

Influence of Tacticity of Poly(methyl methacrylate) on the Compatibility with Poly(vinyl phenol)

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ABSTRACT: Isotactic, atactic, and syndiotactic poly(methyl methacrylate) (PMMA) were mixed with poly(vinyl phenol) (PVPh) separately in tetrahydrofuran to make three polymer blend systems. Differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy were used to study the miscibility of these blends. Isotactic PMMA was found to be more miscible with PVPh than atactic or syndiotactic PMMA. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1773–1780, 1997

Key words: tacticity, poly(methylmethacrylate), compatibility, poly(vinylphenol)

INTRODUCTION

It has been known for years that the stereoregularity of polymer chains influences polymer–polymer miscibility. Due to its availability in both syndiotactic and isotactic forms, poly(methyl methacrylate) (PMMA) has been used frequently in the investigation of the effect of tacticity on miscibility. Several articles have shown that the tacticity of PMMA influences blend compatibility when PMMA is blended with a chemically different polymer. Some of these systems include poly(vinylidene fluoride) (PVDF)–PMMA,^{1–3} poly(ethylene oxide) (PEO)–PMMA,^{4–6} poly(vinyl chloride) (PVC)–PMMA^{7–8} and poly(styrene-co-vinyl phenol) (MPS)–PMMA.⁹ For the PVDF–PMMA system, isotactic PMMA was found to be more miscible than syndiotactic one. For PVC–PMMA and MPS–PMMA systems, PVC or MPS forms miscible blends with syndiotactic PMMA, whereas it does not form miscible blends with isotactic PMMA. For the PEO–PMMA system, the results are not consistent. One result is that isotactic PMMA is more miscible than syndiotactic PMMA.⁴ The other result is that syndiotactic PMMA is more miscible than isotactic PMMA.^{5–6}

The reason may be the differences in the molecular weights and the preparation methods of the samples. Because atactic PMMA is mainly composed of syndiotactic PMMA, the result of atactic one is often similar to syndiotactic PMMA.

It has been reported, on the basis of experimental data as well as theoretical predictions, that PMMA forms a single amorphous phase with PVPh over the entire composition range and at all accessible temperatures.^{10–14} Some contradicting data on the miscibility of PMMA and PVPh have been reported, however.^{15,16} These are believed to be related to the blend preparation method, which directly influences phase behavior.¹² In this article, the miscibility of PMMA–PVPh blends prepared by solution casting with different tacticities of PMMA were investigated. Transparency and a single glass transition temperature for each composition of the blends are used as criteria for miscibility. Also, the carbonyl groups of PMMA will form hydrogen bonds with the hydroxyl groups of PVPh. Thus, the wavelength shift of absorbance of the carbonyl groups can be observed by infrared (IR) spectroscopy. Therefore, differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) measurements were carried out to study the glass transition temperatures and the degree of hydrogen bonding of the polymer blends. The aim of this work is to find out the influence

Table I Polymer Compositions and Their Shapes

Polymer Compositions	Solid or Film
PVPh : iPMMMA	
100 : 0	s
74.9 : 25.1	s
50.1 : 49.9	f
25.6 : 74.4	f
0 : 100	f
PVPh : aPMMA	
75.0 : 25.0	s
49.2 : 50.8	s
24.9 : 75.1	s
0 : 100	f
PVPh : sPMMA	
75.5 : 24.5	s
50.1 : 49.9	s
24.8 : 75.2	s
0 : 100	s

of tacticity of PMMA on the compatibility with PVPh.

EXPERIMENTAL

Materials

Isotactic, atactic, and syndiotactic PMMA (designated as iPMMMA, aPMMA, and sPMMA in this study) and PVPh were purchased from Poly-science, Inc., Warrington, PA. According to the supplier information, the molecular weights (M_w) of iPMMMA, aPMMA, and sPMMA are the same, at about 100,000. The molecular weight (M_w) of PVPh is about 30,000. PVPh was mixed with each PMMA individually with different weight compositions. The actual compositions are shown Table I. Films of the polymer blends were made by solution casting onto glass plates. Tetrahydrofuran (THF) was used as the solvent for most compositions; but for PMMA, toluene was used instead. THF and toluene are ACS reagent purchased from Fisher Scientific, Fair Lawn, New Jersey. The final drying step for all the films took place in a vacuum oven for more than one day at 92–105°C. Then the films were cooled down to room temperature slowly by air cooling. Although the drying temperature were sometimes lower than the glass transition temperatures of the polymers, the films were transparent after air cooling without any observable phase separation.

Differential Scanning Calorimetry and Fourier Transform Infrared Spectroscopy

The glass transition temperatures (T_g s) of the polymer blends were determined using a DuPont 2000 thermal analyzer. The scanning range for temperature was from 30 to 200°C and a heating rate of 20°C min was used in every measurement. The experiments were performed in the ambient environment of nitrogen gas. In the first thermal scan, the samples stayed at 200°C for one minute. Then the samples were quenched to 0°C immediately using an ice water bath. The samples were quenched quickly enough to prevent any crystallization, as detected by DSC. There was also no trace of solvent in the films detected by DSC. The inflection point of the specific heat jump of the second thermal scan was taken as the glass transition temperature.

The polymer blends were ground with KBr powder to make samples for FTIR studies. Spectra were obtained with 64 scans at a resolution of 4 cm^{-1} . The wavelength range was from 400 to 4000 cm^{-1} .

RESULTS AND DISCUSSION

All the polymers after preparation appeared to be transparent, indicating possible compatibility. The shapes of most of the polymers were more like powdered solids than films, owing to the brittleness of the two polymers (PVPh and sPMMA). Table I is a list of all the polymer compositions studied and their shapes.

Glass Transition Temperatures

The complete thermal scans of the three polymer blends are shown in Figures 1–3. T_g s of iPMMMA, aPMMA, sPMMA, and PVPh were measured to be 75, 105, 124, and 156°C individually. If aPMMA is assumed to be composed solely of iPMMMA and sPMMA, aPMMA is estimated to be 61% sPMMA and 39% iPMMMA from the T_g difference. According to Figures 1–3, there is a single glass transition temperature for most compositions. The only two exceptions (shown in Figures 2 and 3) are PVPh : aPMMA (49.2 : 50.8) and PVPh : sPMMA (50.1 : 49.9), with two glass transition temperatures indicating heterogeneity. The results can be seen more clearly in Figure 4. For the two compositions having two T_g s, the lower T_g one is quite close to the T_g of pure PMMA. Judging from this, the

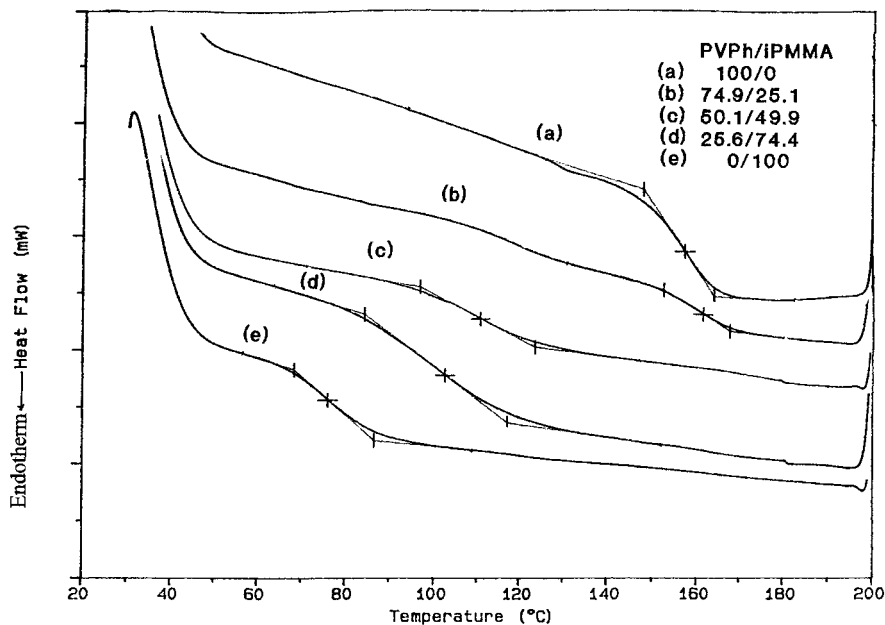


Figure 1 DSC thermograms of PVPh-PMMA blends.

composition with higher T_g can be assumed to be composed of PMMA and PVPh, and the one with lower T_g consists of mainly PMMA. Aside from the two T_g points, the glass transition temperatures for these blends are mostly quite close to the values predicted by the additivity rule (the dashed lines in Figure 4). However, the T_g of PVPh : iPMMA (74.9 : 25.1) is much higher than

the value predicted by the additivity rule, and this value is even higher than that of aPMMA or sPMMA with a similar composition. The T_g of PVPh : iPMMA (25.6 : 74.4) is above the weight-averaged value. However, the T_g of aPMMA or sPMMA with a similar composition falls below the average value. The importance of the elevation of T_g will be expounded in the next paragraph.

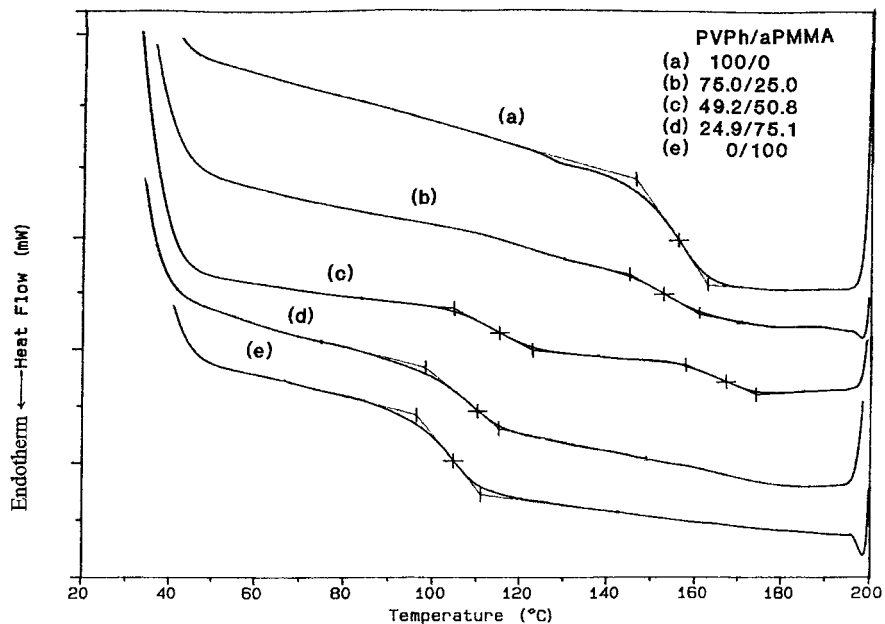


Figure 2 DSC thermograms of PVPh-PMMA blends.

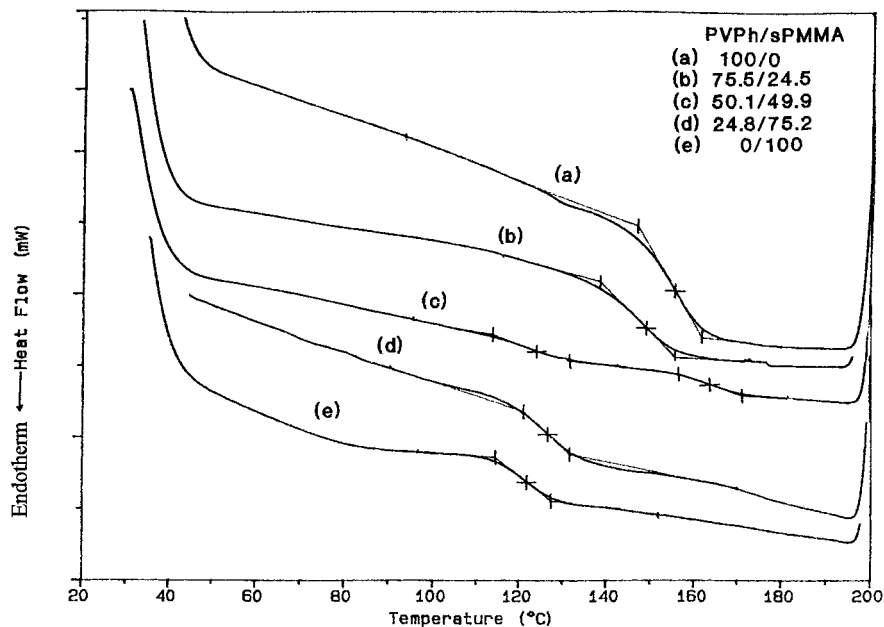


Figure 3 DSC thermograms of PVPh-PMMA blends.

Several empirical equations have been proposed to describe the composition dependence of T_g for miscible blends that involve strong specific interaction. Three publications¹⁷⁻¹⁹ offer theoretical insights into the underlying reason for the experimental observations. In the limiting case, these equations reduce to the following simple expression²⁰:

$$T_g = W_1 T_{g1} + W_2 T_{g2} + q W_1 W_2 \quad (1)$$

where W_1 and W_2 denote, respectively, the weight fractions of the components 1 and 2, and q is a parameter that depends on the net polymer-polymer interaction (i.e., hydrogen bonding in this article). The following comments can be drawn by

using the eq. (1). For compositions such as approximately 25 or 75% PMMA in the blends, the degree of hydrogen bonding of iPMMA with PVPh is higher than that of aPMMA or sPMMA.

The glass transition temperature regions (ΔT_g) were calculated as the differences between the onset and the end points of T_g . The calculated results are shown in Figure 5. It is interesting to notice that a broadening of the glass transition temperature regions occur when iPMMA is added to the PVPh-iPMMA system. For PVPh-aPMMA or PVPh-sPMMA system (those compositions with two T_g s not included), a broadening of the glass transition temperature regions is not observed. In the literature, a broadening of T_g regions has often been attributed to the presence of

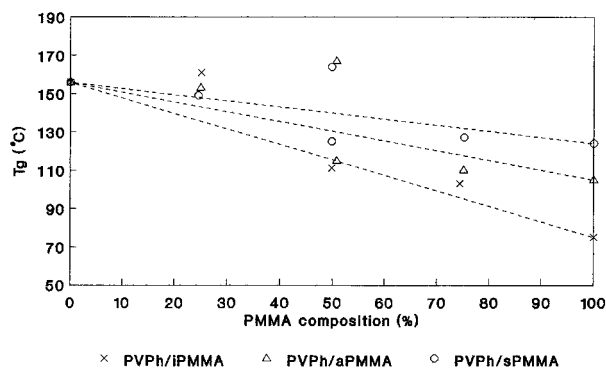


Figure 4 The glass transition temperatures of the three polymer blends.

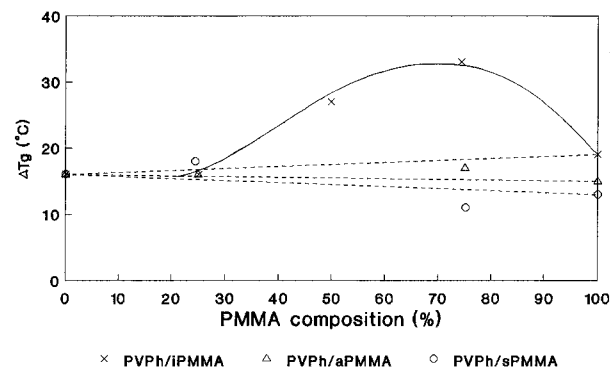


Figure 5 The glass transition temperature regions of the three polymer blends.

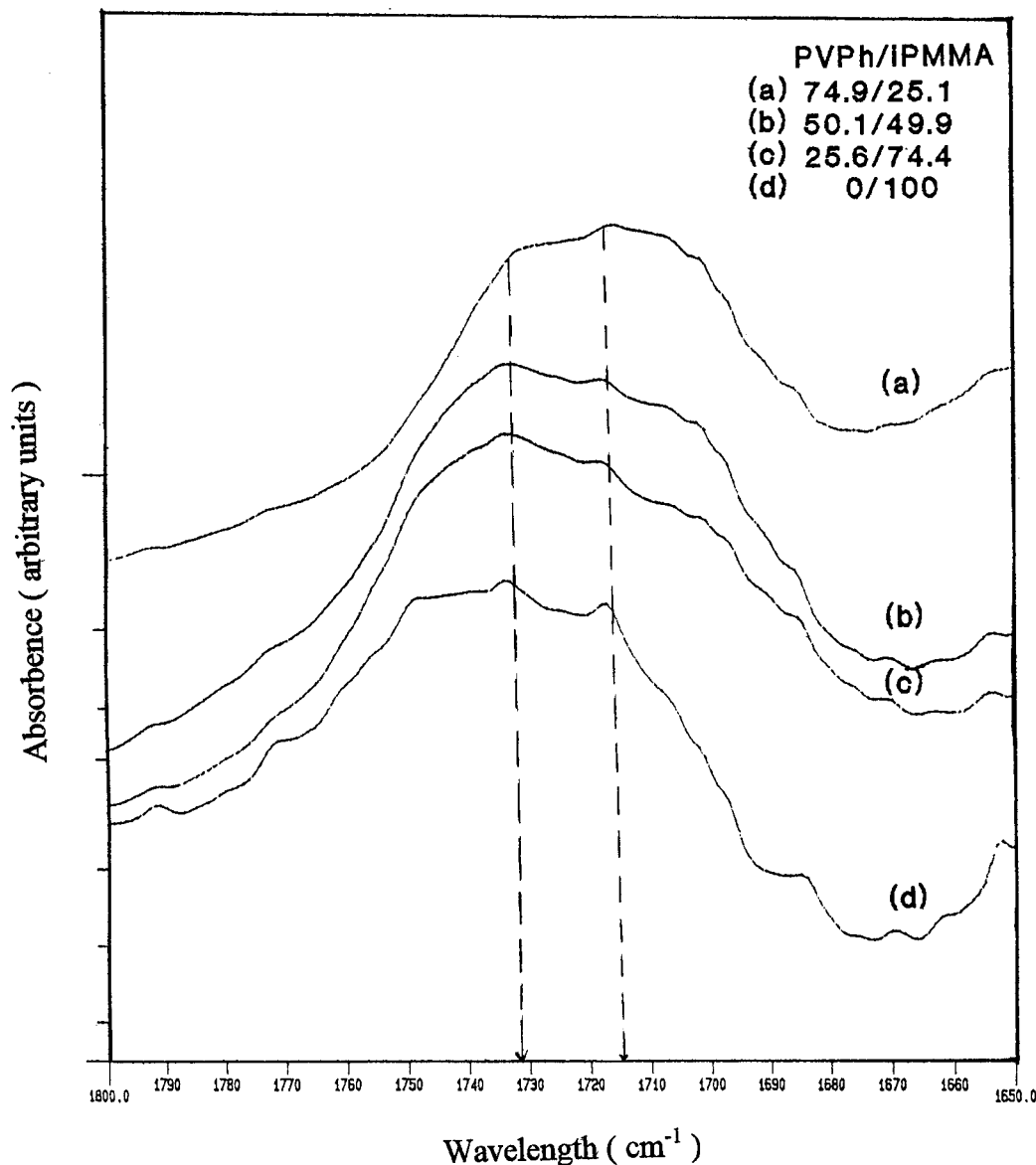


Figure 6 FTIR spectra of PVPh-iPMMA blends.

microheterogeneities where local fluctuations are added to the density fluctuations.^{21,22} However, it has been shown that such a broadening may also result from normal density fluctuations without invoking the presence of composition fluctuations.²³ The T_g difference between PMMA and PVPh is the biggest (81°C) for iPMMA, so it is not fair to determine the miscibility of the studied blends solely from this aspect.

FTIR Studies

The FTIR measurements are shown in Figures 6–8 only for the region of the wavelength from 1650

to 1800 cm^{-1} . For the three blend systems, there are two peaks observed. One is the free carbonyl group stretching in 1732 cm^{-1} . The other one in 1715 cm^{-1} can be assigned to the hydrogen-bonded carbonyl groups. Because sPMMA is easy to ground with KBr powder, in Figures 6–8, the FTIR spectrum of sPMMA is used to represent all the PMMAs. Because the samples were prepared as KBr-polymer disks, there was some scattering in the signals. However, the following qualitative comments can be made. In Figure 6, the degree of hydrogen bonding increases with the increasing composition of PVPh (from 0 to 74.9%) in the blends. However, there is little difference in the

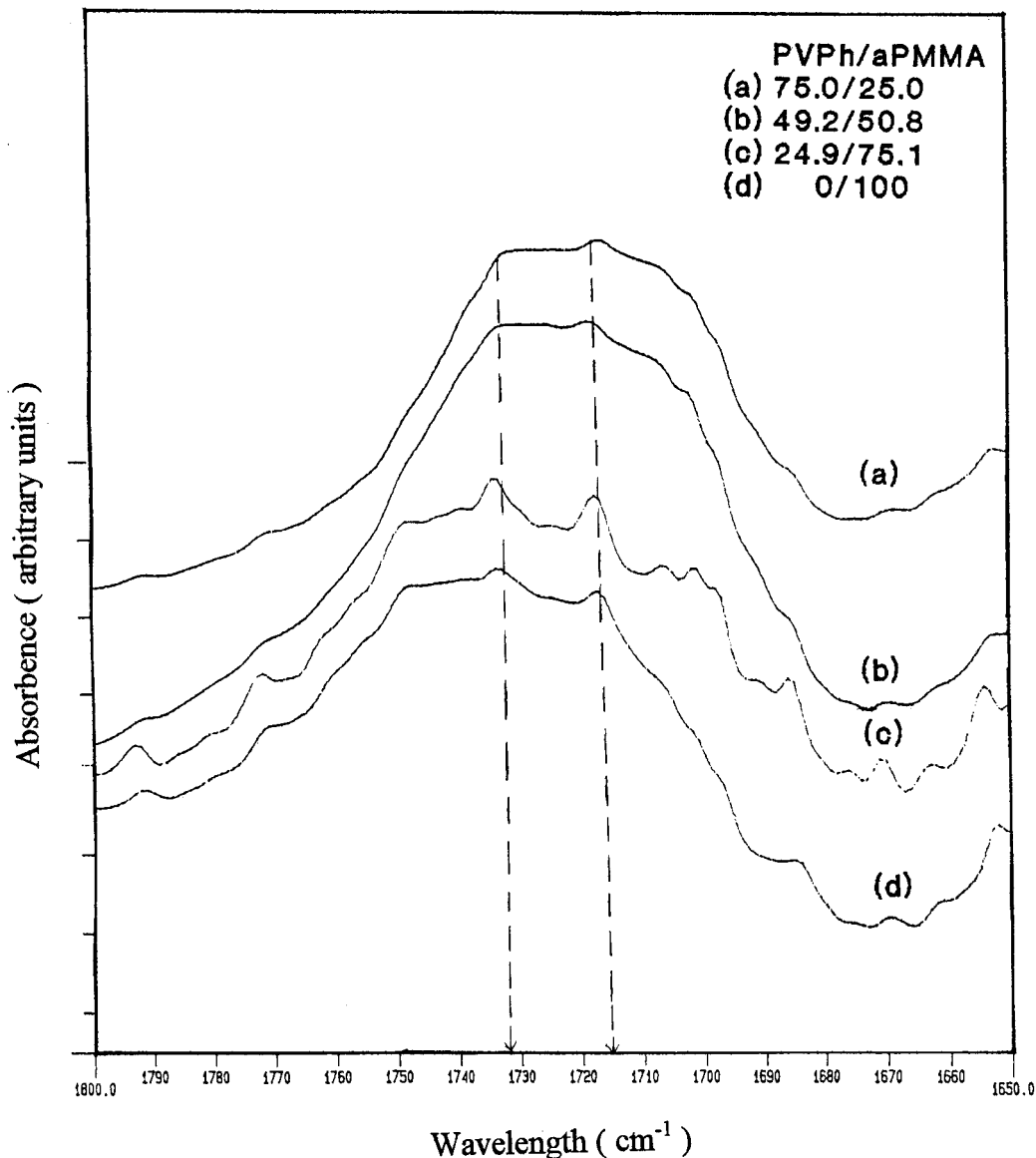


Figure 7 FTIR spectra of PVPh-aPMMA blends.

degree of hydrogen bonding between 25.6 and 50.1% PVPh in the blends. In Figures 7 and 8, the degree of hydrogen bonding also increases with the increasing composition of PVPh in the blends, but there is a very low degree of hydrogen bonding for one composition (about 25% PVPh in the blend). Comparing the curve of PVPh : iP-MMA (25.6 : 74.4) to that of aPMMA or sPMMA having a similar composition, it seems that iP-MMA has the highest degree of hydrogen bonding with PVPh. Comparing the (a) curves (about 75% PVPh in the blends) in Figures 6-8 also seems to support the fact that the degree of hydrogen bonding is highest for iP-MMA.

For the PMMA-PVPh blends to be more miscible, there is a need for more PMMA-PVPh interactions and less PMMA-PMMA and PVPh-PVPh interactions. PMMA-PMMA interactions are weak, but PVPh-PVPh interactions are strong because of self-associated hydrogen bonding.²⁴ Thus, PVPh-PVPh interactions need to be taken into the consideration in the blends. If the PVPh-PVPh interactions are stronger than the PMMA-PVPh interactions, PVPh-PVPh interactions will not be broken, and the PMMA-PVPh blends will be immiscible. In the studied blends, iP-MMA forms more hydrogen bonding interactions with PVPh than aPMMA or sPMMA. Therefore, the iP-MMA-PVPh blends are

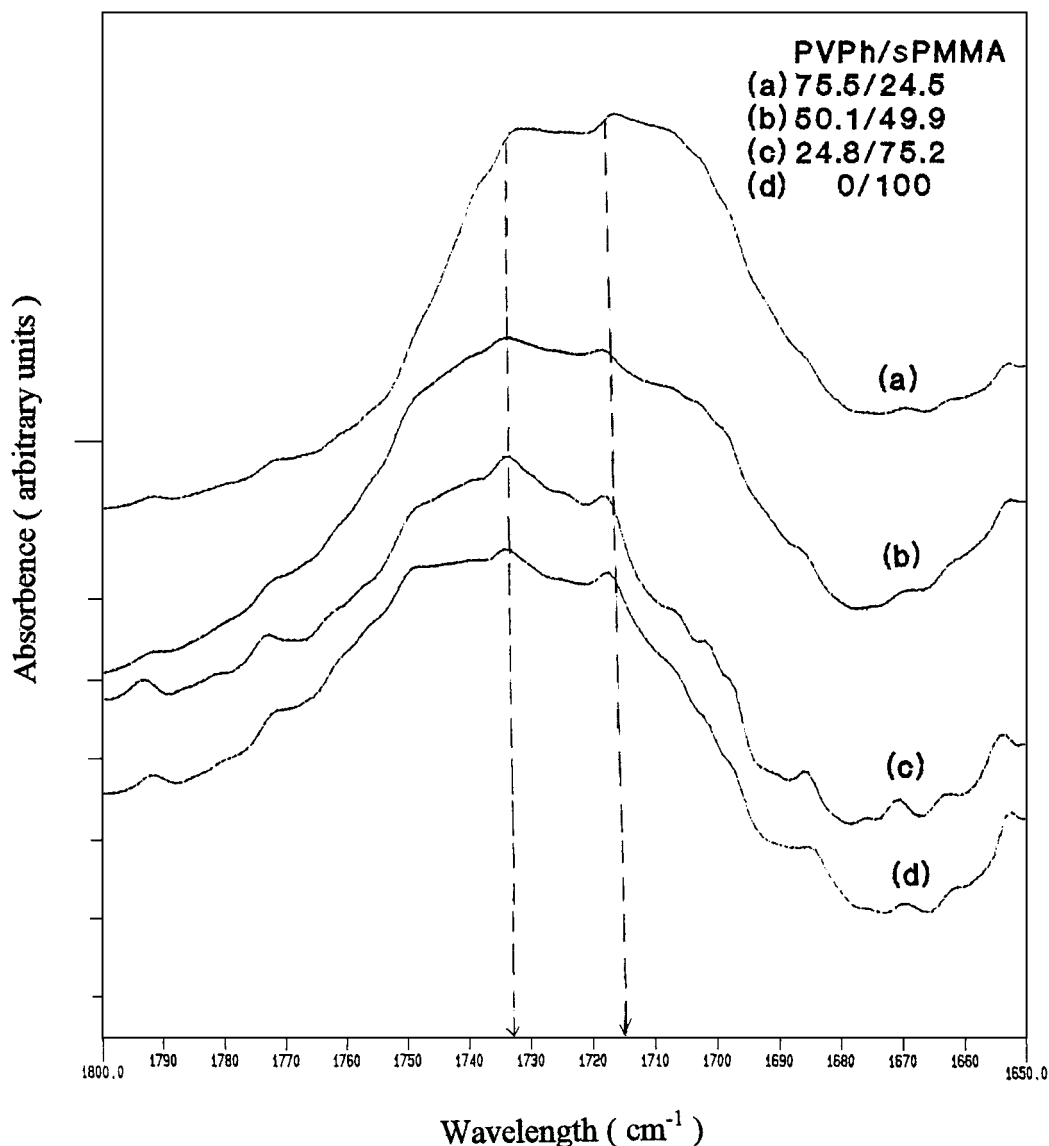


Figure 8 FTIR spectra of PVPh-sPMMA blends.

more miscible than the aPMMA-PVPh or sPMMA-PVPh blends.

The degree of the annealing effect on these polymer blends was not investigated in this article but will be an interesting subject to look into. More work needs to be done to clarify this effect.

CONCLUSIONS

iPMMA is more miscible than aPMMA or sPMMA when it was blended with PVPh in THF for the compositions studied. The results are corroborated by the glass transition temperature measurements and FTIR spectra. There is a single

glass transition temperature for each composition in the blends of PVPh and iPMMA. However, there are two glass transition temperatures for one composition of PVPh-aPMMA or PVPh-sPMMA blends. From FTIR spectra, the degree of hydrogen bonding of iPMMA with PVPh is the highest among these three PMMAs.

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REFERENCES

1. E. Roerdink and G. Challa, *Polymer*, **19**, 173 (1978).
2. E. Roerdink and G. Challa, *Polymer*, **21**, 509 (1980).

3. A. P. A. M. Eijkelenboom, W. E. J. R. Mass, W. S. Veeman, G. H. Werumeus Buning, and J. M. J. Vankan, *Macromolecules*, **25**, 4511 (1992).
4. G. Ramana Rao, C. Castiglioni, M. Gussoni, G. Zeroi, and E. Martuscelli, *Polymer*, **26**, 811 (1985).
5. E. John and T. Ree, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 385 (1990).
6. C. Silvestre, S. Cimmino, E. Martuscelli, F. E. Karasz, and W. J. MacKnight, *Polymer*, **28**, 1190 (1987).
7. J. W. Schurer, A. de Boer, and G. Challa, *Polymer*, **16**, 201 (1975).
8. E. J. Vorenkamp, G. ten Brinke, J. G. Meijer, H. Jager, and G. Challa, *Polymer*, **26**, 1725 (1985).
9. Lei Jong, E. M. Pearce, and T. K. Kwei, *Polymer*, **34**, 48 (1993).
10. C. J. Serman, P. C. Painter, and M. M. Coleman, *Polymer*, **32**, 1049 (1991).
11. C. T. Chen and H. Morawetz, *Macromolecules*, **22**, 159 (1989).
12. C. J. T. Landry and D. M. Teegarden, *Macromolecules*, **24**, 4310 (1991).
13. S. H. Goh and K. S. Siow, *Polym. Bull.*, **17**, 453 (1987).
14. C. J. Serman, Y. Xu, P. C. Painter, and M. M. Coleman, *Macromolecules*, **22**, 2015 (1989).
15. X. Zhang, K. Takegoshi, and K. Hikichi, *Macromolecules*, **24**, 5756 (1991).
16. S. R. Fahrenholtz and T. K. Kwei, *Macromolecules*, **14**, 1076 (1981).
17. P. C. Painter, J. F. Graf, and M. M. Coleman, *Macromolecules*, **24**, 5630 (1991).
18. P. R. Couchman, *Macromolecules*, **24**, 5772 (1991).
19. Xinya Lu and R. A. Weiss, *ACS Polym. Mater. Sci. Eng. Prep.*, **64**, 75 (1991).
20. T. K. Kwei, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 306 (1984).
21. R. E. Prud'homme, *Polym. Eng. Sci.*, **22**, 90 (1982).
22. W. J. MacKnight, F. E. Karasz, and J. R. Fried, *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Chap. 5.
23. W. M. Prest Jr. and F. J. Roberts Jr., paper presented at the 28th IUPAC Macromolecular Symposium, Amherst, MA, July 12–16, 1982.
24. M. M. Coleman, J. F. Graf, and P. C. Painter, *Specific Interaction and the Miscibility of Polymer Blends*, Technomic, Lancaster, PA, 1991.