

# Interpolymer-Specific Interactions and Miscibility in Poly(styrene-*co*-acrylic acid)/Poly(styrene-*co*-*N,N*-dimethylacrylamide) Blends

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**ABSTRACT:** The miscibility or complexation of poly(styrene-*co*-acrylic acid) containing 27 mol % of acrylic acid (SAA-27) and poly(styrene-*co*-*N,N*-dimethylacrylamide) containing 17 or 32 mol % of *N,N*-dimethylacrylamide (SAD-17, SAD-32) or poly(*N,N*-dimethylacrylamide) (PDMA) were investigated by different techniques. The differential scanning calorimetry (DSC) analysis showed that a single glass-transition temperature was observed for all the mixtures prepared from tetrahydrofuran (THF) or butan-2-one. This is an evidence of their miscibility or complexation over the entire composition range. As the content of the basic constituent increases as within SAA-27/SAD-32 and SAA-27/PDMA, higher number of specific interpolymer interactins occurred and led to the formation of interpolymer complexes in butan-2-one. The qualitative Fourier transform infrared (FTIR) spectroscopy study carried out for SAA-27/SAD-17 blends re-

vealed that hydrogen bonding occurred between the hydroxyl groups of SAA-27 and the carbonyl amide of SAD-17. Quantitative analysis carried out in the 160–210°C temperature range for the SAA-27 copolymer and its blends of different ratios using the Painter–Coleman association model led to the estimation of the equilibrium constants  $K_2$ ,  $K_A$  and the enthalpies of hydrogen bond formation. These blends are miscible even at 180°C as confirmed from the negative values of the total free energy of mixing  $\Delta G_M$  over the entire blend composition. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1011–1024, 2007

**Key words:** miscibility; interpolymer complexes; poly(styrene-*co*-acrylic acid); poly(styrene-*co*-*N,N*-dimethylacrylamide); FTIR; DSC; TGA; hydrogen bonding; equilibrium constants

## INTRODUCTION

It has been reported that depending on the nature of the solvent, the nature and densities of the interacting species incorporated within two dissimilar polymers, miscible polymer blends, or interpolymer complexes can be formed, as interpolymer hydrogen bonding developed between the two polymers is progressively intensified.<sup>1–7</sup> This is a convenient approach to elaborate new materials with properties different from those of the initial polymers. Jiang et al.<sup>8</sup> have reviewed the interpolymer complexation and miscibility enhancement by hydrogen bonding, for synthetic polymers.

Poly(*N,N*-dimethylacrylamide) (PDMA) is capable of interacting through specific interactions of hydrogen bonding type with proton-donating polymers at the two interacting sites namely the carbonyl amide group and the nitrogen atom.<sup>9</sup> Several binary miscible blends and interpolymer complexes containing PDMA are reported in the literature.<sup>10–15</sup>

Poly(acrylic acid) (PAA), a proton-donating polymer forms miscible blends and interpolymer complexes

with a large number of proton-accepting polymers or copolymers.<sup>16–22</sup> This biocompatible polymer has been used in many applications as a biomaterial. Its poor thermal stability and relatively low decomposition temperature, however, limit its uses in some specific applications.

The complexing ability and the stability of interpolymer complexes depend on a number of factors such as the temperature, the thermodynamic quality of the solvent, the acidity of the proton donor, the basicity of the proton acceptor, and the accessibility of the interacting species introduced within the polymer chains. Several studies<sup>23–26</sup> showed that spacing the hydrogen bonding moieties on the polymer chain optimizes the extent of intermolecular interactions between the two polymers in a blend.

The intermolecular interactions of hydrogen bonding type that occur between two dissimilar polymers in blends or complexes can be analyzed by techniques such as viscometry, light scattering, Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), solid-state nuclear magnetic resonance (NMR) spectroscopy, and X-ray photoelectron spectroscopy.

As an extension of our previous studies on miscibility enhancement by introduction of small amounts of interacting species within polymer chains,<sup>27–29</sup> or

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complexation as the densities of interacting species increase, via hydrogen bonding<sup>30</sup> and because of the hydrophobic properties and low water absorption ability of polystyrene, several random copolymers of styrene with *N,N*-dimethylacrylamide (SAD) and of styrene with acrylic acid (SAA) were prepared by free-radical polymerization to reduce the strong self-association of PAA, and dilute the interactions that occurred between PAA and PDMA and that led to their complexation. A progressive increase of styrene moieties will control the complexation and will favor the formation of miscible polymer blends with a good dispersion upon solvent evaporation. Besides their use as a model blend system to study the effect of styrene content on interpolymer interactions and because of the interactions between the two components of the blend, the resulting materials may be used in several fields, particularly in microporous polymer membranes generated by the solvent evaporation from the cast polymer blend solution.

In addition, the thermal stability and specific interactions of the pure SAA copolymers and their miscible blends or interpolymer complexes with SAD-17, SAD-32, or PDMA have been analyzed by DSC and thermogravimetry (TGA) in the 25–500°C temperature range. The hydrogen bonding in the SAA-27 copolymer and its miscible blends with poly(styrene-*co*-*N,N*-dimethylacrylamide) containing 17 mol % of *N,N*-dimethylacrylamide cast from tetrahydrofuran (THF) is

**TABLE I**  
Characteristics of the Copolymers

Polymer	$[\eta]$	$M_n$ ( $10^{-4}$ )	$M_w$ ( $10^{-4}$ )	$I$	$T_g$ (°C)
SAD-17	–	6.08	12.7	2.09	108.0 <sup>Butanone</sup>
SAD-32	–	6.04	12.8	2.12	102.0 <sup>Butanone</sup>
SAA-27	–	10.00	14.6	1.46	135.0 <sup>Butanone</sup>
PDMA	1.20 <sup>Methanol</sup>	–	–	–	–

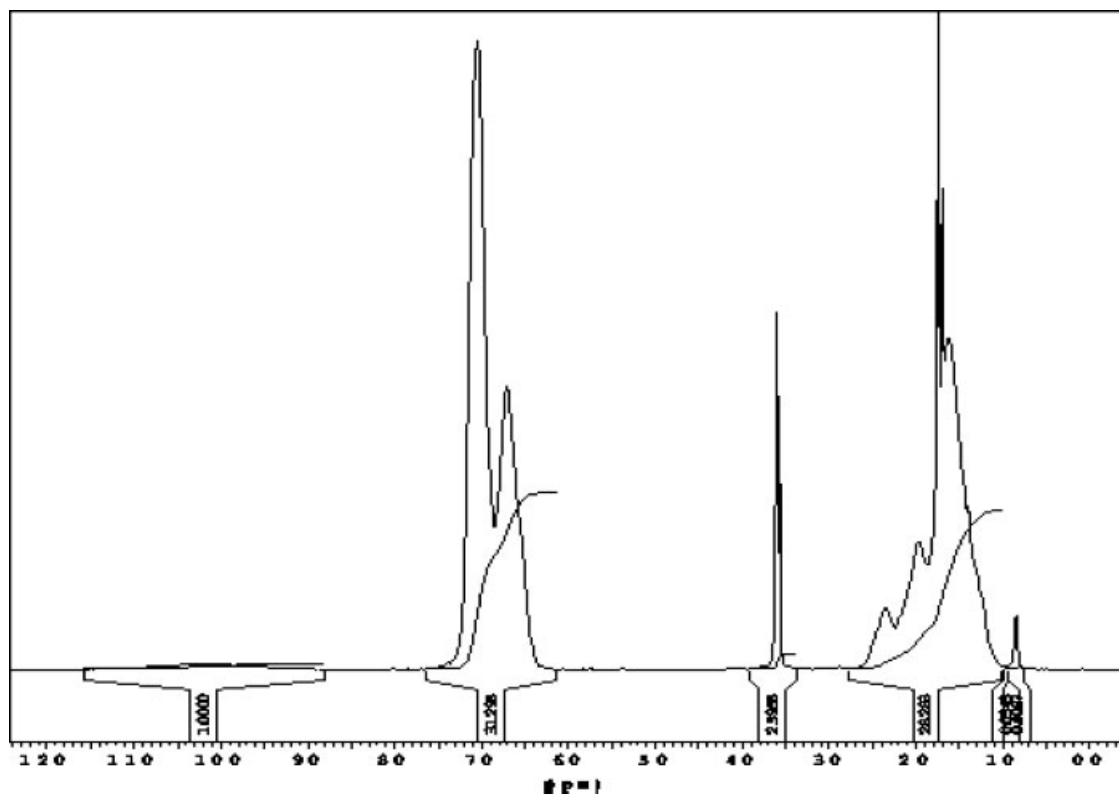
$I$  is the polymolecularity index.

characterized by FTIR spectroscopy qualitatively and quantitatively in the 50–210°C temperature range. Moreover, using the Painter–Coleman association model<sup>31</sup> the self-association ( $K_2$ ) and interassociation ( $K_A$ ) equilibrium constants and the enthalpy of hydrogen bonding formation of the SAA-27 copolymer and of its blends with SAD-17 were determined. The total free energy of mixing and the different contributions over the entire composition range as a function of copolymer composition were then calculated for this system.

## EXPERIMENTAL

### Polymer synthesis and characterizations

PDMA, random copolymers of styrene, and *N,N*-dimethyl acrylamide containing 17 or 32 mol % of *N,N*-dimethylacrylamide (SAD-17, SAD-32) and of styrene with acrylic acid SAA of different compositions (be-



**Figure 1**  $^1\text{H-NMR}$  spectrum of SAA-27 copolymer.

**TABLE II**  
Statistical Distribution of the Monomer Sequences  
in the SAA-27 Copolymer

Copolymer	F <sub>SS</sub>	F <sub>SA</sub>	F <sub>AA</sub>	F <sub>SSS</sub>	F <sub>SAS</sub>	F <sub>SSA</sub>	F <sub>AAA</sub>
SAA-27	0.493	0.474	0.033	0.456	0.769	0.438	0.015

tween 18 and 32 mol %) of acrylic acid were prepared by bulk free-radical polymerization using azo-bis-isobutyronitrile as the initiator at 60°C. These copolymers were purified by repeated dissolution/precipitation and to remove the residual solvent they were then dried to constant weight in a vacuum oven for several days at 60°C. Average molecular weights of the copolymers determined by GPC using a Waters HPLC are listed in Table I.

The copolymer compositions were determined not only by elemental analysis and UV spectroscopy at 262 nm where only the styrene units absorb but also by <sup>1</sup>H-NMR.

Figure 1 shows as an example, the <sup>1</sup>H-NMR spectrum of SAA-27. The composition of this copolymer is obtained using the equations below:

$$3x + 3y = a + b; \quad 5x = c \text{ and} \\ \% \text{ Styrene} = x/(x + y)$$

where  $x$  and  $y$  are the molar ratios of styrene and acrylic acid respectively;  $(a + b)$  and  $c$  are the integrals of the corresponding protons as shown in Figure 1.

The obtained values were in an acceptable agreement. Average values of these compositions were used to calculate the monomer reactivity ratios of the SAA copolymers determined using the Finemann and Ross method.<sup>32</sup> The values were found to be  $r_s = 0.34$  and  $r_{AA} = 0.65$  corresponding to the styrene and acrylic acid monomers respectively. The low  $r_s$ ,  $r_{AA}$  value (less than unity) indicates that these monomers have a tendency towards alternation. Using the relations of Harwood,<sup>33</sup> the statistical distribution of the monomer sequences were calculated for SAA-27 and are shown in Table II.

**TABLE III**  
Characteristics of SAA-27/SAD-32 Complexes

	Complex number				
	1	2	3	4	5
Feed composition <sup>a</sup>	20.0	30.0	50.0	70.0	80.0
Feed composition <sup>b</sup>	22.3	33.1	53.5	73.0	82.2
Bulk composition <sup>b</sup>	55.5	60.0	77.1	79.5	82.7
Yield of the complex	24.8	32.8	63.2	29.4	21.5
wt % SAA-27/SAD-32					
$T_g$ (°C)	117.0	124.5	129.0	132.9	133.2

<sup>a</sup> wt % of SAA-27.

<sup>b</sup> mol % of SAA-27.

### Thermal measurements

Blends of different ratios of SAA-27/SAD-17 were prepared by codissolution of the copolymers in a common solvent (THF or butan-2-one). Films were generated from polymeric solutions by evaporation of solvent with pure copolymers or blends. In the case of SAA-27/SAD-32 and SAA-27/PDMA mixtures in butan-2-one that 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 ( $T_g$ ) of the pure components and of their mixtures of different ratios as blends or complexes were determined with a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 K/min. Several scans were carried out to obtain reproducible values and the  $T_g$  was taken as the mid point of the heat capacity change.

The TGA thermograms of the as-cast and without any thermal pretreatment copolymers and of their mixtures as blends or complexes were determined under nitrogen using TA Instrument TGA 2590 thermogravimetric analyzer at a heating rate of 20 K/min from 25°C to 500°C.

### FTIR measurements

For FTIR measurements, thin films of the SAA-27 and SAD-17 copolymers and of their SAA-27/SAD-17 blends were prepared by casting from a 2–3% w/v solution in THF 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. Since both SAA-27 and SAD-17 are slightly hygroscopic, removal of THF and water traces from these copolymers and their blends that may remain as residues was ascertained by FTIR using specific vibration modes of water and THF.

All infrared measurements were recorded on heating from room temperature to 210°C and then on cooling to 25°C on a Nicolet 560 FTIR spectrometer with a spectral resolution of 2 cm<sup>-1</sup>. Sixty scans were signal averaged. All the spectra were recorded after the same stabilization time. The quantitative study

**TABLE IV**  
Characteristics of SAA-27/PDMA Complexes

	Complex number				
	1	2	3	4	5
Feed composition <sup>a</sup>	20.0	30.0	50.0	70.0	80.0
Feed composition <sup>b</sup>	12.3	19.4	36.0	56.7	69.2
Bulk composition <sup>b</sup>	35.3	46.3	50.6	53.0	50.3
Yield of the complex	56.3	80	71.4	46.7	24.4
wt % SAA-27/PDMA					
$T_g$ (°C)	132.5	130.0	131.5	132.0	129.0

<sup>a</sup> wt % of SAA-27.

<sup>b</sup> mol % of SAA-27.

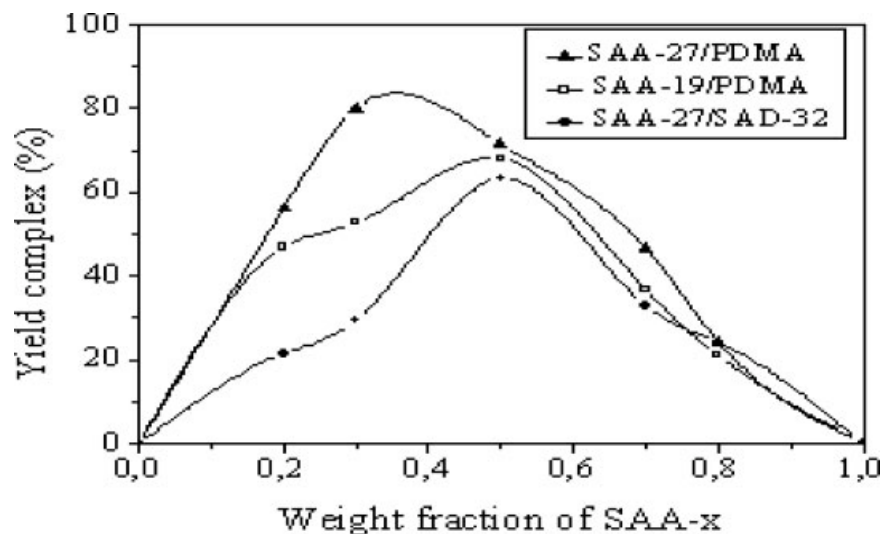


Figure 2 Illustration of yield versus feed composition for SAA-27/SAD-32 and SAA-27/PDMA complexes.

that concerns blends cast from THF was carried out at temperatures above  $T_g$  on cooling, using a micro-processor-temperature and processor controller Omega CN3201.

## RESULTS AND DISCUSSION

### Complexation behavior

Prior to the DSC and FTIR analyses, SAA-18/SAD-17, SAA-27/SAD-17, SAA-27/SAD-32, SAA-27/PDMA, and SAA-18/PDMA mixtures of different ratios in THF or butan-2-one were prepared. Depending on the nature of the solvent and the interacting densities introduced within the polystyrene matrix, homogeneous mixtures or complexation were observed and characterized. All these binary systems formed homogeneous solutions in THF. This may be due to the hydrogen-bonding ability of THF with the SAA copolymers that affects the interactions between the unlike species. Indeed, in this particular case, a preliminary FTIR study showed that the interactions developed between the SAA-27 copolymer and either of THF or the amide groups of the basic polymer are of slightly different strength as characterized by the bands of liberated carbonyl groups appearing at  $1729$  and  $1726\text{ cm}^{-1}$  for SAA-27/THF and SAA-27/SAD-17, respectively.

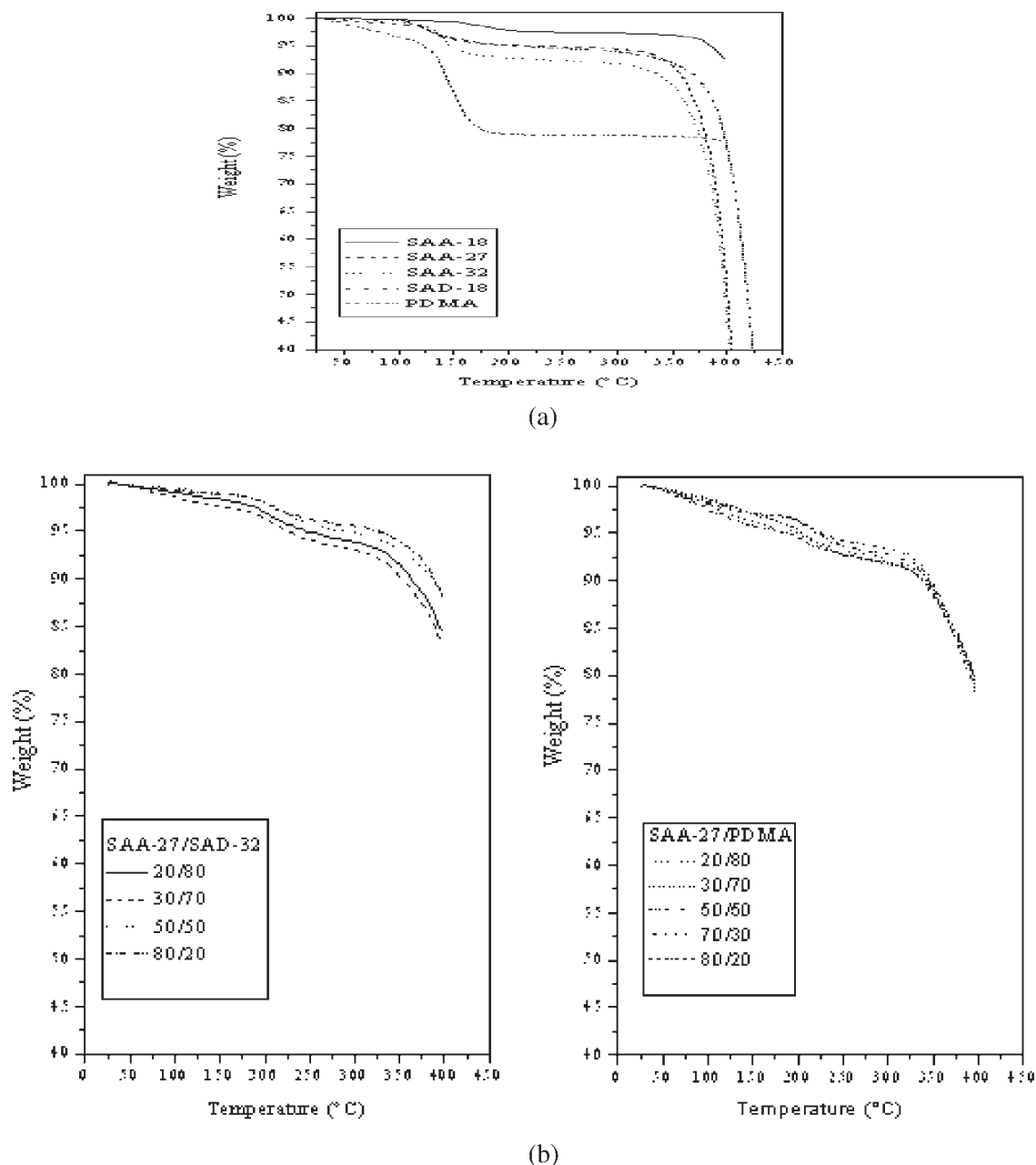
While homogeneous solutions were observed with SAA-18/SAD-17 blends, cloudy solutions were obtained with SAD-17 and SAA-27 when butan-2-one was used as the common solvent. As the content of the basic copolymer is increased within the polystyrene matrix, polymer complexes were obtained by mixing appropriate dilute butan-2-one solutions of PDMA or SAD-32 with SAA-27 or SAA-18 copolymers over the entire feed composition. Butan-2-one has a weaker hydrogen-bonding ability than THF and thus favors the formation of interpolymer complexes. The

instantaneously formed interpolymer complexes as precipitates were isolated from the solution and then dried in a vacuum oven at  $60^\circ\text{C}$  for several days to constant weight. These interpolymer complexes were soluble in THF.

The nitrogen content in the SAA-27/SAD-32 and SAA/PDMA interpolymer complexes was determined by elemental analysis. Tables III and IV show the yields and the compositions of these complexes. The yields of these complexes in the range of 21–80 wt %, formed with all systems were found to depend on the feed composition of the constituents and the densities of interacting species introduced within the polystyrene chains. The compositions of the SAA-27/SAD-32 complexes are in the range 55.5–82 centered at 53 mol % of SAA-27. This suggests that SAA-27 prefers to form in butan-2-one 1 : 1 ratio complexes with SAD-17. As can be seen from Figure 2, the complex yield first increases, goes through a maximum that depends on the amount of carboxylic and amide groups within the polymer chains, and then decreases as the content of SAA in the feed composition increases. The stoichiometry of the interpolymer complexes was found to vary with the densities of the interacting species.

### Thermal analysis

Prior to the quantitative analysis of the interpolymer interactions, a thermogravimetric study was carried out to get preliminary information on the thermal stability of the copolymers and of their mixtures. Figure 3(a) shows the thermogravimetric curves of the different acidic and basic as-cast and without any heat pretreatment copolymers. A two-step process of degradation is detected with these copolymers. A first loss of mass is observed in the  $120$ – $150^\circ\text{C}$  temperature range for the SAA-27 copolymer. The corresponding very low



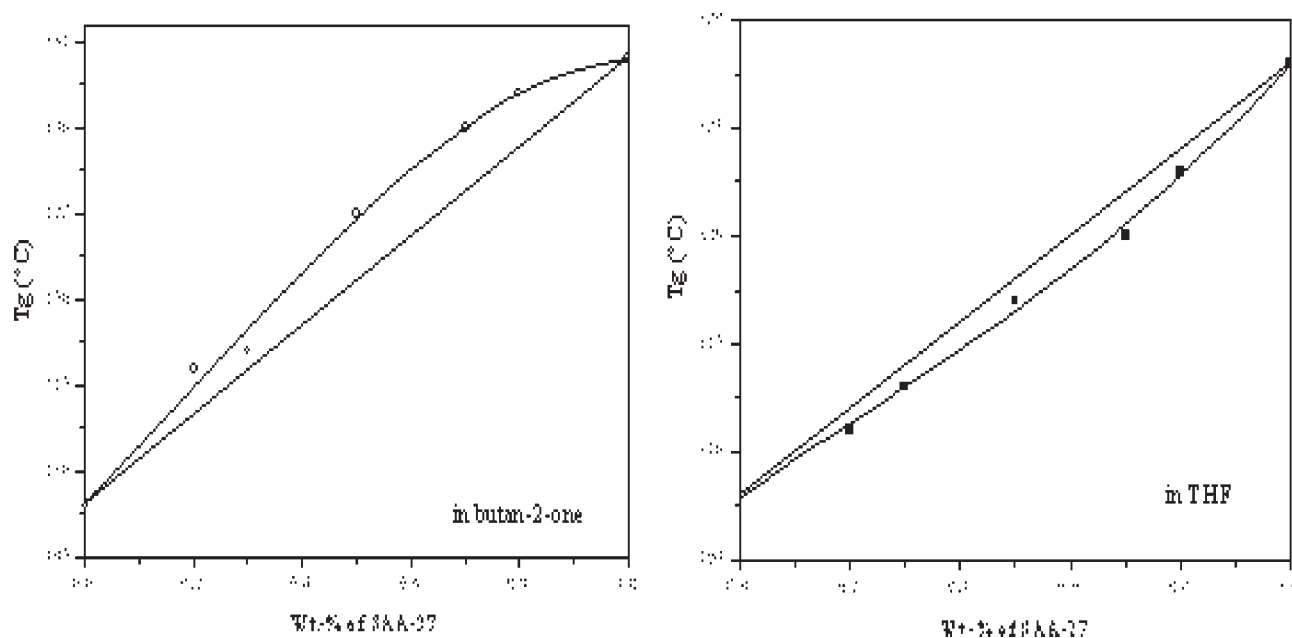
**Figure 3** (a) TGA curves of SAA-18, SAA-27, SAA-32, and PDMA copolymers. (b) TGA curves of SAA-27/SAD-32 and SAA-27/PDMA mixtures.

mass loss of 5% observed with the as-cast SAA-27 was attributed mainly to moisture absorption or anhydride formation and its level off between 160°C and 310°C confirms the significant thermal stabilization of SAA-27 copolymer compared with PAA. The second degradative step starts only above 310°C. A practically similar thermal degradation process with an increase of the first loss of mass is observed with copolymers of higher content of interacting groups as with the basic components SAD-32, PDMA, or acidic copolymers SAA-32. Lower first mass losses were however observed with SAA-18 and SAD-17. The thermal degradation mechanism of PAA is discussed in the litera-

ture.<sup>19</sup> The thermal stabilization, observed upon mixing SAA-27 with SAD-32 or PDMA [Fig. 3(b)], of less than 4% first mass loss observed with most of these mixtures, is attributed to both the hydrophobic effect of styrene moieties within the polymeric matrix and the specific interactions of hydrogen bonding type that occurred between the carboxylic and the amide groups.

As it is shown, the hygroscopicity of these copolymers increases with an increase of the interacting species. Since the presence of some molecules of water or solvent that may remain as residues, acting as plasticizer in the as-cast blends, may affect the glass-transition temperature,<sup>34</sup> the DSC study was carried out with





**Figure 4** Variation of the glass-transition temperature with SAA-27 composition for SAA-27/SAD-17 mixtures cast from butan-2-one or THF.

precautions until reproducible  $T_g$  values within few degrees were obtained. Because of some rearrangements and more accessibility of the interacting species upon heating the sample above  $T_g$ , additional hydrogen bonding interactions between the constituents of the mixture may occur and lead to higher  $T_g$ .<sup>35</sup>

The single glass-transition temperature, observed for these SAA-27/SAD-17, SAA-27/SAD-32, and SAA-27/PDMA binary systems cast from both THF or butan-2-one, is considered as an evidence of their miscibility or complexation because of the presence of specific interactions of hydrogen bonding type that occurred between the carboxylic acid groups and the carbonyl amide groups. Figure 4 shows the variation of the glass-transition temperature with SAA-27 composition for these systems. Positive deviations from the linear average line were observed with these binary mixtures when butan-2-one is used as the common solvent. As can be seen from Figure 4 different behavior is displayed for  $T_g$ -composition with the as-cast SAA-27/SAD-17 mixtures. The  $T_g$  of the blends of this system cast from butan-2-one were, however, higher than those prepared in THF. Similar observations, attributed to the influence of casting solvents on polymer blend miscibility, known as “ $\Delta\chi$  effect” are reported in the literature.<sup>36–38</sup> A similar positive deviation was observed in our recent study of blends of poly(*n*-butyl methacrylate-*co*-methacrylic acid) containing 18 mol % of methacrylic acid with SAD-17.<sup>39</sup>

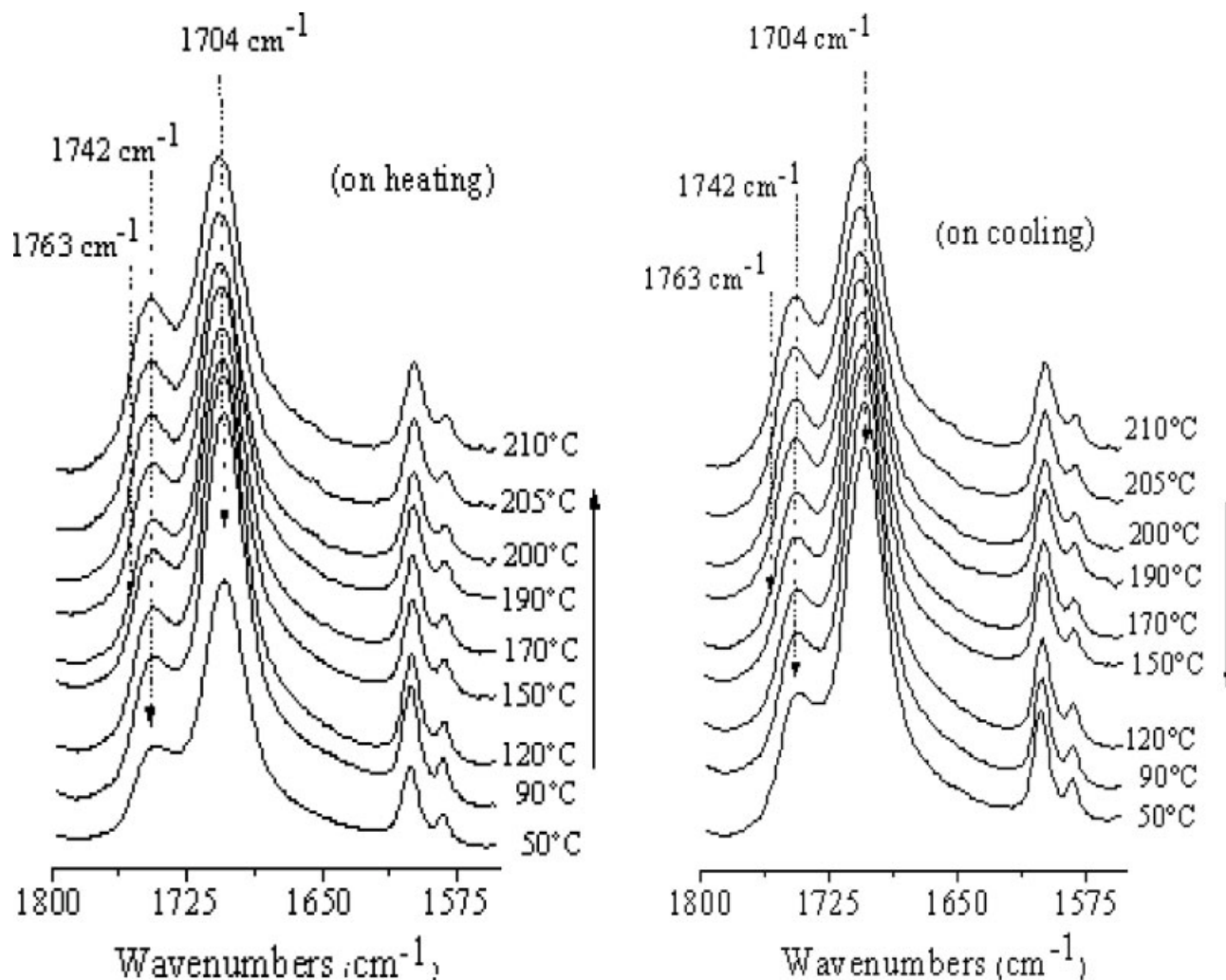
As the density of the interacting species is increased, a single phase as with blends, is observed with SAA-27/SAD-32 and SAA-27/PDMA interpolymer complexes. As can be seen from Tables III and IV, the  $T_g$  of

the complexes is higher than those calculated from the additivity rule, resulting from higher number of interpolymer interactions. While the  $T_g$  values of the SAA-27/SAD-32 complexes varied with the composition, practically the same single  $T_g$  is observed with the SAA-27/PDMA complexes of different original mixtures.

#### FTIR analysis

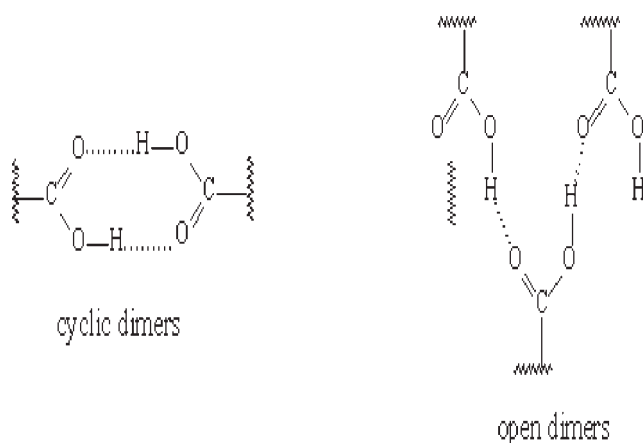
We have used FTIR spectroscopy, a technique of choice, to study the specific interactions of hydrogen bonding type that occurred between the constituents of the blends in the main regions where significant changes were observed. The self-association dimensionless equilibrium constants of SAA-27 and its interassociation constants with SAD-17 were determined for the miscible SAA-27/SAD-17 blends cast from THF. A similar thermodynamic study was carried out with other acidic and basic copolymers and their blends of different compositions to optimize the extent of intermolecular interactions between these two polymers in a blend.<sup>40</sup>

Figure 5 shows the scale-expanded infrared spectra of SAA-27, recorded in the carbonyl 1800–1550  $\text{cm}^{-1}$  region on heating from 50°C to 210°C and on cooling to room temperature. Besides the styrene ring stretching bands at 1601 and 1583  $\text{cm}^{-1}$ , the spectrum of the SAA-27 copolymer shows two resolved main bands and a small shoulder at ~1742, 1704, and 1686  $\text{cm}^{-1}$  characteristic of the free, associated carboxylic groups, and inner hydrogen bonded carbonyl groups respectively. The maxima of these bands shift slightly to higher wavenumbers as the temperature is raised.



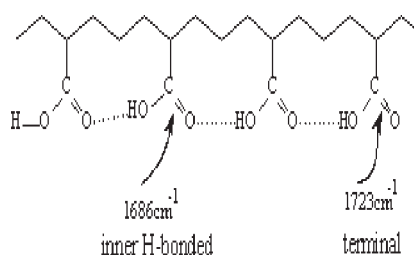
**Figure 5** Scale-expanded FTIR spectra of SAA-27 copolymer in the 1800–1550  $\text{cm}^{-1}$  region recorded as a function of as-indicated heating or cooling temperature.

This is due to the presence of dimers of different structures ranging from cyclic, in their great majority, to open chains and free carbonyl of different strength as illustrated in Scheme 1.

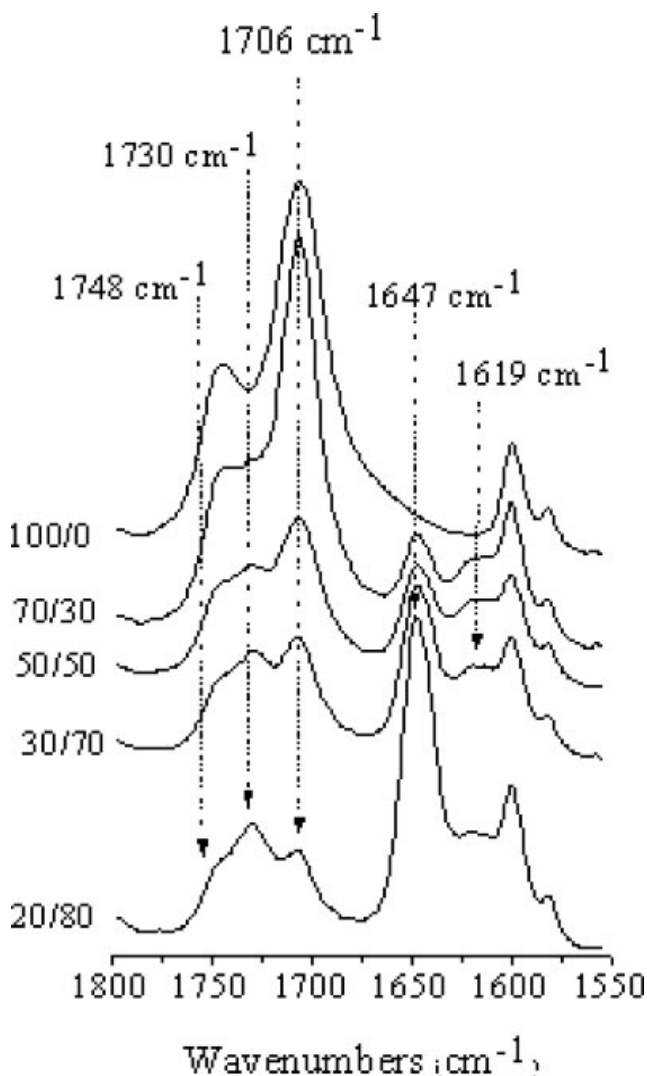


**Scheme 1** Dimerization possibilities.

In agreement with the TGA results, only very small amount of anhydrides characterized by weak shoulders at 1763 and 1772  $\text{cm}^{-1}$  are formed when SAA-27 is heated up to 210°C and then cooled down to room temperature. As expected, a decrease of the relative intensities of the hydrogen bonded to the free bands of SAA-27 is observed with an increase of temperature. The presence of any THF traces would show a band around 1729  $\text{cm}^{-1}$  characteristic of liberated carbonyl



**Scheme 2** Possibilities for carbonyl groups in relation to hydrogen bonding.



**Figure 6** Scale-expanded FTIR spectra of SAA-27/SAD-17 blends in the 1800–1550  $\text{cm}^{-1}$  region recorded at 180°C temperature on cooling.

groups due to carboxyl–ether interactions. Besides, THF absorbs strongly at 2978  $\text{cm}^{-1}$ , and the absence of this band in the SAA-27 FTIR spectrum is another evidence of a sample free of solvent. Similar carboxylic acid–THF interaction is reported by Cleveland et al.<sup>41</sup> for poly(styrene-*co*-methacrylic acid)/polytetrahydrofuran.

Jo et al.<sup>42</sup> reported similar observations for this type of copolymers. However as shown in Scheme 2, four bands were observed by Dong et al.<sup>43</sup> with PAA in the carbonyl region at 1686, 1705, 1723, and 1742  $\text{cm}^{-1}$ .

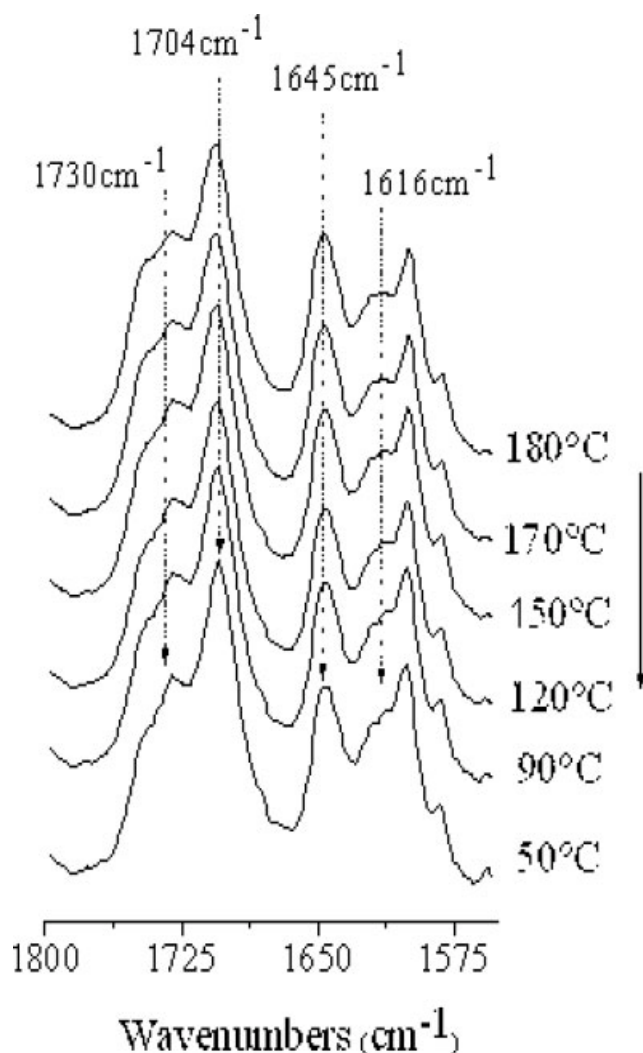
Harthcock<sup>44</sup> carried out a FTIR study of various ethylene-*co*-acrylic copolymers and observed from the deconvoluted room temperature spectra different hydrogen bonded carbonyl structures depending on the acrylic acid content in the copolymer. At room temperature, two hydrogen bonded carbonyl bands were observed at 1696 and 1710  $\text{cm}^{-1}$  for the 9% acrylic acid copolymer. The 1696  $\text{cm}^{-1}$  band is

assigned to planar cyclic dimers while the 1710  $\text{cm}^{-1}$  is attributed to open dimer structure in a more “short range” hydrogen bonded structure. One hydrogen bonded band was however observed at 1706  $\text{cm}^{-1}$  with a 6.5% acrylic acid copolymer and assigned to an open dimer “long range order” structure. Scheme 1 illustrates the various carbonyl stretching vibrations in this type of copolymers as cyclic dimers or open chains.

The SAD-17 copolymer shows a strong absorption at about 1642  $\text{cm}^{-1}$  attributed to the free amide carbonyl groups and a styrene ring stretching bands at 1601 and 1583  $\text{cm}^{-1}$ .

Similar free amide band is reported in the literature<sup>9</sup> for dry PDMA. It has also been reported<sup>9</sup> that there are two possible PDMA sites, the carbonyl oxygen and the nitrogen atoms, for hydrogen bonding with the acidic SAA-27 copolymer.

When the SAD-17 copolymer, transparent in the carboxyl 1800–1650  $\text{cm}^{-1}$  region, is added to the



**Figure 7** Scale-expanded FTIR spectra obtained on a film of SAA-27/SAD-17 (50/50) blend recorded as a function of as-indicated cooling temperature.



TABLE V  
Curve Fitting Data from the Carbonyl Bands of SAA-27 Copolymer on Heating from 50°C to 210°C and Cooling to Room Temperature

T (°C)	v (cm <sup>-1</sup> )				Width at ½ height (cm <sup>-1</sup> )				Mole fraction		K <sub>2</sub>
	V <sub>free</sub>	V <sub>dim</sub>	V <sub>styrene</sub>	V <sub>styrene</sub>	W <sub>free</sub>	W <sub>dim</sub>	W <sub>styrene</sub>	W <sub>styrene</sub>	f <sub>free</sub>	f <sub>dim</sub>	
160	1745	1705	1600	1582	19	34	10	5	0.164	0.836	15.500
170	1745	1705	1600	1582	19	34	11	6	0.189	0.811	14.744
180	1745	1706	1599	1582	20	34	11	6	0.188	0.812	11.461
190	1745	1706	1599	1582	20	34	12	6	0.191	0.809	11.156
195	1746	1706	1599	1582	20	34	12	7	0.212	0.788	8.791
200	1746	1706	1599	1582	21	34	12	7	0.226	0.774	7.563
205	1746	1706	1599	1582	21	34	12	7	0.234	0.766	7.028
210	1746	1707	1599	1582	22	35	12	7	0.240	0.760	6.539
210	1746	1707	1599	1582	22	35	12	7	0.245	0.755	6.302
205	1746	1707	1599	1582	22	34	12	8	0.241	0.759	6.528
200	1746	1706	1599	1582	21	34	12	8	0.234	0.766	7.020
195	1746	1706	1599	1582	21	34	12	7	0.227	0.773	7.528
190	1746	1706	1599	1582	21	34	12	7	0.216	0.784	8.476
180	1746	1706	1599	1582	20	35	11	7	0.200	0.800	9.987
170	1746	1706	1599	1582	20	34	11	6	0.190	0.810	11.300
160	1745	1705	1600	1582	19	34	11	6	0.178	0.822	12.900

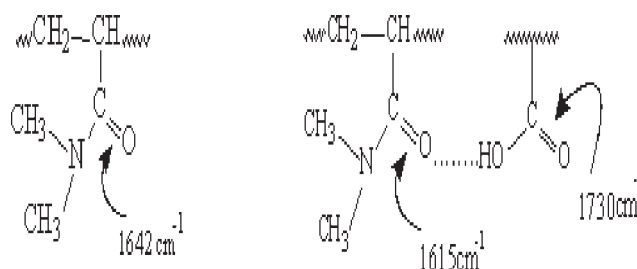
SAA-27 copolymer, a progressive decrease of the band at 1704 cm<sup>-1</sup> characteristic of dimer dissociation is observed. A new band of increasing intensity appeared at 1730 cm<sup>-1</sup> as the content of the basic SAD-17 copolymer is added to the blend. This band is characteristic of SAA-27 carbonyl groups that are liberated as a result of interactions that occurred between the hydroxyl group of the acidic copolymer and the SAD-17 carbonyl amide groups.

Moreover, the analysis of the FTIR spectra of these blends also confirms qualitatively in the amide stretching 1800–1550 cm<sup>-1</sup> region the presence of interactions between the carboxylic groups and the carbonyl amide groups even at temperatures above the glass-transition temperatures of the two components of the blends by the appearance of a new band around 1616 cm<sup>-1</sup>, characteristic of the associated amide. The difference between the frequency of the free and the associated amide bands of 30 cm<sup>-1</sup> for blends containing an excess of SAA-27 decreases slightly as the fraction of SAD-17 increases in the blend. This difference is an indication of the presence of relatively strong specific interactions. It can be seen from Figure 6 that the intensity of the associated amide band relative to the free one increases with an increase of the SAA-27 content in the blend. A small peak is observed at 1652 cm<sup>-1</sup> with blends containing an excess of the acidic copolymer. This may be indicative of the presence of a small fraction of other types of complexes that are formed. Similar behavior was observed by Lichkus et al.<sup>45</sup> with blends of poly(ethylene-*co*-acrylic acid) and poly(ethylloxazoline) and by Meaurio et al.<sup>9</sup> for the blends of poly(mono-*n*-alkyl itaconates) with PDMA or poly(ethylloxazoline). A 24 cm<sup>-1</sup> shift to lower wavenumber was observed in this region with blends of PAA and poly(vinylpyrrolidone).<sup>19</sup> A shift of 44 cm<sup>-1</sup> to lower wave number was reported by Motzer et al.<sup>46</sup> for poly(sty-

rene-*co*-methacrylic acid)/poly(styrene-*co*-vinylpyrrolidone) blends.

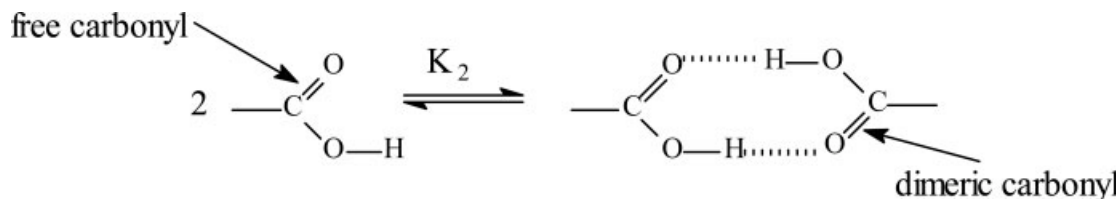
Figure 7 displays the spectra of the 1 : 1 ratio SAA-27/SAD-17 blends recorded on cooling from 180°C to 50°C. In agreement with the DSC, these results confirm the miscibility of these blends from the observed recovery of the hydrogen bonding. Phase separation does not occur at 180°C. Depending on the composition and temperature, different complexes are formed as observed from the presence of several structures obtained from the redistribution of the carbonyl bands upon mixing SAA-27 with SAD-17. Both bands characterizing the carboxylic dimers and the liberated carbonyl groups as a result of specific interactions that occurred between the two species shifted slightly to higher wavenumbers as the temperature or the composition is increased.

Using a Lorentzian curve-fitting procedure, the areas of the free and hydrogen bonded carbonyl groups for SAA-27 were determined at temperatures above the glass-transition temperature on heating from 160°C to 210°C and on cooling from 210°C to 160°C. In this temperature range, the copolymers remain stable as evidenced by TGA.



Scheme 3 Free amide carbonyl and carboxylic acid–amide interassociation.

The self-association equilibrium constant  $K_2$  for cyclic carboxylic dimers described by:



is related to the fraction of the free carbonyl groups given by:

$$f_F^{c=O} = \frac{\varepsilon A_F}{\varepsilon A_F + A_D} \quad (1)$$

where  $A_F$  and  $A_D$  are the areas of the free and dimeric carbonyl groups respectively, and  $\varepsilon$  an absorptivity ratio equals to 1.1.<sup>47</sup> The results are summarized in Table V.

Considering that negligible amount of anhydrides are formed in this temperature range,  $K_2$  can be determined from FTIR measurements of the fraction of the free carbonyl groups given by:

$$K_2 = \frac{1 - f_F^{c=O}}{2(f_F^{c=O})^2} \quad (2)$$

Neglecting the small amount of open chain carboxylic dimers that may be formed upon heating, the calculated  $K_2$  values from the equation above for the different temperatures as shown in Table V decreased with the temperature. The corresponding standard self-association constants  $K_2^{\text{std}}$  were obtained using molar volumes for the repeat units in SAA-27 and extrapolation to 25°C.

The most important interactions that may occur upon blending dry SAA-27 with SAD-17 are shown in Scheme 3:

The interassociation equilibrium constant describing the interactions that occurred between the acrylic acid and the amide groups within the blends that assumes the formation of 1 : 1 complexes only

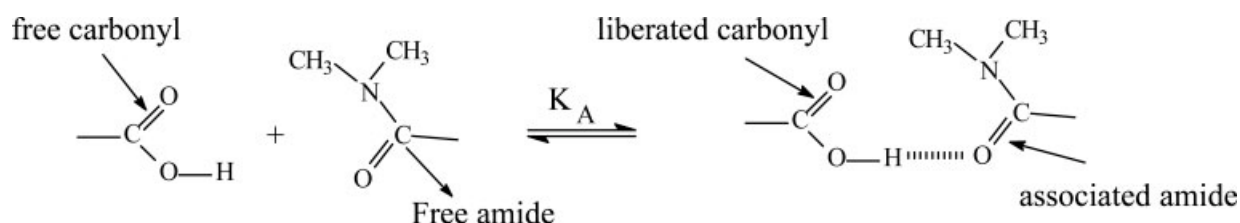


TABLE VI  
Curve Fitting Data from Infrared Spectra of SAA-27/SAD-17 Blends in the 1800–1550  $\text{cm}^{-1}$  Region on Cooling from 180°C to 150°C

$T$ (°C)	180°C			170°C			160°C			150°C		
	$\nu$ ( $\text{cm}^{-1}$ )	$W$ ( $\text{cm}^{-1}$ )	$f$	$\nu$ ( $\text{cm}^{-1}$ )	$W$ ( $\text{cm}^{-1}$ )	$f$	$\nu$ ( $\text{cm}^{-1}$ )	$W$ ( $\text{cm}^{-1}$ )	$f$	$\nu$ ( $\text{cm}^{-1}$ )	$W$ ( $\text{cm}^{-1}$ )	$f$
70/30	1748	14	0.113	1748	14	0.108	1747	14	0.101	1747	13	0.094
	1734	21	0.174	1734	21	0.173	1734	21	0.169	1734	21	0.168
	1706	24	0.712	1706	24	0.719	1706	24	0.730	1706	24	0.739
	1647	18	0.494	1647	18	0.489	1647	18	0.480	1647	19	0.476
	1619	26	0.506	1619	26	0.511	1619	26	0.520	1618	25	0.524
50/50	1748	14	0.124	1747	14	0.118	1747	14	0.108	1747	14	0.101
	1733	22	0.246	1733	22	0.248	1732	22	0.254	1732	22	0.254
	1706	30	0.630	1706	30	0.634	1706	29	0.638	1705	29	0.645
	1647	19	0.513	1647	19	0.503	1647	19	0.492	1647	19	0.483
	1619	27	0.487	1619	27	0.497	1619	28	0.508	1618	28	0.517
30/70	1746	15	0.141	1746	15	0.133	1746	14	0.123	1745	15	0.112
	1730	21	0.353	1730	22	0.360	1730	22	0.366	1730	22	0.380
	1706	25	0.506	1706	25	0.507	1706	25	0.511	1706	24	0.508
	1647	19	0.578	1647	19	0.567	1647	19	0.555	1646	19	0.550
	1619	28	0.422	1619	28	0.433	1619	28	0.445	1619	28	0.450

TABLE VII  
Calculated Equilibrium Constants of SAA-27/SAD-17 Blend on Cooling from 180°C to 150°C

T (°C)	180°C			170°C			160°C			150°C		
	$K_2$	$K_A^{C=O}$	$K_A^{amid}$	$K_2$	$K_A^{C=O}$	$K_A^{amid}$	$K_2$	$K_A^{C=O}$	$K_A^{amid}$	$K_2$	$K_A^{C=O}$	$K_A^{amid}$
70/30	39.8	19.3	12.9	43.8	20.2	13.8	51.3	21.6	15.3	60.2	23.3	16.8
50/50	41.4	14.4	15.4	45.5	15.5	16.7	54.0	17.5	19.0	64.2	19.6	21.3
30/70	42.2	11.4	17.2	47.5	11.6	19.0	56.3	13.1	21.7	66.8	15.0	24.3

is defined in terms of volume fractions by:

$$K_A = \frac{\phi_{BA}}{\phi_{B_1}\phi_{A_1}} \left[ \frac{r}{1+r} \right] \quad (3)$$

The equation below describes the mass balance:

$$1 = \phi_{B_1} + \phi_{A_1} + \phi_{BA} + \phi_{B_2} \quad (4)$$

The stoichiometry of this system is given by:

$$\Phi_B = \phi_{B_1} \left[ 1 + \frac{K_A \phi_{A_1}}{r} \right] + 2K_2 \phi_{B_1}^2 \quad (5)$$

$$\Phi_A = \phi_{A_1} (1 + K_A \phi_{B_1}) \quad (6)$$

The fractions of the three carbonyl bands in the SAA-27/SAD-17 blends of different ratios as a function of the volumes fractions are given by the following expressions:

$$f_{free}^{C=O} = \frac{\phi_{B_1}}{\Phi_B} \quad (7)$$

$$f_{dim}^{C=O} = \frac{\phi_{B_2}}{\Phi_B} \quad (8)$$

$$f_{lib}^{C=O} = 1 - (f_{free}^{C=O} + f_{dim}^{C=O}) \quad (9)$$

$$\phi_{BA} = f_{lib}^{C=O} \Phi_B (1 + r) \quad (10)$$

where  $\phi_i$ ,  $\Phi_i$ , and  $r$  are the volume fraction of the polymer segment containing the  $i$  species, volume fraction of interacting polymer in the blend and the ratio of the molar volumes  $V_A/V_B$  respectively, while the index  $B$  and  $A$  relates to self-associated polymer (B) which can interassociate with polymer (A).

We have, in a first step, attempted a quantitative analysis of the interactions between SAA-27 and SAD-17 in the 1800–1550  $\text{cm}^{-1}$  region using a Lorentzian curve-fitting procedure to determine the fraction of each of the carbonyl species in the blends containing between 30% and 70% of the basic SAD-17 copolymer at different temperatures. The SAD-17 does not absorb in the carboxylic 1800–1660  $\text{cm}^{-1}$  region. The results summarized in Table VI show that the fraction of the carboxylic dimers decreases with the SAD-17 content, while an increase of the liberated carbonyl groups resulting from the hydroxyl–carbonyl amide interactions is observed.

The fraction of the relative areas of the two (free and associated amide) bands were then determined in the same 1800–1550  $\text{cm}^{-1}$  region using a Gaussian and Lorentzian spectral curve-fitting procedure respectively, for amide and styrene bands from the following relation:

$$f_{free}^{amid} = \frac{A_{1645}}{A_{1645} + \frac{a_{1645}}{a_{1616}} A_{1616}} \quad (11)$$

where  $A_{1645}$  and  $A_{1616}$  are the areas of the bands at 1645 and 1616  $\text{cm}^{-1}$ , respectively, and  $a_{1645}$  and  $a_{1616}$

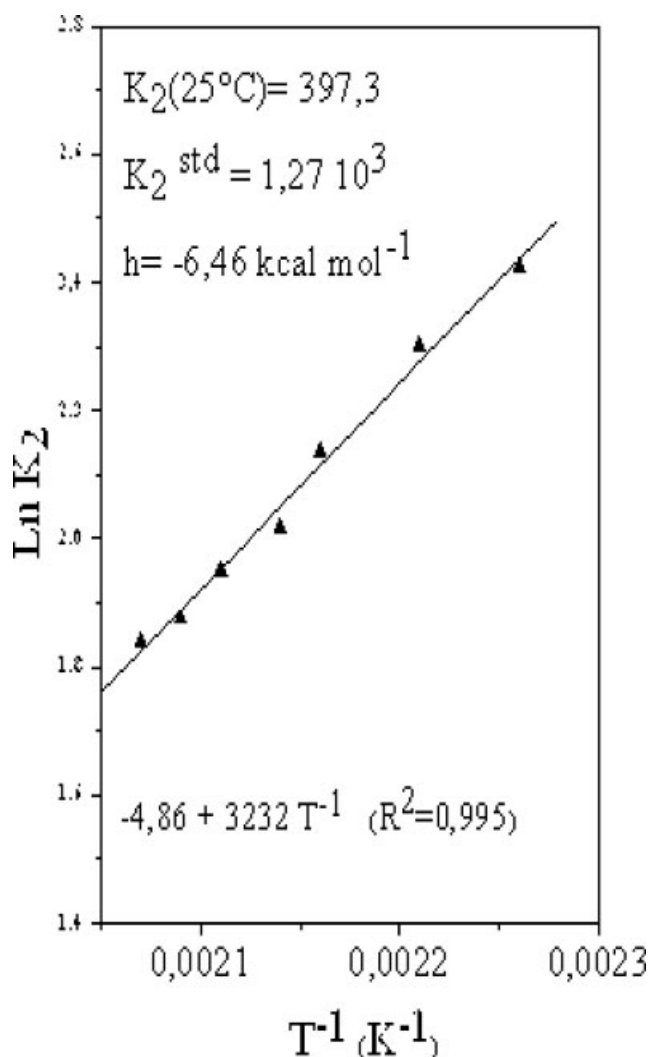
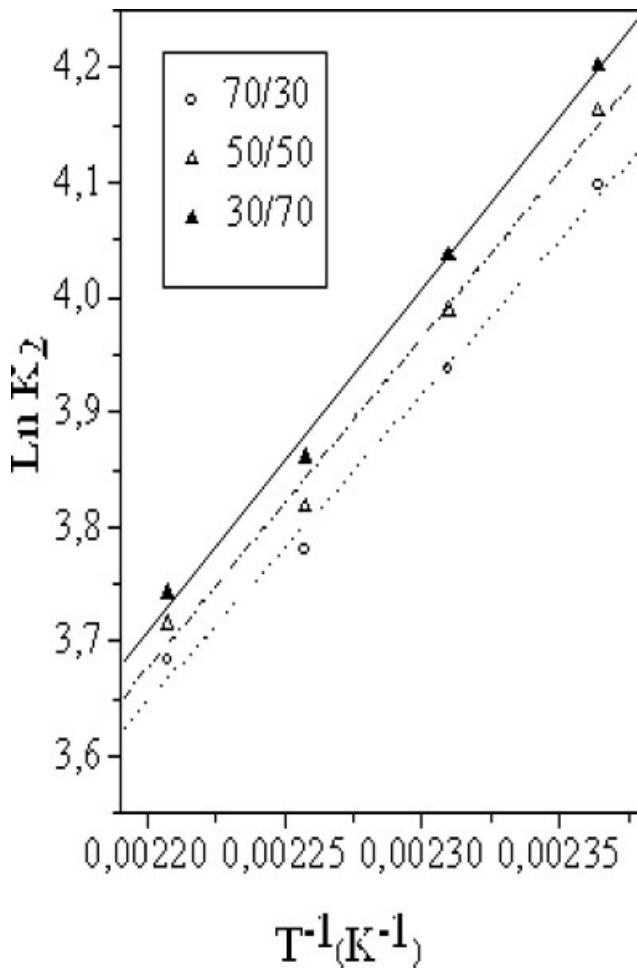


Figure 8 Van't Hoff plot of  $K_2$  (logarithmic scale) versus temperature (reciprocal scale) of SAA-27 copolymer.



**Figure 9** Van't Hoff plot of  $K_2$  (logarithmic scale) versus temperature (reciprocal scale) of SAA-27/SAD-17 blends.

are the absorptivities of the two bands, assuming an absorptivity ratio of 1.<sup>10</sup> The curve-fitting data from the infrared spectra of SAA-27/SAD-17 blends in this region are shown in Table VI. Very broad bands of the associated amide are observed with blends containing an excess of the basic SAD-17 copolymer at high temperature.

The fractions of the free and associated carbonyl amide bands in the SAA-27/SAD-17 blends of different ratios as a function of the volumes fractions are given by the following expressions:

$$f_{\text{free}}^{\text{amid}} = \frac{\Phi_{A_1}}{\Phi_A} \quad (12)$$

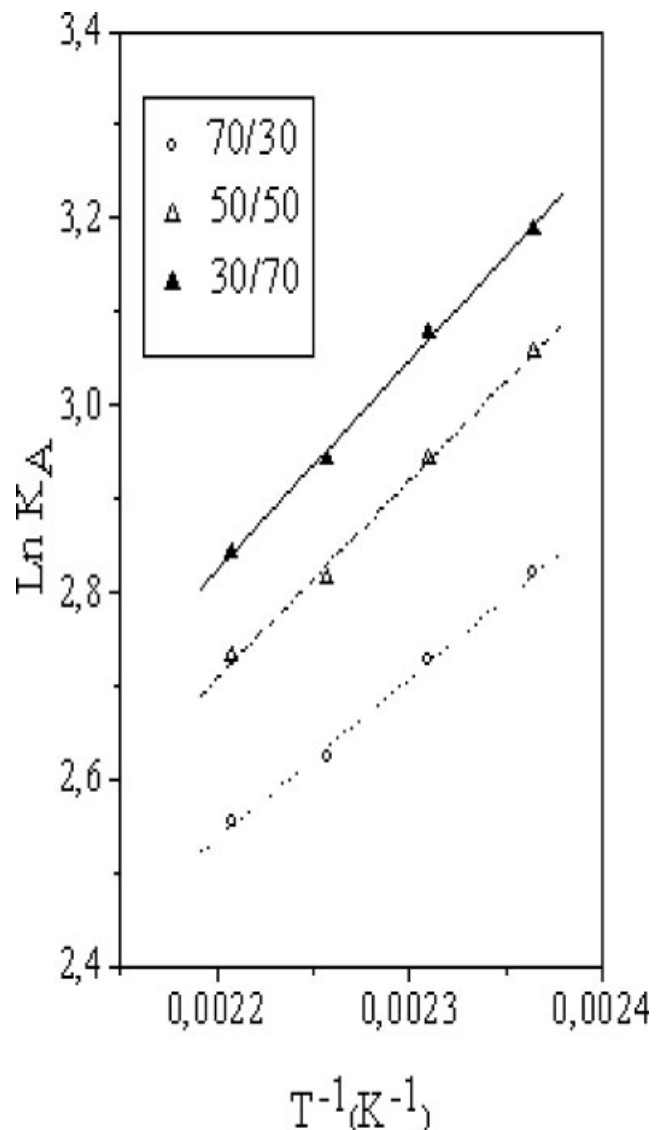
$$f_{\text{ass}}^{\text{amid}} = \frac{\Phi_{BA}}{\Phi_A} \left[ \frac{r}{1+r} \right] \quad (13)$$

Using the Painter–Coleman association model,<sup>31</sup> the interassociation constants  $K_A$  were calculated in the carbonyl region, at different temperatures assuming the formation of 1 : 1 complexes and that equilibrium

has been attained. As can be seen from Table VII  $K_A^{C=O}$  decreases with the temperature.

In a similar way as in the carboxyl region and using the same association model,<sup>31</sup> the interassociation constants  $K_A^{\text{amid}}$  were calculated in the carbonyl amide region, using the volume fraction, on cooling at temperatures higher than  $T_g$  assuming the formation of 1 : 1 complexes and that equilibrium has been attained. As can be seen from Table VII,  $K_A^{\text{amid}}$  decreases with the temperature. The values of the enthalpy of hydrogen bond formation for the SAA-27 copolymer and its blends with SAD-17, obtained from the slope of a Van't Hoff plot of  $\ln K$  versus the reciprocal of temperature shown in Figures 8–10 are summarized in Table VIII.

According to the Painter–Coleman association model, the free energy of mixing of polymer blends when



**Figure 10** Van't Hoff plot of  $K_A$  (logarithmic scale) versus temperature (reciprocal scale) of SAA-27/SAD-17 blends.



TABLE VIII  
Thermodynamic Data Obtained of SAA-27/SAD-17 Blends on Cooling in the 180°C to 150°C Temperature Range

Weight fraction of SAA-27	$K_2$ (25°C)	$K_2^{\text{Std}}$ ( $10^{-3}$ )	$-h_b$ (kcal mol $^{-1}$ )	$K_A$ (25°C)	$K_A^{\text{Std}}$ ( $10^{-3}$ )	$-h_a$ (kcal mol $^{-1}$ )
100/0	397.3	1.27	6.46	–	–	–
70/30	867.7	2.55	5.38	91.7	0.27	3.42
50/50	1070.0	3.15	5.70	172.7	0.51	4.22
30/70	1270.6	3.74	5.95	220.3	0.65	4.44

The molar volume of SAA-27 is calculated by group contributions as 294.61 cm $^3$  mol $^{-1}$ .

strong specific interactions are present is described by the following expression:

$$\frac{\Delta G_M}{RT} = \frac{\Phi_A}{M_A} \ln \Phi_A + \frac{\Phi_B}{M_B} \ln \Phi_B + \Phi_A \Phi_B \chi_{AB} + \frac{\Delta G_H}{RT} \quad (14)$$

The Flory–Huggins parameter  $\chi$  is given by

$$\chi = (\delta_A - \delta_B)^2 \frac{V_{\text{ref}}}{RT} \quad (15)$$

where  $\delta_i$  is the solubility parameter which can be determined by group molar contribution.

The term  $\Delta G_H/RT$  is the favorable contribution to the change in the free energy of mixing due to the presence of intermolecular hydrogen bonding interactions and is given by:

$$\begin{aligned} \frac{\Delta G_H}{RT} = & \Phi_B \ln \left( \frac{\phi_{B_1}}{\phi_{B_1}^0} \right) + \frac{\Phi_A}{r} \ln \phi_{A_1} \\ & + \Phi_B \left[ \phi_{B_1}^0 (1 + K_2 \phi_{B_1}^0) \right] - \phi_{B_1} (1 + K_2 \phi_{B_1}) \\ & - \left[ \frac{\Phi_B}{h} \ln \Phi_B + \frac{\Phi_A}{r} \ln \Phi_A \right] \quad (16) \end{aligned}$$

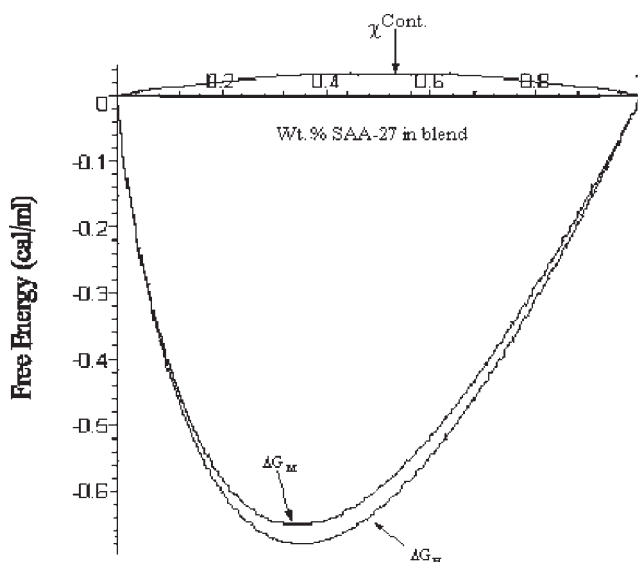


Figure 11 Calculated values of the total free energy and the relative contributions as a function of SAA-27 of SAA-27/SAD-17 blend at 180°C.

where

$$\bar{h}^0 = \frac{1 + 2K_B \phi_{B_1}^0}{1 + K_B \phi_{B_1}^0} \quad (17)$$

The variation of the total free energy of mixing and the different contributions were calculated as a function of the blend composition at 180°C, using the different characteristics of the copolymers and the self-association and interassociation constants  $K_2$  and  $K_A = 10$  deduced from the best fit of the data for these blends. Figure 11 displays the obtained results that confirm the miscibility of these blends at 180°C from the negative values of  $\Delta G_M$  and the positive second derivative with respect to composition over the entire blend composition. Since the two copolymers contain mainly polystyrene, their small  $\Delta\chi$  contribution calculated from group contribution acts in favor of their miscibility.

In a forthcoming publication we will present results of a study extended to other copolymers and their blends of different ratios by SEM and solid-state NMR and calculate the total free energy of mixing and the different contributions over the entire composition range using the Painter–Coleman association model.

## CONCLUSIONS

This study showed that depending on the nature of the solvent used, THF or butan-2-one, the densities of carboxylic or amide groups introduced within polystyrene matrix, homogenous solutions, or interpolymer complexes are observed as a result of interpolymer hydrogen bonding that occurred between the acid groups of SAA-27 and the amide carbonyl of the SAD copolymers or PDMA. This was first evidenced by DSC by the appearance of a single  $T_g$  for each of the blends and complexes. FTIR results confirm then the presence of these hydrogen bonding interactions qualitatively by the appearance of two new bands at 1730 and 1616 cm $^{-1}$  characteristic of the liberated carboxyl groups and associated amide carbonyl groups respectively, and quantitatively from the evaluation of the fractions of the liberated carboxyl groups and the associated amide in the 1800–1550 cm $^{-1}$  region.

Self-association equilibrium constants of the SAA-27 and its interassociation constants with SAD-17 were determined in the studied temperature range in both carbonyl and amide regions, using the Painter–Coleman Association Model. The enthalpies of hydrogen bond formation for the SAA copolymer and for its blends of different ratios with SAD-17 were obtained from Van't Hoff plots. These blends are miscible even at 180°C as confirmed from the negative values of the total free energy of mixing  $\Delta G_M$  and the positive second derivative with respect to composition over the entire blend composition.

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