

# Interpolymer Interactions and Miscibility in Poly(*n*-butyl methacrylate-*co*-methacrylic acid)/Poly(styrene-*co*-*N,N*-dimethyl acrylamide) Blends

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**ABSTRACT:** The miscibility of poly(*n*-butyl methacrylate-*co*-methacrylic acid) containing 18 mol % methacrylic acid (BMAM-18) and poly(styrene-*co*-*N,N*-dimethyl acrylamide) containing 17 mol % *N,N*-dimethyl acrylamide (SAD-17) was investigated with viscometry, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy. The DSC analysis showed a single glass-transition temperature for all the blends, indicating that these copolymers were miscible over the entire composition range. The glass-transition temperatures of these blends were higher than those calculated with the additivity rule. This was characteristic of the presence of specific interactions. The interactions between BMAM-18 and the tertiary amide of SAD-17 were studied with FTIR spectroscopy, which revealed that hydrogen-bonding interactions occurred between the hydroxyl

groups of BMAM-18 and the carbonyl amide of SAD-17. A new band characterizing these interactions appeared around 1613 cm<sup>-1</sup>. The quantitative results showed that the fraction of the associated amide increased with an increase in the amount of the acidic BMAM-18 copolymer. Although BMAM-18 and SAD-17 led to homogeneous solutions in butan-2-one, as the concentration of *N,N*-dimethyl acrylamide increased to 32 mol % [as within the poly(styrene-*co*-*N,N*-dimethyl acrylamide) containing 32 mol % *N,N*-dimethyl acrylamide], complexation occurred when this latter compound was mixed with BMAM-18 in butan-2-one. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2717–2724, 2006

**Key words:** blends; differential scanning calorimetry (DSC); FT-IR; gels; miscibility

## INTRODUCTION

Miscible polymer blends are one of the most convenient approaches for elaborating materials with properties different from and in some cases superior to those of the constituents of the blends. The formation of a binary, miscible polymer blend requires, however, the presence of sufficient amounts of interacting species within two constituents of different natures. Many miscible blends have been reported in the literature.<sup>1–6</sup> Inoue et al.<sup>7</sup> published very recently a review of hydrogen-bonded polymer blends over the last 2 decades.

Techniques such as Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), solid-state NMR spectroscopy, and X-ray photoelectron spectroscopy are among those intensively used to analyze the specific interactions in miscible blends.<sup>8–16</sup> Poly(*N,N*-dimethyl acrylamide) (PDMA) is capable of interacting through specific interactions of a hydrogen-bonding type with proton-donating polymers at the two interacting sites, namely, the carbonyl amide group and the nitrogen atom.<sup>17</sup>

Several binary, miscible blends containing PDMA and poly(vinyl acetate-*co*-vinyl alcohol), poly(vinyl alcohol),<sup>18</sup> poly(vinyl phenol),<sup>19</sup> poly(2-hydroxypropyl methacrylate),<sup>20</sup> or poly(monoalkyl itaconate)<sup>21</sup> have been reported in the literature. Goh et al.<sup>20</sup> also studied the complexation behavior between PDMA and poly(2-hydroxypropyl methacrylate). These authors<sup>20</sup> showed that interpolymer complexes were obtained over the entire feed composition in butan-2-one and tetrahydrofuran (THF) but not in *N,N*-dimethylformamide. Katime et al.<sup>22</sup> studied the solvent role in complexation between PDMA and poly(*n*-alkyl itaconate)s.

As an extension of our previous studies on miscibility enhancement by the introduction of small amounts of interacting species within polymer chains<sup>23–26</sup> or complexation as the densities of interacting species increase via hydrogen bonding,<sup>27</sup> poly(styrene-*co*-*N,N*-dimethyl acrylamide) containing 17 mol % *N,N*-dimethyl acrylamide (SAD-17), poly(styrene-*co*-*N,N*-dimethyl acrylamide) containing 32 mol % *N,N*-dimethyl acrylamide (SAD-32), and poly(*n*-butyl methacrylate-*co*-methacrylic acid) containing 18 mol % methacrylic acid (BMAM-18) were prepared by free-radical polymerization. Mixtures of these copolymers of different ratios were prepared. In this contribution,

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the specific interactions in pure BMAM-18 and its miscible blends or interpolymer complexes with the SAD copolymers were analyzed by viscometry, DSC, and FTIR spectroscopy qualitatively and quantitatively.

## EXPERIMENTAL

### Polymer synthesis and characterization

SAD-17, SAD-32, and BMAM-18 were prepared by bulk free-radical polymerization with azobisisobutyronitrile as the initiator at 60°C and with dioxane as the solvent. The copolymers were purified by several reprecipitations from dilute dioxane solutions into an excess of methanol and were dried *in vacuo* for several days at 60°C. The degree of conversion was held below 15 wt %. The acid content within the poly(*n*-butyl methacrylate-*co*-methacrylic acid) copolymer was determined by standard titration in a mixture of benzene and methanol (80/20). The styrene content in the SAD copolymers was determined by UV spectroscopy and elemental analysis.

The average molecular weights and molecular weight distributions of the SAD copolymers, determined by gel permeation chromatography with a Waters high-performance liquid chromatograph (range of detection 500–2000000 Daltons), are listed in Table I.

### Viscometry measurements

The intrinsic viscosity of pure BMAM-18 (listed in Table I) was determined in THF at 25°C in the usual way with an Ubbelohde viscometer.

The reduced viscosities of homogeneous polymer solutions of different ratios were measured in butan-2-one with the Ubbelohde viscometer at 25°C with the total concentration of the two constituents of the blends kept at 0.1 g/dL, which was below the critical concentration, whereas the apparent interpolymer complex viscosities were measured after the filtration of the precipitates or gels.

### DSC measurements

Blends of different ratios of BMAM-18 and SAD-17 were prepared by the codissolution of the copolymers

in a common solvent (butan-2-one). Films were generated from polymeric solutions with the evaporation of the solvent with pure polymers or blends. In the case of BMAM-18/SAD-32 mixtures in butan-2-one, which led to interpolymer complexes, the precipitates were isolated, and all the samples were dried in a vacuum oven for several days at 60°C. The glass-transition temperatures ( $T_g$ 's) of the pure components and their mixtures of different ratios were determined with a PerkinElmer DSC-7 differential scanning calorimeter (Norwalk, CT) at a heating rate of 20 K/min.  $T_g$  was taken as the average value of the midpoint of the heat capacity change of several scans.

### FTIR measurements

Thin films of the copolymers or BMAM-18/SAD-17 blends for FTIR measurements were prepared via casting from a 2–3% (w/v) solution in butan-2-one onto KBr disks. The solvent was first evaporated at room temperature. The disks were then dried in a vacuum oven at 60°C for several days. IR spectra were recorded at room temperature on a Nicolet 550 FTIR spectrometer (Madison, WI) with a spectral resolution of 2 cm<sup>-1</sup>. Sixty scans were signal-averaged.

## RESULTS AND DISCUSSION

### Complexation behavior

Before the DSC, viscometry, or FTIR analysis, BMAM-18/SAD-17 and BMAM-18/SAD-32 mixtures of different ratios in THF or butan-2-one were prepared. Homogeneous solutions were obtained with BMAM-18 and SAD-17 when both solvents were used. BMAM-18 formed, however, homogeneous solutions in THF and interpolymer complexes with SAD-32 or PDMA over the entire feed composition in butan-2-one. The interpolymer complexes, which were gel-like or precipitates, were isolated and then dried in a vacuum oven at 60°C for several days to a constant weight. The composition of the SAD-32 copolymer in these complexes dissolved in THF was obtained by UV spectroscopy in the 240–320-nm range with the calibration curve of SAD-32 and corresponding UV spectra of these complexes. BMAM-18 was transparent in this region. Table II displays the yields and compositions of the complexes, which varied from 23.5 to 78.8 mol % BMAM-18, with the feed composition ranging from 18.2 to 78.7 mol %. The yields of these complexes depended on the feed compositions of the constituents. As can be seen in Figure 1, the complex formation yield first increased, went through a maximum at a BMAM-18 weight feed composition between 50 and 60, and then decreased as the content of BMAM-18 in the feed composition increased.

TABLE I  
Characteristics of the Copolymers

Sample	$[\eta]$	$M_n$ $\times 10^{-4}$	$M_w$ $\times 10^{-5}$	$I$	$T_g$ (°C)
SAD-17	—	6.08	1.27	2.09	108
SAD-32	—	6.04	1.28	2.12	102
BMAM-18	1.38 (THF)	—	—	—	78

$[\eta]$  = intrinsic viscosity;  $M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight;  $I$  = molecular weight distribution.

TABLE II  
Characteristics of the BMAM-18/SAD-32 Complexes

Complex number	0	1	2	3	4	5	6	7	0
Feed composition <sup>a</sup>	0	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1
Feed composition <sup>b</sup>	0	0.182	0.276	0.372	0.472	0.572	0.675	0.787	1
Bulk composition <sup>b</sup>	0	0.159	0.303	0.470	0.534	0.560	0.626	0.819	1
Yield of the complex (wt %)	0	29	46.7	54.5	78.8	77.4	38.9	23.5	0
$T_g$ (°C)	102	98.3	98.6	—	95.3	—	85.5	82.9	78

<sup>a</sup> BMAM-18 (wt %).

<sup>b</sup> BMAM-18 (mol %).

### Viscometry study

The slightly negative deviation from a linear variation of the reduced viscosities as a function of the weight fraction of the BMAM-18 copolymer, observed with BMAM-18/SAD-17 solutions prepared in butan-2-one, is considered evidence of the miscibility of these blends due to the presence of specific interactions of a hydrogen-bonding type, as shown in Figure 2(a). It has been reported in the literature<sup>28</sup> that, according to the type of interaction, complexation between two polymer chains occurs when the reduced viscosity of a blend solution deviates either positively or negatively from the weight-average viscosity of the two constituents of the blend. Indeed, the negative deviation of the apparent viscosities from the linear average viscosity of the respective components observed with BMAM-18/SAD-32 binary systems in the same solvent [Fig. 2(b)] is characteristic of their complexation due to the presence of a higher number of specific intermolecular interactions, which led to the contraction of the polymeric chains. Because a considerable amount of the polymers precipitated, as expected, a viscosity decrease for the solution was observed. As the content of the amide groups increased with PDMA, complexation of the latter occurred over the entire composition range with BMAM-18 and led to a more pronounced negative deviation of the apparent viscosities. As can be seen in Figure 2(c), that shows the difference ( $\Delta\eta$ ) between the measured viscosities and those calculated from the arithmetic average versus the molar fraction of the BMAM-18 copolymer in butan-2-one; the minimum corresponding to the most stable composition of the complex was observed around a 1:1 ratio. This result was in a good agreement with the complexation behavior of this system.

### Thermal analysis

The single  $T_g$ , sometimes higher than those of the pure components, observed for all the blended BMAM-18/SAD-17 and BMAM-18/SAD-32 binary systems is considered evidence of their miscibility or complexation.

Figure 3 displays the variation of  $T_g$  with the BMAM-18 feed composition for BMAM-18/SAD-17. Positive deviations from the linear average line, observed par-

ticularly in the region rich in the basic constituent, are characteristic of the presence of stronger specific interactions of a hydrogen-bonding type that occurred between the carboxylic acid groups of BMAM-18 and the carbonyl amide groups of SAD.

The strength of these interactions for the BMAM-18/SAD-17 system was estimated with a Kwei fitting constant ( $q$ ) as follows:

$$T_g = \frac{W_1 T_{g1} + K W_2 T_{g2}}{W_1 + K W_2} + q W_1 W_2$$

where  $T_{g1}$ ,  $T_{g2}$ ,  $w_1$ , and  $w_2$  are the glass-transition temperatures and weight fractions of components 1 and 2, respectively, and  $K$  is a fitting constant.

The obtained  $q$  value for the BMAM-18/SAD-17 system was 19.

Higher level of interactions were expected as the content of the amide groups was increased, as with SAD-32 (Table I).

As also reported by several authors, the high  $T_g$  values observed with the blends containing an excess of the SAD copolymer enhanced the rigidity of the blends, whereas random mixing was assumed for a blend containing an excess of BMAM-18.

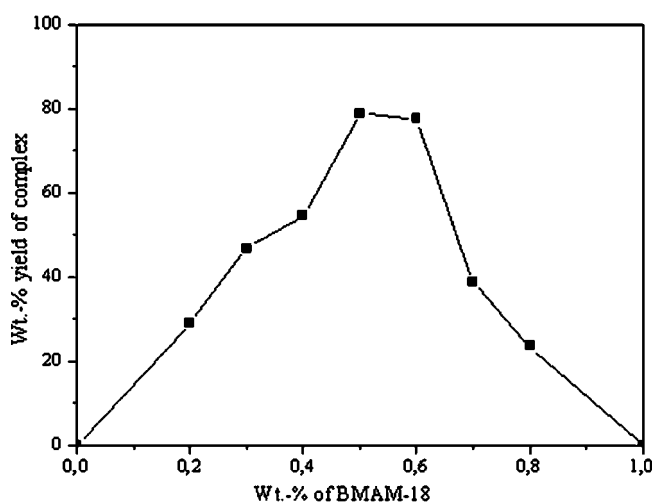
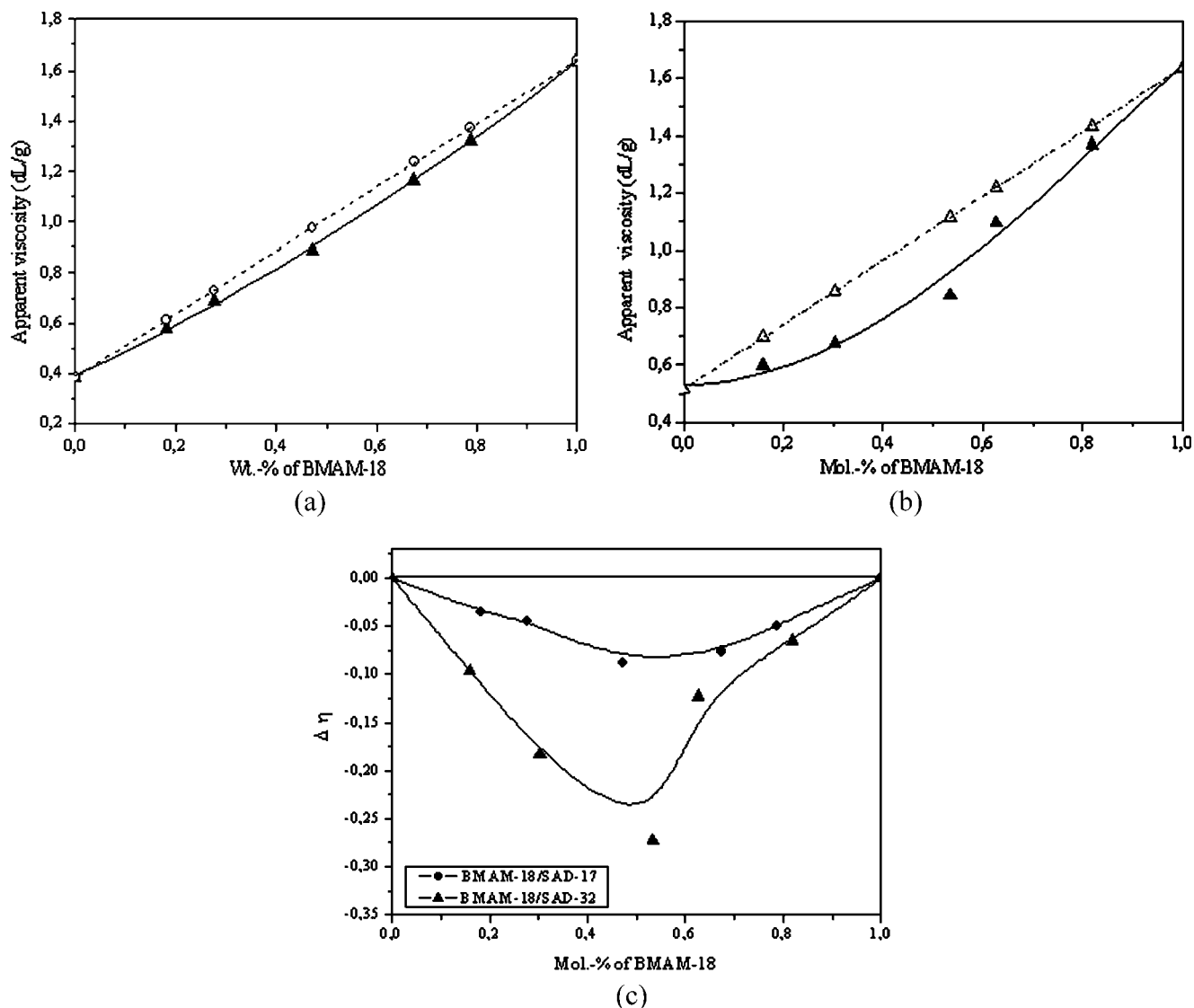


Figure 1 Illustration of the yield versus the feed composition for BMAM-18/SAD-32 complexes.



**Figure 2** (a) Apparent viscosity versus the molar fraction of BMAM-18 of BMAM-18/SAD-17 systems in butan-2-one at 25°C, (b) apparent viscosity versus the molar fraction of BMAM-18 of BMAM-18/SAD-32 systems in butan-2-one at 25°C, and (c)  $\Delta\eta$  versus the molar fraction of BMAM-18 of BMAM-18/SAD-17 and BMAM-18/SAD-32 systems in butan-2-one at 25°C.

### FTIR analysis

FTIR spectroscopy was used to detect the specific interactions that occurred between the constituents of the blends in the three main regions.

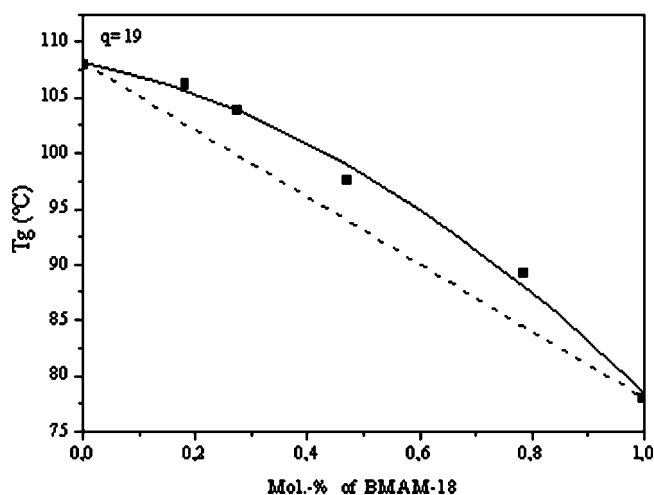
#### Hydroxyl stretching in the 3600–2400-cm<sup>-1</sup> region

Carboxylic acid dimer absorption occurs around 3100 cm<sup>-1</sup> in the hydroxyl region. Figure 4 shows the scale-expanded FTIR spectra of BMAM-18 and BMAM-18/SAD-17 blends recorded at room temperature in the hydroxyl stretching range of 3600–2400 cm<sup>-1</sup>. In addition to the band observed at 3430 cm<sup>-1</sup>, which is characteristic of the overtone of the 1729-cm<sup>-1</sup> band, BMAM-18 exhibits two main bands in this region: a broad band centered around 3265 cm<sup>-1</sup> and attributed

to its eventual hydroxyl-ester interactions and carboxyl dimers and another one around 2620 cm<sup>-1</sup> assigned to carboxylic dimers. Similar bands have been observed for copolymers of methyl methacrylate and methacrylic acid.<sup>29</sup>

When SAD-17 is added to BMAM-18, important perturbations can be observed, depending on the blend ratio, for both bands. The intensities of these two bands appear to decrease, indicating a progressive dissociation of the carboxylic acid and hydroxyl-ester interactions in favor of interpolymer carboxylic acid/amide interactions.

This generates free (no hydrogen bonding) carbonyl groups, whereas a slight increase in the intensity of a band around 3200 cm<sup>-1</sup> can be observed, particularly with a 1 : 1 blend. As a result, a hydrogen bond is also formed between the hydroxyl of the carboxylic acid

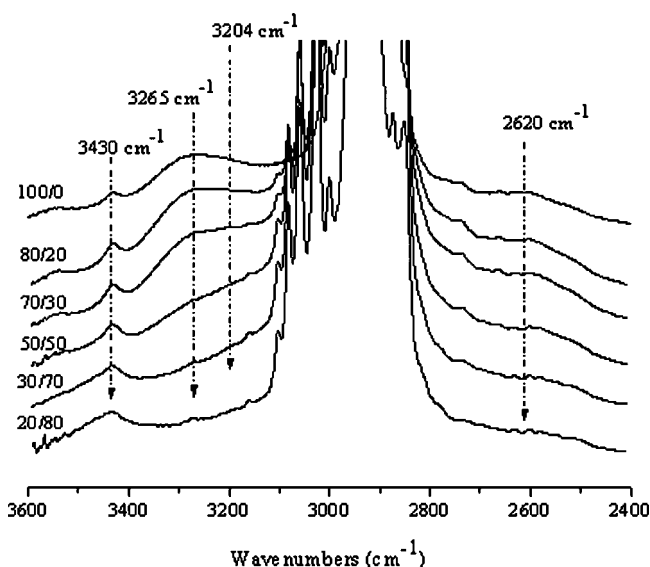


**Figure 3**  $T_g$  versus the molar fraction of BMAM-18 of BMAM-18/SAD-17 mixtures.

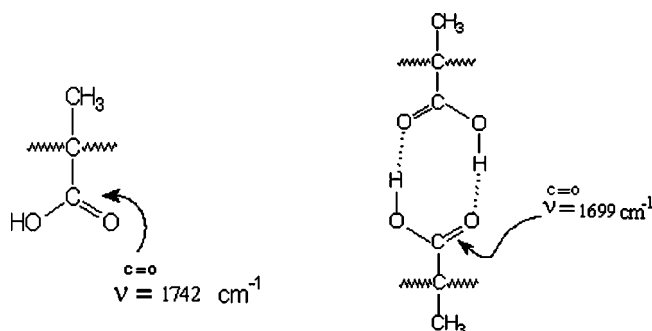
and the amide group. These interactions, evidenced in other regions, are also expected to appear in this region. Indeed, a broader redistribution of these interactions toward lower wave numbers can be observed. In their studies of miscibility behavior and hydrogen bonding in blends of poly(vinyl phenol) and poly(vinylpyrrolidone), Kuo and Chang<sup>30</sup> showed that hydroxyl-carbonyl interactions occur at  $3250\text{ cm}^{-1}$  and that these intermolecular interactions are stronger than the hydroxyl-hydroxyl self-associations interactions.

#### Carbonyl stretching in the $1780\text{--}1650\text{-cm}^{-1}$ region

The scale-expanded FTIR spectrum of BMAM-18 shows in the carbonyl region of  $1780\text{--}1650\text{-cm}^{-1}$  two bands at



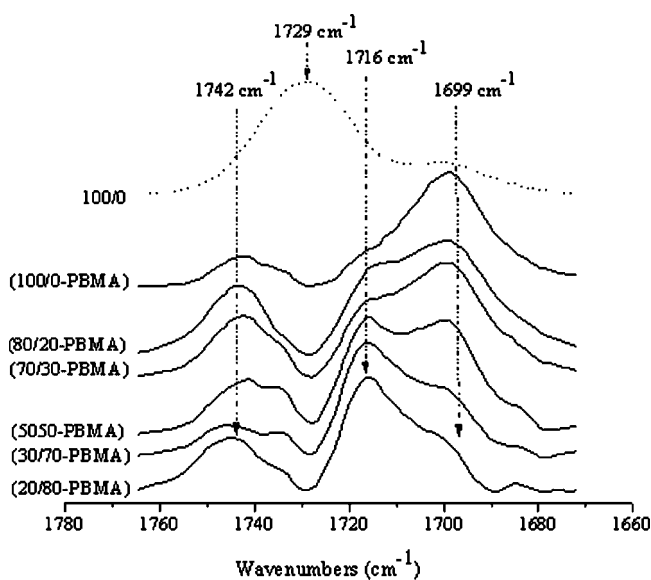
**Figure 4** Scale-expanded FTIR spectra of BMAM-18/SAD-17 blends in the  $3600\text{--}2400\text{-cm}^{-1}$  region recorded at room temperature.



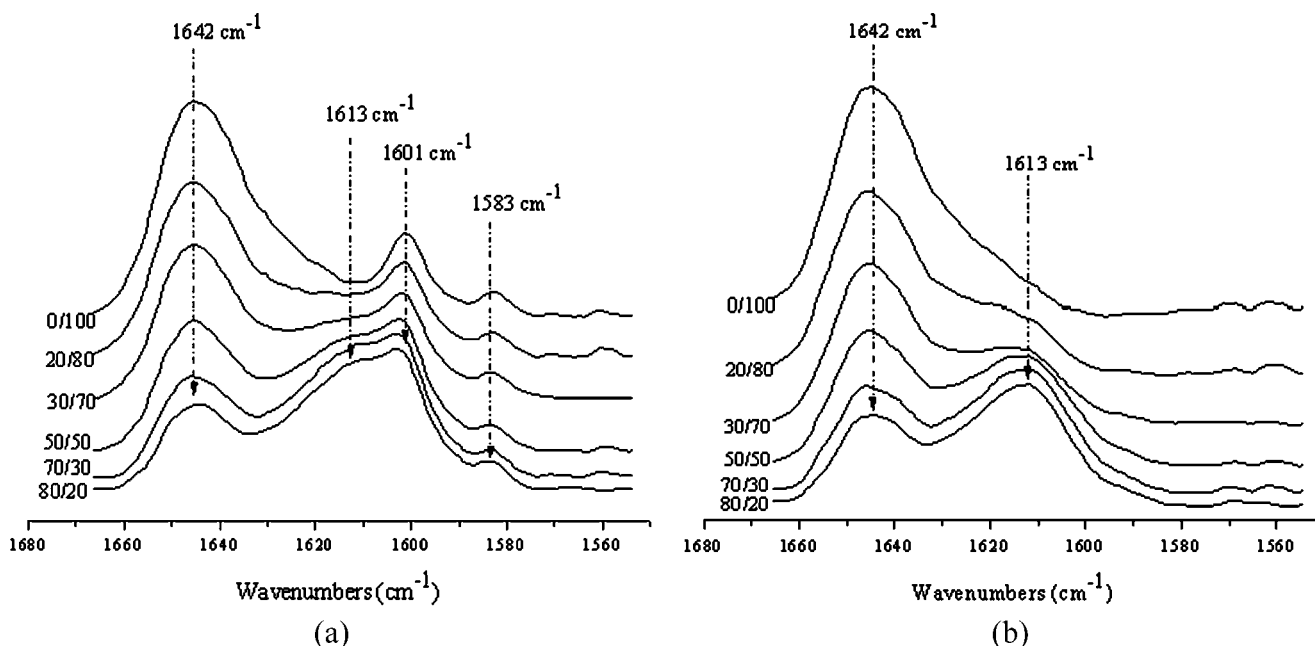
**Scheme 1** Free methacrylic acid and dimer self-association.

$1729$  and  $1699\text{ cm}^{-1}$  that are characteristic of the free carbonyl and carboxyl-ester and carboxyl dimers, respectively. As the basic SAD-17 copolymer, transparent in this region, is added to BMAM-18, a decrease in the band at  $1699\text{ cm}^{-1}$  can be observed that is characteristic of dimers and carboxyl-ester dissociation (Scheme 1).

The subtraction spectrum of PBMA from BMAM-18 shows, in addition to the  $1699\text{-cm}^{-1}$  band (Fig. 5), a weak band at  $1742\text{ cm}^{-1}$  attributed to free carboxylic groups and a small shoulder at  $1716\text{ cm}^{-1}$  attributed to liberated carbonyl groups. Blending the SAD-17 copolymer with BMAM-18 produces a new band of increasing intensity, which is characteristic of carbonyl groups that are liberated as a result of the carboxyl/carbonyl amide group interactions that appear at  $1716\text{ cm}^{-1}$ . A decrease in the intensity of the band at  $1699\text{ cm}^{-1}$  can also be observed. The presence of such interactions confirms the miscibility of these blends, which has already been evidenced by DSC.



**Figure 5** Scale-expanded FTIR spectrum of BMAM-18 and scale-expanded FTIR difference spectra (subtraction of PBMA) of BMAM-18/SAD-17 blends in the  $1780\text{--}1660\text{-cm}^{-1}$  region recorded at room temperature.



**Figure 6** (a) Scale-expanded FTIR spectra of BMAM-18/SAD-17 blends in the 1670–1550- $\text{cm}^{-1}$  region recorded at room temperature and (b) scale-expanded FTIR difference spectra (subtraction of polystyrene) of BMAM-18/SAD-17 blends in the 1670–1550- $\text{cm}^{-1}$  region recorded at room temperature.

#### Amide stretching in the 1670–1550- $\text{cm}^{-1}$ region

Figure 6 displays the FTIR spectra of the SAD-17 copolymer and its blends of different compositions with BMAM-18 in the 1670–1550- $\text{cm}^{-1}$  region, in which BMAM-18 is transparent. The SAD-17 copolymer shows a strong absorption at about 1642  $\text{cm}^{-1}$  attributed to the free amide carbonyl groups and styrene ring stretching bands at 1601 and 1583  $\text{cm}^{-1}$ .

The analysis of the FTIR spectra of these blends confirms qualitatively the presence of the interactions between the carboxylic groups and the carbonyl amide groups by the appearance of a new band around 1613  $\text{cm}^{-1}$ , which is characteristic of the associated amide. Figure 6 shows that the intensity of the associated amide band with respect to the free one increases with an increase in the BMAM-18 content in the blend.

Similar behavior was observed by Katime et al.<sup>17</sup> for blends of poly(mono-*n*-alkyl itaconate)s with PDMA or poly(ethyl oxazoline) (Scheme 2).

#### Quantitative study

A quantitative analysis of these interactions was carried out in this region to determine the fraction of the associated amide.

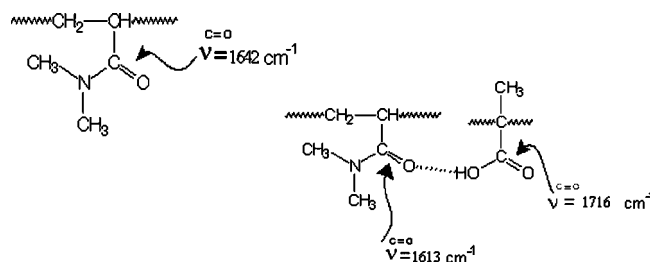
The fractions of the relative areas of the two bands (free and associated amide) were determined in the presence of styrene and after the subtraction of the latter from the spectra of the blends with Gaussian and Lorentzian spectral curve-fitting procedures, respectively, for amide and styrene bands with the following relation:

$$F_{\text{ASS}}^{\text{C=O}} = 1 - \frac{A_{1645}}{A_{1645} + \frac{a_{1645}}{a_{1613}} A_{1613}}$$

where  $F_{\text{ASS}}^{\text{C=O}}$  is the fraction of the associated carbonyl amide groups;  $A_{1645}$  and  $A_{1613}$  are the areas of the bands at 1645 and 1613  $\text{cm}^{-1}$ , respectively; and  $a_{1645}$  and  $a_{1613}$  are the absorptivities of the two bands, assuming an absorptivity ratio of 1.<sup>21</sup>

The curve-fitting data from the IR spectra of BMAM-18/SAD-17 blends in this region at room temperature with Grams 386 are shown in Table III.

As shown in Figure 7, the fraction of the associated amide increases with an increase in the amount of the acidic BMAM-18 copolymer. This maximum inter-association is, however, much lower than 100%, as also reported in the literature, because of several effects, such as functional group accessibility and chain rigidity.



**Scheme 2** Free amide carbonyl and carboxylic acid/amide interassociation.

TABLE III  
Curve-Fitting Data from IR Spectra of BMAM-18/SAD-17 Blends in the Amide Region of 1670–1550 cm<sup>-1</sup> at Room Temperature

	Styrene				Free amide				Associated amide			
	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	Fraction	$W_{1/2}$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	Fraction	
BMAM-18/SAD-17 (w/w)	1582.6	6.00	1601.0	10.00	1645.3	16.45	0.270	1613.2	31.00	0.730		
	1582.4	6.00	1601.1	10.00	1645.5	16.39	0.300	1613.5	32.00	0.700		
	1582.6	6.00	1601.7	10.00	1645.4	17.80	0.399	1614.8	32.00	0.601		
	1582.5	6.00	1601.5	10.00	1645.6	17.68	0.488	1617.8	36.00	0.512		
	1582.7	6.00	1601.2	10.00	1645.7	18.25	0.547	1623.7	36.00	0.453		
	1583.0	6.00	1601.5	10.00	1642.6	25.00	1	—	—	—		
BMAM-18/SAD-17 – polystyrene (w/w)	—	—	—	—	1644.3	18.57	0.350	1614.6	25.47	0.650		
	—	—	—	—	1644.7	18.93	0.392	1614.4	26.05	0.608		
	—	—	—	—	1644.9	19.03	0.449	1615.3	27.75	0.551		
	—	—	—	—	1645.1	18.68	0.559	1618.0	28.64	0.441		
	—	—	—	—	1645.2	19.89	0.653	1620.7	26.44	0.347		
0/100	—	—	—	1642.3	25.00	1	—	—	—			

$\nu$  = wavenumber;  $W_{1/2}$  = width at 1/2 height.

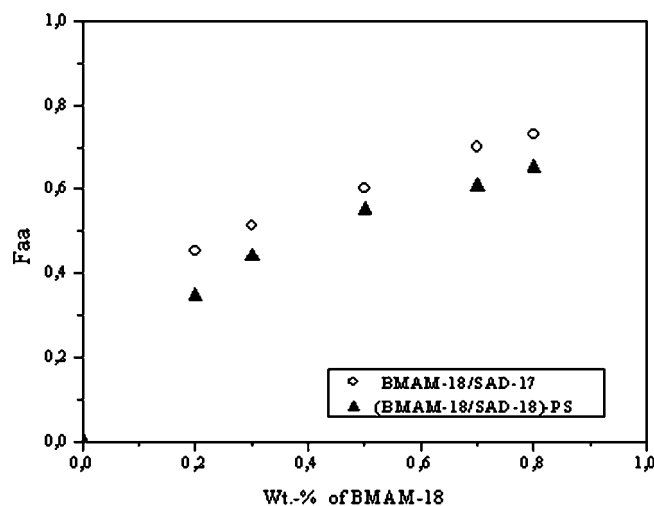


Figure 7 Fraction of associated amide groups ( $F_{aa}$ ) versus the weight fraction of BMAM-18 of BMAM-18/SAD-17 blends.

## CONCLUSIONS

This study shows that BMAM-18 forms miscible blends with SAD-17 in both THF and butan-2-one solutions and interpolymer complexes with SAD-32 in butan-2-one as a result of interpolymer hydrogen bonding occurring between the acid groups of BMAM-18 and the amide carbonyl of the SAD copolymers. This has been evidenced via DSC by the appearance of a single  $T_g$  for each of the blends and complexes higher than those calculated from the weight averages of the pure constituents. FTIR results have confirmed the presence of these hydrogen-bonding interactions qualitatively by the appearance of a new band at 1613 cm<sup>-1</sup> that is characteristic of associated amide carbonyl groups and quantitatively from an evaluation of the fraction of the associated amide carbonyl with the content of BMAM-18. The BMAM-18/SAD-32 complexes have been characterized with UV spectroscopy and by the negative deviation of their apparent viscosities as a function of the fraction of BMAM-18.

## References

- Kuo, S. W.; Chang, S. C.; Chang, F. C. *Macromolecules* 2003, 36, 6653.
- Kuo, S. W.; Huang, C. F.; Chang, F. C. *J Polym Sci Part B: Polym Phys* 2001, 39, 1348.
- Luo, X. F.; Hu, X.; Zhao, X. Y.; Goh, S. H.; Li, X. D. *Polymer* 2003, 44, 6285.
- Zheng, S. X.; Mi, Y. L. *Polymer* 2003, 44, 1067.
- Lau, C.; Mi, Y. L. *Polymer* 2002, 43, 823.
- Li, X. D.; Goh, S. H. *Polymer* 2002, 43, 6853.
- He, Y.; Zhu, B.; Inoue, Y. *Prog Polym Sci* 2004, 29, 1021.
- Zheng, S. X.; Guo, Q. P.; Mi, Y. L. *J Polym Sci Part B: Polym Phys* 1998, 36, 2291.
- Yi, J. Z.; Goh, S. H. *Polymer* 2001, 42, 9313.
- Crispim, E. G.; Schuquel, I. T. A.; Rubira, A. F.; Muniz, E. C. *Polymer* 2000, 41, 933.

11. Iriondo, P.; Iruin, J. J.; Fernandez-Berridi, M. J. *Macromolecules* 1996, 29, 5605.
12. Jong, L.; Pearce, E. M.; Kwei, T. K. *Polymer* 1993, 34, 48.
13. Mugica, A.; Callahorra, M. E.; Cortazar, M. *Macromol Chem Phys* 2002, 203, 1088.
14. Kuo, S. W.; Chan, S. C.; Chang, F. C. *Polymer* 2002, 43, 3653.
15. Goh, S. H.; Liu, Y.; Lee, S. Y.; Huan, C. H. A. *Macromolecules* 1999, 32, 8595.
16. Yi, J. Z.; Goh, S. H. *Polymer* 2002, 43, 4515.
17. Meaurio, E.; Cesteros, L. C.; Katime, I. *Macromolecules* 1997, 30, 4567.
18. Parada, L. G.; Cesteros, L. C.; Meaurio, E.; Katime, I. *Polymer* 1998, 39, 1019.
19. Wang, L. F.; Pearce, E. M.; Kwei, T. K. *J Polym Sci Part B: Polym Phys* 1991, 29, 619.
20. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *J Appl Polym Sci* 1994, 53, 837.
21. Meaurio, E.; Velada, J. L.; Cesteros, L. C.; Katime, I. *Macromolecules* 1996, 29, 4598.
22. Meaurio, E.; Cesteros, L. C.; Katime, I. *Polymer* 1998, 39, 379.
23. Djadoun, S.; Karasz, F. E.; Metref, F. *Makromol Chem Macromol Symp* 1994, 78, 155.
24. Djadoun, S.; Karasz, F. E.; Hadj Hamou, A. S. *Thermochim Acta* 1996, 282, 399.
25. Hadj Hamou, A. S.; Habi, A.; Djadoun, S. *Eur Polym J* 1997, 33, 1105.
26. Bennour, S.; Metref, F.; Djadoun, S. *J Appl Polym Sci* 2005, 98, 806.
27. Abdellaoui, N.; Djadoun, S. *J Appl Polym Sci* 2005, 98, 658.
28. Zhang, G.; Jiang, M.; Zhu, L.; Wu, C. *Polymer* 2001, 42, 151.
29. Kochneva, I. S.; Roshupkin, V. P. *Polym Sci* 1991, 33, 2104.
30. Kuo, S. W.; Chang, F. C. *Macromolecules* 2001, 34, 5224.