ELSEVIER

Polymer 44 (2003) 1973–1978

polymer

www.elsevier.com/locate/polymer

Miscibility and interactions in poly(methylthiomethyl methacrylate)/poly(vinyl alcohol) blends

J.Z. Yi, S.H. Goh*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, Singapore 117543

Received 6 June 2002; received in revised form 22 November 2002; accepted 27 November 2002

Abstract

Poly(methylthiomethyl methacrylate) (PMTMA) is miscible with poly(vinyl alcohol) (PVA) over the whole composition range as shown by the existence of a single glass transition temperature in each blend. The interaction between PMTMA and PVA was examined by Fourier transform infrared spectroscopy, solid-state nuclear magnetic resonance spectroscopy and X-ray photoelectron spectroscopy. The interactions mainly involve the hydroxyl groups of PVA and the thioether sulfur atoms of PMTMA, and the involvement of the carbonyl groups of PMTMA in interactions is not significant. The measurements of proton spin–lattice relaxation time reveal that PMTMA and PVA do not mix intimately on a scale of 1–3 nm, but are miscible on a scale of 20–30 nm. In comparison, we have previously found that PMTMA is miscible with poly(*p*-vinylphenol) and the two polymers mix intimately on a scale of 1–3 nm.

Keywords: Miscibility; Poly(methylthiomethyl methacrylate); Poly(vinyl alcohol)

1. Introduction

Hydroxyl-containing polymers are capable of forming miscible blends with proton-accepting polymers through hydrogen-bonding interactions involving their hydroxyl groups [1]. However, hydroxyl-containing polymers are self-associated and hence the competition between self-association and interpolymer interaction plays an important role in determining the miscibility behavior of their blends. For example, poly(vinyl alcohol) (PVA) is miscible with three tertiary amide polymers poly(*N*-vinyl-2-pyrrolidone) (PVP) [2–6], poly(*N*,*N*-dimethylacrylamide) [7] and poly(2-methyl-2-oxazoline) [8], but is immiscible with another tertiary amide polymer poly(2-ethyl-2-oxazoline) (PEOx) [9]. In addition, PVA is miscible with self-associated poly(acrylic acid) [10,11] and poly(methyacrylic acid) [10], but not with poly(2-vinylpyridine) (P2VPy) and poly(4-vinylpyridine) (P4VPy) [12].

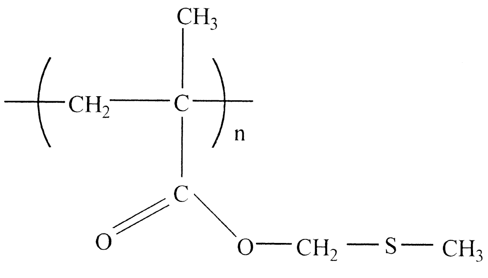
We have recently reported that poly(*p*-vinylphenol) (PVPh) is miscible with poly(methylthiomethyl methacrylate) (PMTMA), mainly arising from interactions between the hydroxyl groups of PVPh and the thioether sulfur atoms of PMTMA [13]. Interactions involving the carbonyl groups of PMTMA are not significant [13]. The result is interesting because PVPh generally interacts with the carbonyl groups of polymethacrylates [14–17]. We suggested that the big sulfur atom in the pendent group of PMTMA might have reduced the accessibility of the carbonyl groups.

Both PVA and PVPh are self-associated. The self-association equilibrium constant of PVA (26.6) is slightly larger than that of PVPh (21.0) [1,18], indicating that PVA has a slightly higher tendency to self-associate. The different self-association tendency of PVA and PVPh may account for their different miscibility behavior of some blend systems. For instance, while PVA is immiscible with P2VPy and P4VPy [12], PVPh is miscible with the two poly(vinylpyridine)s [19–21]. Similarly, PVPh is miscible with PEOx [22,23] but PVA is not [9]. We now report the miscibility and interactions in blends of PVA with PMTMA. It will be shown that although PMTMA is miscible with PVA based on the single-glass transition temperature criterion, PMTMA does not mix with PVA as intimately as with PVPh.

---

* Corresponding author. Fax: +65-67791691.
E-mail address: chmgohsh@nus.edu.sg (S.H. Goh).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00916-3



(PMTMA)

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) ($M_w = 14{,}000$) was supplied by BDH Chemical Ltd. The monomer, methylthiomethyl methacrylate, was prepared by reacting chloromethyl methyl sulfide with methacrylic acid in the presence of triethylamine [13]. PMTMA ($M_w = 12{,}000$) was prepared by solution polymerization in THF at 70 °C using azobisisobutyronitrile as initiator [13].

2.2. Preparation of blends

PMTMA and PVA were separately dissolved in dimethylformamide (DMF) to form 1% (w/v) solutions. Appropriate amounts of PMTMA and PVA solutions were mixed under continuous stirring for 3 h and was then allowed to evaporate to dryness to give a polymer blend. The blend was dried in vacuo at 60 °C for 2 weeks.

2.3. DSC measurements

The glass transition temperature (T_g) values of various blends were measured with a TA Instruments 2920 differential scanning calorimeter using a heating rate of 20 °C/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values. The initial onset of the change of slope in the DSC curve is taken to be the T_g.

2.4. FTIR characterization

FTIR spectra were acquired using a Bio-Rad 165 FTIR spectrophotometer. Samples were prepared by grinding the blends with KBr and compressing the mixture to form disks. The disks were stored in a desiccator to avoid moisture absorption. All spectra were recorded at 140 °C to ensure the exclusion of absorbed moisture. Sixteen scans were signal-averaged at a resolution of 4 cm^{-1}.

2.5. NMR measurements

High-resolution solid-state ^{13}C NMR experiments were carried out on a Bruker DRX-400 MHz NMR spectrometer operating at resonance frequencies of 400 and 100 MHz for ^{1}H and ^{13}C, respectively. The high-resolution solid-state ^{13}C NMR spectra were obtained by using the cross polarization (CP)/magic angle spinning (MAS)/high-power dipolar decoupling (DD) technique. A 90° pulse width of 2.75 μs and a contact time of 3 ms were used in ^{13}C CP/MAS experiments. The MAS rate was 8 kHz for measurements of both ^{13}C spectra and relaxation time. The ^{13}C chemical shift of the methine carbon of solid adamantane (29.5 ppm relative to TMS) was used as an external reference standard.

2.6. XPS measurements

X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MkII spectrometer equipped with a Mg Kα X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Various samples were ground to fine powders and were then mounted on standard sample studs by means of a double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA, and a pass energy of 20 eV was used in the analyzer. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. All core-level spectra were referenced to the saturated hydrocarbon C1s peak at 285.0 eV.

3. Results and discussion

3.1. General characteristics of blends

Blends containing 70 and 90 mol% PVA were cloudy and the DSC curves showed that the blends were semicrystalline (Fig. 1). The two blends became clear when heated above the melting point of PVA. Blends of other composition were transparent. All the blends exhibited a single T_g, indicating miscibility. As shown in Fig. 2, the T_g–composition curve for PMTMA/PVA blends can be fitted by the Kwei equation [24,25]:

$$T_g(\text{blend}) = [(w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)] + qw_1w_2$$

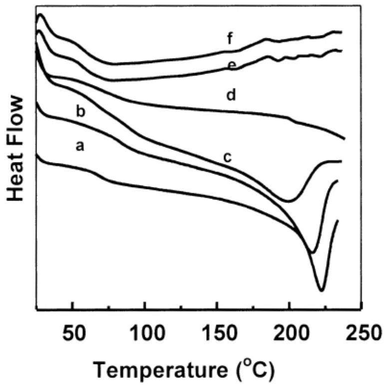


Fig. 1. DSC curves of PVA/PMTMA blends containing (a) 100, (b) 90, (c) 70, (d) 50, (e) 30, and (f) 0 mol% PVA.

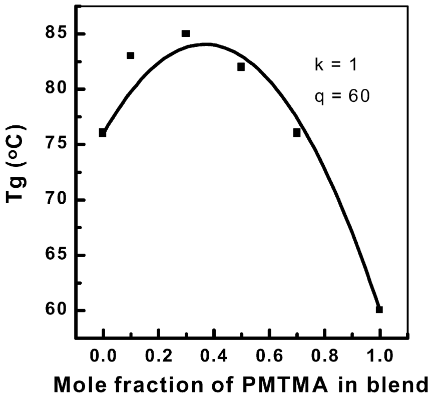


Fig. 2. T_g–composition curve of PMTMA/PVA blends.

where k and q are fitting constants. The curve in Fig. 2 was drawn using $k = 1$ and $q = 60$. The k and q values for PMTMA/PVPh blends are 1 and 86, respectively [13]. The q value is commonly taken as a measurement of number of specific interactions [25]. Therefore, the larger q value for the PMTMA/PVA blends appears to suggest the existence of a larger number of interactions in the PMTMA/PVPh blends than in the PMTMA/PVA blends. Table 1 lists the thermal characteristics of PMTMA/PVA blends. The degree of the crystallinity of PVA is calculated by the following equation:

$$\chi_c = \Delta H_f / (\Delta H_f^0 W)$$

where ΔH_f is the apparent enthalpy of the fusion of PVA in the blend, W, the weight fraction of PVA, and ΔH_f^0 is the enthalpy of fusion per gram of completely crystalline PVA (156 J/g for PVA [26]). For polymer blends containing a crystalline component, the variation in values of T_m and χ_c is usually attributed to interactions between the components [27–29]. The T_m and χ_c values decrease with increasing PMTMA content in the blend, indicating that the presence of interaction between PVA and PMTMA.

3.2. FTIR characterization

Fig. 3 shows the IR spectra in the 3000–3800 cm^{-1} region (O–H stretching) of PVA and various PMTMA/PVA blends. The hydroxyl band of pure PVA consists of a broad band centered at 3483 cm^{-1}, attributed to a wide distribution of hydrogen-bonded hydroxyl groups. The center of the broad hydroxyl band of the blend shifts to a lower frequency (3427 cm^{-1}), showing the existence of the intermolecular hydrogen-bonding interactions between PVA and PMTMA. The hydroxyl band of PVPh also shows a low-frequency shift upon blending with PMTMA [13]. Similar to the PMTMA/PVPh blends, there is no significant peak shift of the carbonyl band in the blend, indicating that the involvement of carbonyl groups in interaction with PVA is not significant (Fig. 4). In contrast, the amide carbonyl band of PVP progressively shifts towards a lower frequency upon blending with PVA, showing the existence of hydrogen-bonding interactions between carbonyl and hydroxyl groups [2].

Table 1
Thermal characteristics of PMTMA/PVA blends

	T_g (°C)	T_m (°C)	ΔH_f (J/g)	χ_c (%)
PVA	76	225	62.4	40
Blend 1	83	216	23.6	19
Blend 2	85	201	8.8	13
Blend 3	82	Nd	Nd	Nd
Blend 4	76	Nd	Nd	Nd
PMTMA	60			

Nd = not detected.

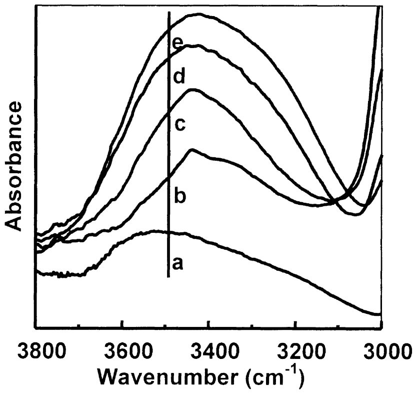


Fig. 3. FTIR spectra, recorded at 140 °C, of the hydroxyl stretching region of PMTMA/PVA blends containing (a) 100, (b) 90, (c) 70, (d) 50, and (e) 30 mol% PVA.

3.3. NMR characterization

Fig. 5 shows the ^{13}C CPMAS spectra of PVA, PMTMA and their blends, from which useful information can be drawn. First, the methine carbon resonance of PVA is split into three peaks in its ^{13}C CPMAS spectrum. The three peaks are designated as peak 1, peak 2 and peak 3 in order of decreasing frequency. The intensity of peak 2 is the strongest; hence the PVA used in this study is slightly

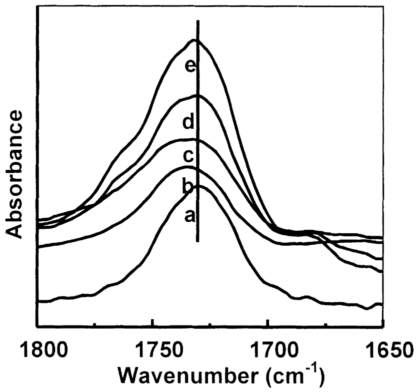


Fig. 4. FTIR spectra, recorded at 140 °C, of the carbonyl stretching region of PMTMA/PVA blends containing (a) 0, (b) 30, (c) 50, (d) 70, and (e) 90 mol% PVA.

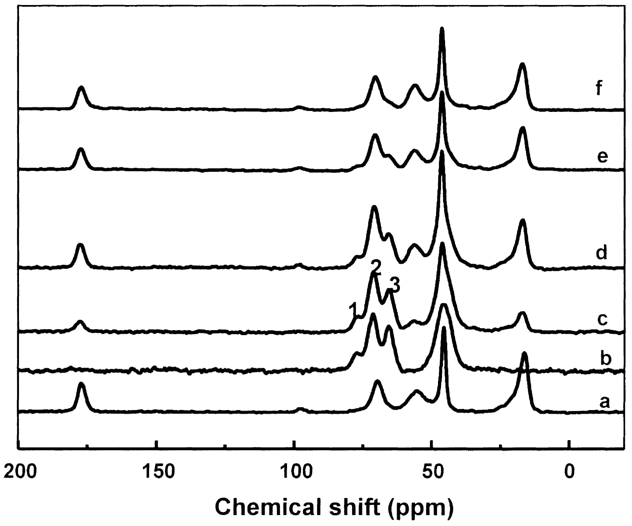


Fig. 5. ^{13}C CP/PAS spectra of PMTMA/PVA blends containing: (a) 0, (b) 100, (c) 90, (d) 70, (e) 50, and (f) 30 mol% PVA.

heterotactic [30]. According to Terao et al. [30] the splitting of the methine carbon resonance reflects the stereoregularity of PVA. They assigned peak 1 to *mm* triad with two intramolecular hydrogen bonds, peak 2 to *mm* and *mr* triads with one hydrogen bond, and peak 3 to *mm*, *mr*, and *rr* triads with no intramolecular hydrogen bond. As shown in Fig. 5, peak 3 of the methine carbon of PVA is markedly weakened with increasing PMTMA content. When the PMTMA content is more than 72%, the three peaks of methine carbon of PVA become very poorly resolved, almost merging into one broad peak. At the same time, the line widths of the three peaks are also reduced with increasing PMTMA content. Therefore, from the changes of the three peaks of methine carbon, it is concluded that the addition of PMTMA disrupts the self-association of PVA. The higher the PMTMA content, the more disruptions of the intramolecular and intermolecular hydrogen bonds of PVA are.

On the other hand, the carbonyl carbon resonance peak at 177.3 ppm shows little change in shape and position upon blending. Therefore, both ^{13}C and FTIR studies show that interactions involving the carbonyl groups of PMTMA, if any, are very weak and not significant. In contrast, the carbonyl resonance peak of PVP is shifted downfield by 2 ppm upon the addition of PVA [4]. It is difficult to see the change of the SCH$_2$-carbon resonance peak at 69 ppm due to its overlapping with the methine carbon resonance peak of PVA. The NMR results, therefore, are unable to show that the thioether sulfur atoms in PMTMA interact with the hydroxyl groups in PVA.

The scale of mixing in polymer blends can be determined through measurements of proton spin–lattice relaxation time in the rotating frame, $T_{1\rho}(H)$, and in the laboratory frame, $T_1(H)$. If the two polymer chains in a blend mixed intimately, spin-diffusion occurs quickly among the chemically different components, which equilibrates the magnetization, and so single $T_{1\rho}(H)$ and $T_1(H)$ values are obtained. If not, different $T_{1\rho}(H)$ and $T_1(H)$ values are obtained for the carbons corresponding to different polymers. A single $T_1(H)$ value indicates mixing to a scale of about 20–30 nm, whereas a single $T_{1\rho}(H)$ value indicates mixing on a scale of about 1–3 nm [4,5,10,16,17,23,31]. The $T_{1\rho}(H)$ values are determined through delayed-contact ^{13}C CP/MAS experiments, using Eq. (1):

$$\ln(M_\tau/M_0) = -\tau/T_{1\rho}(H) \qquad (1)$$

where τ is the spin-lock time used in the experiment, and M_0 and M_τ are the intensity of peak at zero time and at τ, respectively.

Fig. 6 shows the plots of $\ln(M_\tau/M_0)$ vs. τ, for the carbonyl carbon of PMTMA and PVA/PMTMA blends, and for the methylene carbon at 45 ppm for PVA. The experimental data are in good agreement with Eq. (1). From the slope of the fitted line, the $T_{1\rho}(H)$ value was determined (Table 2). The carbon resonance peaks of pure PMTMA show a single-exponential decay and have similar $T_{1\rho}(H)$ values around 16 ms. On the other hand, the carbon resonance peaks of PVA show a bi-exponential decay and two $T_{1\rho}(H)$ values exist. The slow decay component (11.2 ms) would be attributed to crystalline phase, and the fast decay component (4.5 ms) to an intermediate phase [10,30]. Two $T_{1\rho}(H)$ values for various PMTMA/PVA blends based on the carbon resonance peaks of PMTMA exist. One is around 16 ms, which is attributed to PMTMA-rich phase; the other is around 4 ms, which is attributed to miscible PMTMA/PVA interphase. Therefore, two $T_{1\rho}(H)$ values for each blend based on PMTMA carbon resonance peaks show that the two polymers do not mix intimately to a scale of 1–3 nm, where the spin-diffusion occurs within the $T_{1\rho}(H)$ time. In comparison, PMTMA and PVPh mix intimately on a scale of 1–3 nm [13]. The strong self-association tendency of PVA is likely the main reason that it does not mix with PMTMA as intimately as PVPh does.

To examine miscibility on a somewhat larger scale, the

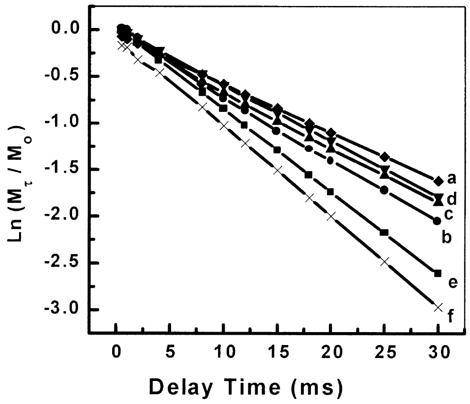


Fig. 6. Logarithmic plot of resonance of relative ^{13}C resonance intensity vs. delay time in PMTMA/PVA blends: (a) 0; (b) 90; (c) 70; (d) 50; (e) 30; (f) 100 mol% PVA.

Table 2
$T_{1\rho}(H)$ values of PMTMA, PVA and PMTMA/PVA blends

Resonance line (ppm)	$T_{1\rho}(H)$ (ms)					
	PMTMA	10/90[a]	30/70[a]	50/50[a]	70/30[a]	PVA
16.5	16.3	16.5 (74%) 4.9 (26%)	17.8 (80%) 4.8 (20%)	16.8 (95%) 4.0 (5%)	19.3 (97%) 2.2 (3%)	
45						4.5 (53%) 11.2 (47%)
177.3	16.1	16.2 (72%) 4.6 (28%)	17.6 (79%) 4.7 (21%)	16.6 (94%) 3.8 (5%)	19.0 (96%) 2.0 (4%)	
70						4.3 (54%) 11.0 (46%)

[a] Mole ratio of PMTMA to PVA in the blend.

$T_1(H)$ values of PVA/PMTMA blends were measured and the results are summarized in Table 3. Only one composition-dependent $T_1(H)$ value for each blend sample is obtained, the value of which is intermediate to those of PMTMA and PVA. Therefore, the PMTMA/PVA blends are homogeneous on a scale of 20–30 nm.

3.4. XPS characterization

The involvement of thioether sulfur atoms in specific interactions with PVA is confirmed by XPS. Fig. 7 shows the S2p spectra of PMTMA and the PMTMA/PVA blends. For PMTMA, the S2p spin–orbit split doublet is located at 163.48 and 164.68 eV, with an intensity ratio of 2 to 1, attributed to $S2p_{3/2}$ and $S2p_{1/2}$, respectively. The S2p peaks of the blends are broader, indicating a change in the environment of sulfur upon blending. Each peak can be curve-fitted by two doublets, with the original doublet located at 163.48 and 164.68 eV (full curves). The peak synthesis is based on the principle that the new doublet also maintains an intensity ratio of 2:1 for $S2p_{3/2}$ and $S2p_{1/2}$, and the difference in the binding energy values of $S2p_{3/2}$ and $S2p_{1/2}$ is also kept at 1.2 eV. In all the cases, the sum of the intensities of the two doublets agrees well with the experimental signals. The presence of a new high-BE S2p doublet at 164.14 and 165.34 eV (dashed curves) shows the interactions between the sulfur atoms in PMTMA and PVA. It is noted that the fractions of high-BE S2p peak of PMTMA/PVA blends are slightly smaller than those of the corresponding PMTMA/PVPh blends (Table 4). Therefore, both the XPS results and the q value of T_g–composition curve suggest a slightly larger number of interactions in the PMTMA/PVPh blends.

Table 3
$T_1(H)$ values of PMTMA, PVA and PMTMA/PVA blends

Resonance line (ppm)	$T_1(H)$ (s)					
	PMTMA	10/90[a]	30/70[a]	50/50[a]	70/30[a]	PVA
16.5	0.62	5.9	5.5	2.6	1.5	
45						7.5
177.3	0.63	5.8	5.7	2.8	1.4	
70						7.4

[a] Mole ratio of PMTMA to PVA in the blend.

4. Conclusions

PMTMA/PVA blends are miscible over the whole composition range based on the single-T_g criterion. Upon blending with PMTMA, the hydroxyl band of PVA shows a low-frequency shift, showing that the hydroxyl groups of PVA are interacting with PMTMA. However, the carbonyl band and the ^{13}C carbonyl resonance peak of PMTMA do not show significant changes upon blending with PVA, indicating that the involvement of carbonyl groups of PMTMA in interactions with PVA is not significant. XPS shows the development of a new high-BE S2p doublet in each blend. Therefore, the miscibility of the PMTMA/PVA blends arises mainly from interactions between the hydroxyl groups of PVA and thioether sulfur atoms of PMTMA. The $T_{1\rho}(H)$ and $T_1(H)$ results show that the blends are homogeneous on a scale of 20–30 nm but not of 1–3 nm.

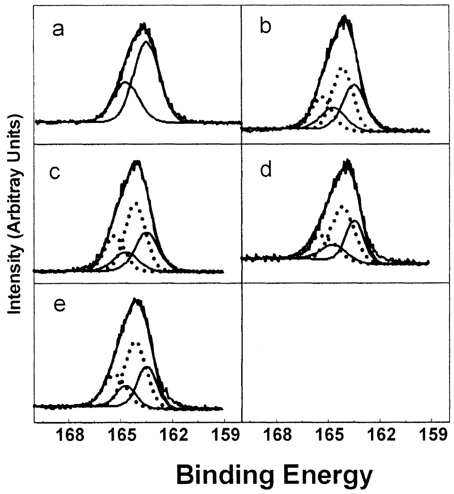


Fig. 7. XPS S2p core-level spectra of PMTMA (a), and PMTMA/PVA blends Containing (b) 30, (c) 50, (d) 70, and (e) 90 mol% PVA.

Table 4
XPS characteristics of PMTMA/PVA blends

Blend	1	2	3	4
Feed composition[a]	0.22	0.53	0.70	0.86
Feed composition[b]	0.10	0.30	0.50	0.70
S2p peak (eV)	163.48, 164.68 164.14, 165.34	163.48, 164.68 164.14, 165.34	163.48, 164.68 164.14, 165.34	163.48, 164.68 164.14, 165.34
Fraction of high-BE S2p peak	0.63 (Not available)[c]	0.61 (0.68)[c]	0.59 (0.63)[c]	0.54 (0.54)[c]

[a] Weight fraction of PMTMA.
[b] Mole fraction of PMTMA.
[c] Fraction of high-BE S2p peak in corresponding PMTMA/PVPh blends [13].

Acknowledgements

We thank Mr H.K. Wong for assistance in XPS measurements.

References

[1] Coleman MM, Painter PC. Prog Polym Sci 1995;20:1.
[2] Ping ZH, Nguyen QT, Neel J. Makromol Chem 1989;190:437.
[3] Ping ZH, Nguyen QT, Neel J. Makromol Chem 1990;191:185.
[4] Zhang X, Takegoshi K, Hikichi K. Polymer 1992;33:712.
[5] Feng H, Feng Z, Shen L. Polymer 1993;34:2516.
[6] Cassu SN, Felisberti MI. Polymer 1999;40:4845.
[7] Parada LG, Cesteros LC, Meaurio E, Katime I. Polymer 1998;39:1019.
[8] Aoi K, Takasu A, Okada M. Macromol Rapid Commun 1995;16:757.
[9] Parada LG, Cesteros LC, Meaurio E, Katime I. Macromol Chem Phys 1997;198:2505.
[10] Zhang X, Takegoshi K, Hikichi K. Polym J 1991;23:87.
[11] Danilinc L, de Kesel C, David C. Eur Polym J 1992;28:1365.
[12] Parada LG, Isasi JR, Katime I. J Polym Sci Part B: Polym Phys 1994;32:223.
[13] Yi JZ, Goh SH, Wee ATS. Macromolecules 2001;34:7411.
[14] Serman CJ, Painter PC, Coleman MM. Polymer 1991;32:1049.
[15] Hill DJT, Whittaker AK, Wong KW. Macromolecules 1999;32:5285.
[16] Zhang X, Takegoshi K, Hikichi K. Macromolecules 1991;24:5756.
[17] Zhang X, Takegoshi K, Hikichi K. Macromolecules 1992;25:4871.
[18] Coleman MM, Yang X, Zhang H, Painter PC, Scherer KV. J Polym Sci Part A: Polym Chem 1993;31:2039.
[19] Vivas de Meftahi M, Frechet JMJ. Polymer 1988;29:477.
[20] Dai J, Goh SH, Lee SY, Siow KS. Polym J 1994;26:905.
[21] Zhou X, Goh SH, Lee SY, Tan KL. Appl Surf Sci 1997;119:60.
[22] Wang LF, Pearce EM, Kwei TK. J Polym Sci Part B: Polym Phys 1991;29:619.
[23] Wang J, Cheung MK, Mi Y. Polymer 2001;42:2077.
[24] Kwei TK. J Polym Sci Polym Lett Ed 1984;22:307.
[25] Pennachia JR, Pearce EM, Kwei TK, Bulkin BJ, Chen JP. Macromolecules 1986;19:1973.
[26] Tubbs RK. J Polym Sci A 1965;3:4181.
[27] Koyama N, Doi Y. Polymer 1997;38:1598.
[28] Zhang L, Goh SH, Lee SY. Polymer 1998;39:4841.
[29] Yoshie N, Azuma Y, Sakurai M, Inoue Y. J Appl Polym Sci 1995;56:17.
[30] Terao T, Maeda S, Saika A. Macromolecules 1983;16:1535.
[31] Wang J, Cheung MK, Mi Y. Polymer 2001;42:3087.