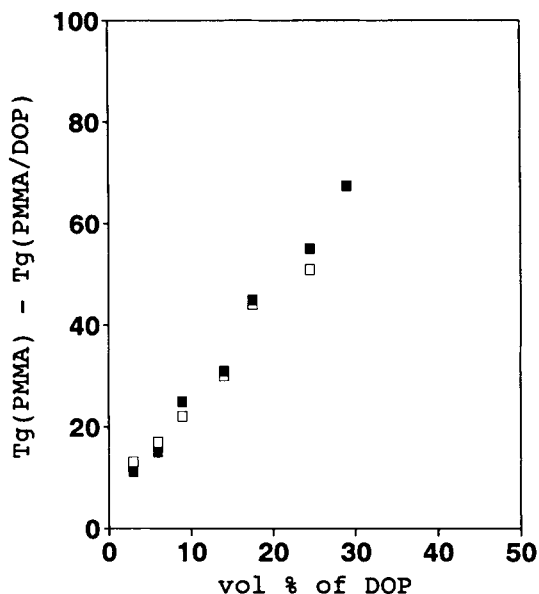
#### *i*-PMMA/PVC Blends: Plasticizer Effect

It is already known, from the work of Vorenkamp et al.,<sup>15</sup> that *i*-PMMA is found to be miscible with PVC for relatively low molar mass only. The cloud point curve for this blend is known to be asymmetric, with a minimum temperature of about 60 to 80% *i*-PMMA, depending on molecular weight. All of the samples of *i*-PMMA/PVC blends, cast from the MEK solution without plasticizer, were cloudy at room temperature and DSC thermograms showed two  $T_g$ s for these mixtures, except for the blend containing 80 wt % PVC.

The  $T_g$  behaviors for the 50 : 50 mixture of *i*-PMMA/PVC showed remarkable enhancement in miscibility by adding a small amount of DMP. As shown in Figure 3,

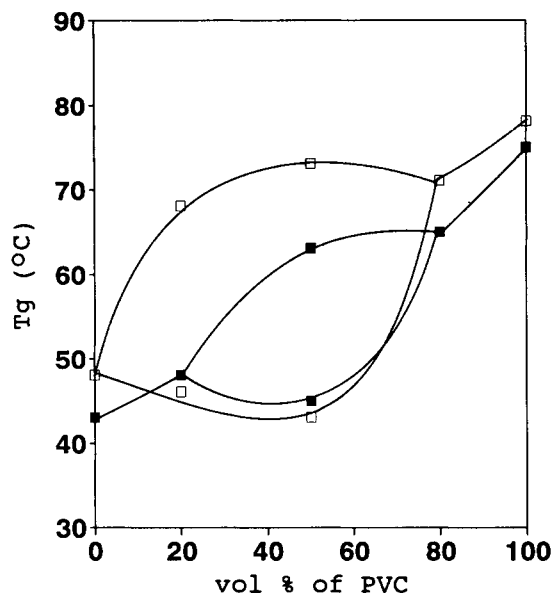
**Table II** Characteristic Parameters Used to Calculate Theoretical  $T_g$ 's of Polymer/Plasticizer Mixtures

Substance	Density at 25°C (g/cm <sup>3</sup> )	$T_g$ (°C)	$\Delta\alpha$			Ref.
			$\alpha_L$	$\alpha_G$	$\times 10^4 \text{ deg}^{-1}$	
<i>a</i> -PMMA	1.188	100.3	5.80	2.72	3.08	11
<i>i</i> -PMMA	1.230	51.3	5.83	2.34	3.49	12
PVC	1.400	78.0	5.2	2.1	3.1	13
DOP	0.986	-82	7.7	3.6	4.1	11
DINP	0.972	-80	8.1	3.7	4.4	14



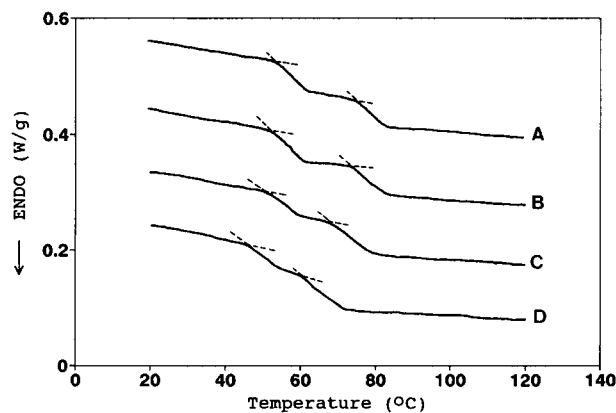
**Figure 2** Effect of DOP concentration on  $T_g$  of atactic PMMA. ( $\square$ ) replotted from the data in Ref. 11, ( $\blacksquare$ ) our data.

each blend still shows two glass transition temperatures, but the intervals between the two  $T_g$ s originated from the phase separation of components that were approached as the DMP concentration increased. On the other hand, the *i*-PMMA/PVC blends, containing more than 1 wt % of DOP, were transparent and showed a single glass transition behavior, while the blends, containing a trace of DOP, were generally translucent as prepared. The  $T_g$  values of the first DSC scan for the *i*-PMMA/PVC blends, containing 0.6 wt % DOP (filled square), and without DOP (open squares), are shown in Figure 4. It is natural that the all  $T_g$ s of the blends, having DOP, appeared at

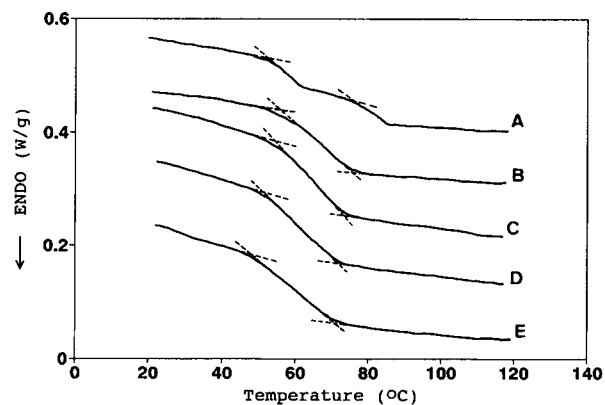


**Figure 4**  $T_g$  behaviors of *i*-PMMA/PVC blends from the first DSC run: ( $\square$ ) without containing DOP, ( $\blacksquare$ ) containing 0.6 wt % DOP.

somewhat lower temperatures than those of the blends without DOP. Significant convergence of two  $T_g$ s within an immiscible region can be observed in the blends containing 0.6 wt % DOP. This behavior was remarkable in the secondary DSC run, as can be seen in Figure 5. This result clearly shows that the miscibility between *i*-PMMA and PVC was enhanced by adding a small amount of DOP. Figure 6 shows the dependency of composition on  $T_g$  behavior for the *i*-PMMA/PVC blends containing 0.6 wt % DOP. Theoretical  $T_g$ s, calculated using the eq. (2) based on isofree volume relationships for three components, are also shown as a solid line.



**Figure 3** DSC thermograms for *i*-PMMA/PVC blends (50 : 50), containing: (A) 0 wt %, (B) 1 wt %, (C) 3 wt %, and (D) 5 wt % DMP.



**Figure 5** DSC thermograms of second run for *i*-PMMA/PVC: (A) without, (B) 0.6 wt %, (C) 1 wt %, (D) 3 wt %, and (E) 5 wt % DOP.

**Table III** Temperature Differences (in °C) between Two  $T_g$ 's ( $\Delta$ ) and Transition Breadth of *i*-PMMA/PVC Blend Containing 50 Wt % PVC

Plasticizer	Free Volume <sup>a</sup> (cm <sup>3</sup> /g)	Content (wt %)				
		0.0	0.6	1.0	3.0	5.0
DMP	0.162	Δ19.9	—	Δ20.0	Δ17.5	Δ14.9
TCP	0.158	Δ19.9	—	Δ15.8	Δ16.2	Δ12.3
DEP	0.181	Δ19.9	—	Δ16.3	18.4	16.1
DOP	0.203	Δ19.9	8.7	18.3	16.8	18.1

<sup>a</sup> Calculated by the method of Van Krevelen.<sup>16</sup>

$$T_g = (V_1\Delta\alpha_1T_{g1} + V_2\Delta\alpha_2T_{g2} + V_3\Delta\alpha_3T_{g3}) / (V_1\Delta\alpha_1 + V_2\Delta\alpha_2 + V_3\Delta\alpha_3) \quad (2)$$

The *i*-PMMA/PVC blends, holding 0.6 wt % DOP, show not only a single glass transition behavior that is a function of blend composition, but also relationships that are somehow agreeable with the theoretical  $T_g$  values. The deviations of observed  $T_g$ s from the theoretical values were decreased with increasing DOP content. At the level of 5 wt % DOP, the  $T_g$  difference between observed and calculated value was within 2°C. It seems that this deviation can be caused by the additional specific interaction induced by plasticizer; further study seems to be required.

Results similar to DOP and DMP were observed in other plasticizers, for example, in TCP and DEP. The temperature difference between two  $T_g$ s for immiscible blend,  $\Delta T_g$ , and the breadth of the  $T_g$  region,  $T_w$ , which is characterized by the difference between the end-point

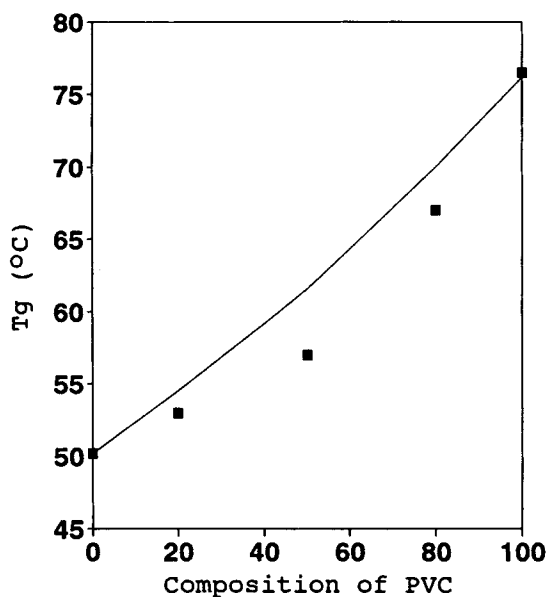
and onset temperature for the blend showing a single  $T_g$ , is listed in Table III, with the calculated free volume of plasticizer. The results in Table III show that the  $T_g$  of the 50 : 50 mixture of *i*-PMMA/PVC blend decreased markedly with an increase in DMP and TCP content, while the  $T_g$  of same mixture, without containing plasticizer, is 19.9°C. This observed miscibility enhancement by plasticizer is remarkable when the DEP is used, that is, the  $\Delta T_g$  decreased with an increment of DEP content and finally showed a single  $T_g$ . Dramatically different results are observed when DOP is the plasticizer, in that one  $T_g$  was observed merely by the addition of 0.6 wt %.

These results indicate that miscibility improves as a function of the plasticizer content, and this miscibility enhancement is also affected by the chemical structure of the plasticizer. It seems that the bulkiness of plasticizer is the main reason for miscibility improvement, since the improvement runs parallel with the values of the free volume fraction of plasticizer. The phase separation temperature on heating, LCST, was also improved at least 40°C for the *i*-PMMA/PVC blends containing 0.6 wt % DOP, since these samples, heated to 150°C in the second scan, showed no sign of phase separation, whereas for those previously reported, LCST is 110°C. However, further studies are required, because it is not known whether or not this is common phenomena for all polymer-polymer blends.

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**Figure 6**  $T_g$  behaviors of *i*-PMMA/PVC blends, containing 0.6 wt % DOP.

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