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Interpolymer Complexes of Poly(N,N-Dimethylacrylamide/Poly(Styrene-co-Acrylic Acid): Thermal Stability and FTIR Analysis

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Summary: This contribution will focus on the elaboration and characterizations of new materials with optimal properties as interpolymer complexes, upon mixing poly (styrene-co-acrylic acid containing 18, 27 and 32 mol % of acrylic acid (SAA-x) and poly (N,N-dimethylacrylamide) (PDMA), through the control of the densities, strength, self-association and accessibility of the interacting species. These elaborated interpolymer complexes, of different structures, investigated by DSC and TGA, exhibited a significant improved thermal stability. Their DSC analysis showed that all these materials showed one composition-dependence glass transition temperature Tg, indicating the formation of a single homogeneous phase. The different behaviors of Tg-initial composition observed with these systems were analyzed by the approaches of Kwei and Brostow et al., recently developed. The specific interactions that occurred within the elaborated materials were evidenced qualitatively by ATR/FTIR spectroscopy, from the appearance of new bands in the 1800–1550 cm^{-1} region.

Keywords: hydrogen bonding; Interpolymer complexes; Poly (N, N-dimethylacrylamide); poly (styrene-co-acrylic acid)

Introduction

Poly (N,N-dimethylacrylamide) (PDMA) is a highly hygroscopic proton acceptor tertiary amide polymer with two possible hydrogen bonding accepting sites and the carbonyl group as the major one.[1,2] This polymer is for instance reported immiscible with poly (ethylene) and poly (vinyl acetate) but due to the presence of specific interactions that it develops, this latter polyamide is miscible with poly (vinyl alcohol) and a wide range of random poly (ethylene-co-vinyl alcohol) and poly (vinyl acetate-co-vinyl alcohol) copolymers and with several other polymers and copolymers containing complementary groups favourable for specific interactions.[2] Accordingly and depending on several factors, this polymer also formed interpolymer complexes.[2–8] One expects that mixing polystyrene, a hydrophobic polymer with PDMA, would to improve the hygroscopic property of the resulting material. Unfortunately these two homopolymers are immiscible. On the other hand, poly (acrylic acid) (PAA) is a polymer largely used in the elaboration of various biomaterials.[9–13] One of its undesirable properties is its low thermal stability that limits however its uses in many specific applications.

PDMA is relatively more thermally stable than poly (acrylic acid). Interpolymer complexes as precipitates are instantaneously formed upon mixing PDMA with PAA in methanol. It may be of very specific interest to elaborate materials with combined optimal properties, particularly improved heat resistant and less hygro-

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scopic as miscible blends or interpolymer complexes, by mixing PDMA and poly (styrene-co-acrylic acid) through the control of the densities of specific groups that optimize the interactions that occur between the complementary constituents of the mixtures.

The density, strength, self-association and accessibility of the interacting species affect the complexation phenomenon.[13,14] M. Jiang et al. reported that interpolymer complexation occurs when the density of specific interactions between the proton-donating and the proton-accepting reaches a certain level.[15]

We will, in this contribution, study the effect of increasing carboxylic acid content within the polystyrene matrix on the interpolymer complexation phenomena of these copolymers with PDMA or copolymers of this latter with styrene (SAD). FTIR spectroscopy will be used to evidence qualitatively the formation of these complexes from the presence of specific interactions that occurred between their constituents. The thermal properties of these materials will be investigated by TGA and DSC. Their Tg- composition behaviors will be analyzed by Kwei[16] and Brostow et al[17] approaches.

Experimental Part

Polymer Synthesis and Characterizations

Poly (N,N-dimethylacrylamide) (PDMA), random copolymers of styrene, and N,N-dimethyl acrylamide containing 17 or 32 mol % of N,Ndimethylacrylamide (SAD-17, SAD-32) and of styrene with acrylic acid SAA of different compositions (18, 27 and 32 mol %) of acrylic acid were prepared by bulk free-radical polymerization using azo-bis-isobutyronitrile as the initiator at 60 °C and keeping the conversion low. These copolymers were purified by repeated dissolution/precipitation in THF/methanol and to remove the residual solvent they were then dried to constant weight in a vacuum oven for several days at 60 °C. They were characterized as previously described[18–20] by elemental analysis, UV spectroscopy and proton NMR. Their average molecular weights were examined by size exclusion chromatography using a Waters HPLC (elution with THF on cross-linked polystyrene: rate 1 ml/min, calibration with polystyrene standards). Intrinsic viscosities [η], average molecular weights, polymolecularity indices (PID) and glass transition temperatures (Tg) of these polymers cast from butan-2-one are listed in Table 1.

Preparation of Blends and Interpolymer Complexes

SAA copolymers and PDMA or SAD copolymers were separately dissolved in THF or butan-2-one. Appropriate amounts of acidic solutions were mixed together to PDMA or SAD solutions.

ATR/FTIR Measurements

Mixtures of different ratios of SAA18, SAA27, SAA32 and PDMA or SAD32 were prepared by co-dissolution of the polymers in a butan-2-one. The formed interpolymer complexes as precipitates were isolated and dried in a vacuum oven for several days at 60 °C. ATR/FTIR spectra of these complexes were recorded at room temperature on a Vertex 70 FTIR/ATR spectrometer with a spectral resolution of 2 cm^{-1}. 60 scans were signal-averaged.

Thermal Measurements

The glass-transition temperatures (Tg) of the copolymers and their mixtures of different ratios were determined with a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 K/min.

Table 1.
Characteristics of polymers.

Polymer	[η]	Mn 10^{-4}	Mw 10^{-4}	PID	Tg (°C)
SAD-17	–	6.08	1.27	2.09	108.0
SAD-32	–	6.04	1.28	2.12	102.0
SAA-18	1.74^{THF}	–	–	–	130.0
SAA-27	–	10.00	14.6	1.46	135.0
SAA-32	–	2.47	4.27	1.73	149.0
PDMA	$1.20^{Methanol}$	–	–	–	110.0

Tg was taken as the average value of the midpoint of the heat capacity change of several scans.

TGA Measurements

A Thermogravimetric analysis of these complexes was carried out on a TA instrument TGA 2590 under nitrogen atmosphere from 25 °C to 500 °C at a heating rate of 20K/min.

Results and Discussion

Complexation

The results of this study showed that homogeneous phases are observed when each of the SAA copolymers is mixed together with SAD17 or PDMA in THF while cloudy solutions were observed when SAA32 was mixed with SAD17 in butan-2-one. Precipitate interpolymer complexes of compact structures were formed with these acidic copolymers and PDMA when the common solvent is butan-2-one. Indeed, the competition between polymer-solvent and polymer-polymer interactions governs the complex formation processes. SAA-27 also formed soluble interpolymer complexes in THF and precipitate interpolymer complexes with SAD-32 over the entire feed composition in butan-2-one.[18]

All these SAA/PDMA interpolymer complexes, as precipitates, were isolated and then dried in a vacuum oven at 60 °C for several days to constant weight.

Figure 1 displays the complex yields of these two systems. As it can seen in this Figure, the complex yield of the SAA18/PDMA system, in the range of 21 -68%, first increases, goes through a maximum around 50% by weight of SAA18 then decreases as the content of SAA18 in the feed composition increases.

Similar behavior but with higher yields of interpolymer complexes, varying slightly with the initial feed composition and a maximum yield practically constant within a broader range, shifting towards initial composition containing an excess of PDMA, was observed in butan-2-one when PDMA is mixed with SAA32, a copolymer containing a higher content of carboxylic groups.

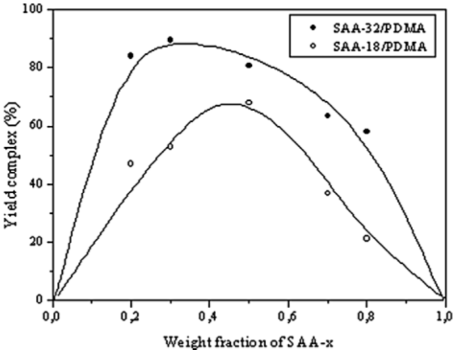


Figure 1.
Illustration of yield versus feed composition for SAA-18/PDMA and SAA-32/PDMA complexes.

The composition of these complexes was obtained from the nitrogen content determined by elemental analysis. Table 2 summarizes the results.

Thermal Analysis

DSC

It is worth recalling that we previously showed[19] that while SAA18/SAD17 formed homogeneous phase in butan-2-one, turbid solutions were observed in the same common solvent with SAA32/SAD17 systems. All these blends, as-cast from butan-2-one, exhibited a single Tg. The Tg of SAA18/SAD17 blends varied positively from the weight average of the pure constituents as shown in Figure 2. While

Table 2.
Characteristics of SAA-18/PDMA and SAA-32/PDMA complexes

SAA-18/PDMA	1	2	3	4	5
Feed composition[a]	20.0	30.0	50.0	70.0	80.0
Feed composition [b]	20.2	30.2	50.3	70.2	80.3
Bulk composition [b]	39.5	49.0	58.5	74.2	83.8
Yield of the complex wt%.	47.0	52.7	68.0	36.8	21.1

SAA-32/PDMA	1	2	3	4	5
Feed composition[a]	20.0	30.0	50.0	70.0	80.0
Feed composition [b]	21.0	31.1	51.3	71.1	80.8
Bulk composition [b]	29.5	49.1	55.0	61.7	86.04
Yield of the complex wt%.	83.8	89.2	80.6	63.3	57.9

[a]Wt.-% of SAA-x,[b]Mol.-% of SAA-x

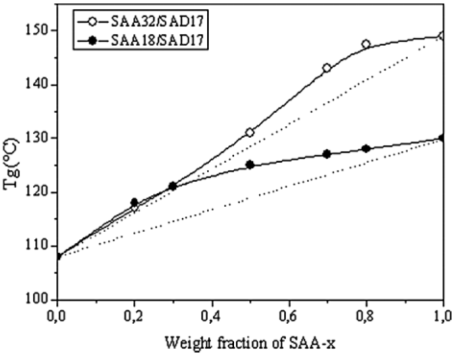


Figure 2.
Variation of the glass transition temperature with SAA-x composition for SAA-32/SAD-17 and SAA-18/SAD-17 mixtures cast from butan-2-one.

Table 3.
Fitting parameters using equation of Brostow et al.

System	Kwei	Brostow et al.		
SAA18/SAD17	$q=24$	$a_0^F=24$	$a_1^F=17$	$a_2^F=3$
SAA32/SAD17	$q=13$	$a_0^F=10$	$a_1^F=-33$	$a_2^F=42$
SAA18/PDMA	$q=33$	$a_0^F=31$	$a_1^F=-6$	$a_2^F=15$
		$a_0^B=15$	$a_1^B=-48$	$a_2^B=-11$
SAA32/PDMA	$q=-45$	$a_0^F=-24$	$a_1^F=97$	$a_2^F=-191$
		$a_0^B=-34$	$a_1^B=58$	$a_2^B=-275$

F: Complex Feed Composition, B: Complex Bulk Composition

this system shows a good fitting of the experimental data to the Kwei equation with a q constant of 24 (Table 3), the positive deviation decreased with an increase of the content of carboxylic groups within the polystyrene matrix in the case of SAA32/SAD17. A positive deviation is observed only for blends containing an excess of SAA32.

The same study also confirmed that spacing the carboxylic groups within polystyrene matrix optimized the hydrogen bonding interactions in poly (styrene-co-acrylic acid)/poly (styrene-co-N, N-dimethylacrylamide) homoblends.[19]

The single Tg observed with each interpolymer complex of the systems under study is an indication of the formation of single phase. As shown in Figure 3, different behaviors of Tg-initial composition are observed with these systems.

The Tg of the complexes resulting from SAA18/PDMA binary system are higher than those calculated from the additivity rule, resulting from a high number of interpolymer interactions. While the Tg values of the SAA18/PDMA complexes varied with the composition, practically the same single Tg is observed with the SAA32/PDMA complexes of different original mixtures. Table 4 gathers the different values of glass transition temperatures Tg and ΔTg of SAA18/PDMA and SAA32/PDMA complexes. We can note that the stoichiometry of the interpolymer complexes was found to vary with the densities of the interacting species. A better homogeneity is obtained with (50/50) composition for SAA18/PDMA complex. This suggests that SAA- 18 prefers to form in butan-2-one 1: 1 ratio complexes with

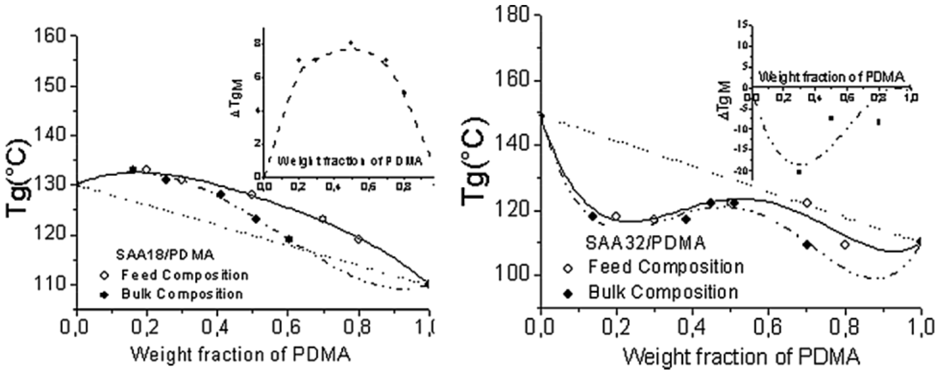


Figure 3.
Brostow et al. fits with feed and bulk complex composition for SAA-x/PDMA.

Table 4.
Values of glass transition temperatures Tg and ΔTg of SAA18/PDMA and SAA32/PDMA complexes

Complex	Tg	Δ Tg
SAA18/PDMA		
100/0	130	10
80/20	133	28
70/30	131	27
50/50	128	22
30/70	123	24
20/80	119	25
0/100	110	14
SAA32/PDMA		
100/0	149	12
80/20	118	33
70/30	117	30
50/50	122	28
30/70	122	24
20/80	109	23
0/100	110	14

PDMA, while a better homogeneity is observed with (20/80) for SAA32/PDMA complex. The SAA32 copolymer is expected to develop a higher number of specific interactions, this may be due to a more important self-association effect as the density of carboxylic groups increases within the acidic copolymer.

The positive deviation from the linear average line observed with the system above is characteristic of the presence of strong specific interpolymer interactions.

An analysis of these specific interactions was carried out using the well-known Kwei[16] approach and the recently one proposed by Brostow et al.[17] and Kalogeras[21,22] described by the equations below:

Kwei equation (K =1)

$$T_{g,blend} = w_1 T_{g,1} + w_2 T_{g,2} + q w_1 w_2 \tag{1}$$

Brostow equation*:*

$$T_{g\,(blend)} = w_1 T_{g,1} + (1-w_1) T_{g,2} + w_1(1-w_1)[a_0 + a_1(2w_1-1) + a_2(2w_1-1)^2] \tag{2}$$

Where Tg, 1 or 2 and w1 or 2 are the glass transition temperatures of the pure components and their corresponding weight fractions, respectively. q and a_i are adjustable parameters determined from experimental Tg-composition curves.

It is well known that "q" constant measures the extent of specific interactions that occurred between the two copolymers. Accordingly, the obtained q values confirmed that indeed stronger interpolymer interactions occurred for the SAA-x/SAD-17 systems (Table 3) A higher q value (of 24) obtained with SAA-18/SAD-17 is due to stronger and more important favourable interpolymer interactions that led to highly interassociated polymer systems.

The Tg-Feed composition of the SAA18/PDMA system is fairly described by the Kwei equation. The relatively high value of 33 obtained with this system indicates that important favourable interpolymer interactions occurred and also led to highly inter-associated polymer complexes.

The highest Tg value, observed with the complex prepared from an initial SAA18 composition of 80% by weight deviated slightly from the best Kwei equation fit and does not correspond to the highest complexation yield, obtained for 50% by weight of SAA18.

The Tg of the interpolymer complexes are not necessarily higher than the average value of their constituents. Indeed, the results obtained with the SAA32/PDMA system showed a negative deviation from the additivity rule when the proton-donating polymer SAA32 is in excess. This is due to the self-association of carboxylic groups within the SAA32.

However, better fitting results are obtained when the Brostow et al. equation is used with only three parameters listed in Table 3, as shown in Figure 3.

In a previous article,[23] the different Tg-composition behaviors of the SAAx/SAD17 blends cast from THF, were well analyzed by the Brostow et al. recently developed approach.

The results of these analyses showed that both Kwei and Brostow et al. approaches interpreted very well the Tg-composition behavior of the SAA18/SAD17 system cast from butan-2-one. The decrease of q and a0 values with an increase of the carboxylic acid density as within SAA32/SAD17 is an evidence of carboxylic self-association contribution in the decrease of interpolymer interactions. The moderate a1 and a2 absolute values indicate a less complex Tg-composition behavior with a slight deviation of the maximum of interactions from the volume fraction of low Tg SAD17 from 0.5.

The a_0 parameter is a measure of the extent of the specific interaction strength. The positive values, close to Kwei q constant, indicate that strong specific inter-polymer interactions occurred within these blends. In agreement with Kwei constant, the decrease of this parameter from positive value to a negative one as the content of acrylic acid increases within SAA32 copolymer is, among other effects, due to low density of inter-polymer specific interactions and carboxylic self-association within SAA32 copolymer.

The moderate positive $a_0^F = 31$ and relatively low absolute $a_1^F = -6$ values obtained with SAA18/PDMA system, indicate, as shown in inserts of Figure 3, an enhanced up-shift with respect to the linear mixing rule for mixtures, with the low-Tg PDMA volume fraction very close to 0.5. This result is in a good agreement with the illustration of yield versus feed composition for SAA-18/PDMA complexes shown in Figure 1.

A slightly different behaviour but with the same trend of variation is observed with SAA18/PDMA versus bulk composition. The more negative $a_1^B = -48$, indicated that the maximum of interactions occurred when a lower volume fraction than 0.5, of low-Tg PDMA was mixed to SAA of higher Tg. The small a_2^F and a_2^B absolute values obtained with this SAA18/PDMA system reflect its less complex behavior.

The negative $a_0^F = -24$ and $a_0^B = -34$ values and relatively high positive $a_1^F = 97$ and $a_1^B = 58$, observed with SAA32/PDMA indicate that the maximum negative deviation of Tg-composition occurred at a volume fraction of PDMA below 0.5 and, in a good agreement with Figure 1, the maximum density of interactions is observed when low-Tg PDMA is in excess as confirmed in insert of Figure 3. The high absolute values of a_2 parameter reflect the complexity of this system and its anomalous behavior with the composition.

TGA Analysis

A thermogravimetric study was carried out to get preliminary information on the thermal stability of the copolymers and of their mixtures A two-step process of degradation is detected with these copolymers. A first loss of mass is observed in the 110–196 °C temperature range for the SAA-32 copolymer. The corresponding very low mass loss of 5% observed with the as-cast SAA-32 was attributed mainly to moisture absorption or anhydride formation and its level off between 196 °C and 310 °C confirms the significant thermal stabilization of SAA32 copolymer compared with PAA, the thermal degradation mechanism of PAA is clearly explained by Lau, C and all in their article published Polymer 2002, 43, 823. The second degradative step starts only above 310 °C. A practically similar thermal degradation process with an increase of the first loss of mass (21%) is observed with the basic components PDMA.

The thermogravimetric traces (TGA) of SAA32, PDMA and their complexes of different ratios and of their corresponding derivative thermogravimetric d(TGA) are shown in Figure 4 while Table 5 summarizes their thermogravimetric parameters that also includes among others the temperatures at which 5% and 50% degradation occurred. It is evident from these figures that the thermal degradation of SAA32/PDMA complexes proceeds by two steps represented by two peaks in the corresponding d (TGA) curves. The first step, located between 110 °C and 220 °C is attributed to loss of adsorbed water (The acrylic acid and N,N-dimethylacrylamide comonomers have hydrophilic characters). The second step corresponds to the main chain of the complex degradation and to the decarboxylation and carbonization pro-

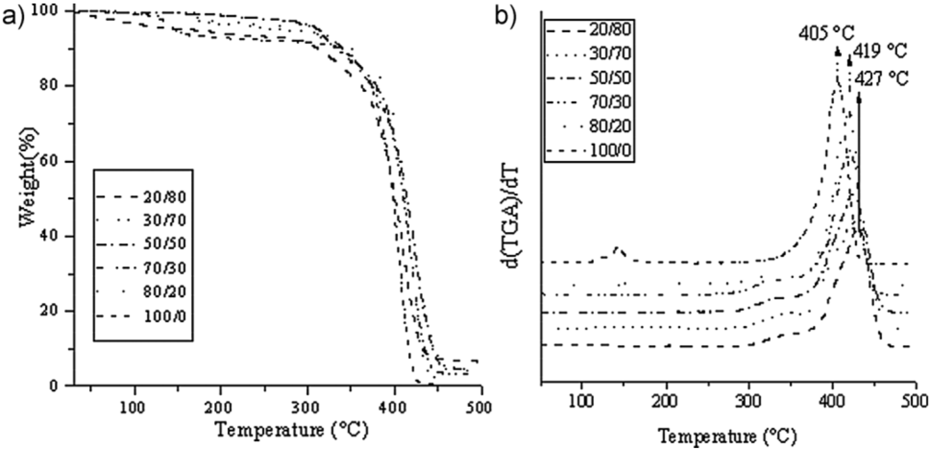


Figure 4.
Thermogravimetric TGA (a) and derivative Thermogravimetric (dTGA)/dT (b) curves of SAA-32(100/0), PDMA(0/100) and their complexes of different ratios.

Table 5.
Thermogravimetric parameters of SAA-27/SAD-32 and SAA-32/PDMA and their different complexes.

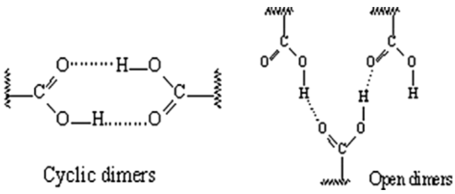
Complex	Stage 1		Stage 2		
	(T^a (°C)	(m^b (%)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	Td_{max} (°C)
SAA-32/PDMA					
0/100	30-226	21.0	121	420	428
20/80	170-201	2.00	165	400	430
30/70	120-220	1.00	273	413	427
50/50	120-196	1.00	312	414	424
70/30	150-196	1.00	306	412	421
80/20	150-205	0.50	294	411	419
100/0	110-196	5.00	146	398	405

cesses, whose temperature of maximum degradation increases with PDMA composition increase in the SAA32/PDMA complexes (T_{max} increase from 419° to 430 °C).

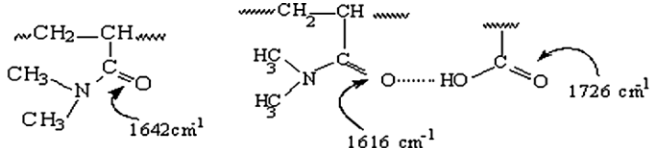
This analysis shows that these as-cast materials absorb an amount of water varying from 21% for PDMA to 1 or 0.5% for complexes. This will affect the interpolymer interactions and explain the enhanced thermal degradation observed with these materials. Indeed, the T5%, T50% and the Td_{max} of the isolated precipitates are higher than those of the pure constituents.

ATR/FTIR Analysis

The formation of SAA/PDMA and SAA/SAD interpolymer complexes is mainly due to the presence of relatively strong and sufficient density of carboxyl-amide specific interactions that occurred between the two components of these systems .We have used FTIR/ATR to identify and quantify these specific interactions. According to the chemical structures of the copolymers and considering the interactions at the carbonyl groups only the major interactions that occurred between the carboxyl and amide groups are described by the schemes below:



Scheme 1.
Possibilities for carbonyl groups in relation to hydrogen bonding.



Scheme 2.
Free amide carbonyl and carboxylic acid-amide interassociation.

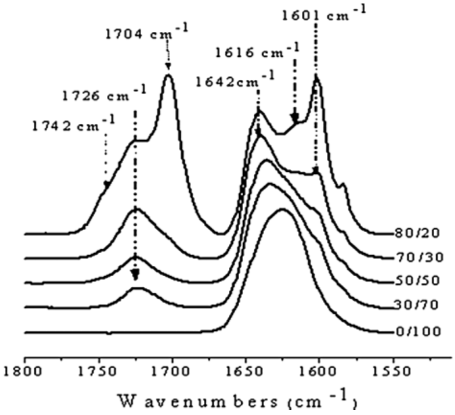


Figure 6.
Scale-expanded infrared spectra of SAA-18/PDMA complexes in 1800-1550 cm^{-1} region.

Qualitatively and as previously reported,[18] the acidic SAA copolymers showed two peaks at 1742 cm^{-1} and 1704 cm^{-1}, attributed to free and associated carboxylic groups, respectively while PDMA or SAD polymers displayed a strong absorption at about 1642 cm^{-1} attributed to the free amide carbonyl groups. The intensities of these bands were affected upon mixing SAA with PDMA or SAD17 and two new bands characterizing the specific interactions, attributed to carbonyl groups that are liberated and associated amide carbonyl groups respectively, appeared at around 1726 cm^{-1} and 1616 cm^{-1}.[18,20] Figure 5, 6 compare scale expanded FTIR spectra of SAA18/SAD17 blends cast from butan-2-one to those of SAA18/PDMA complexes recorded at room temperature in the 1800-1550 cm^{-1}. The intensity of the associated amide band increases with an increase of the SAA18 content in the blend or interpolymer complexes. As the content of amide groups within the proton-acceptor increases, as in the SAA27/SAD-32 systems which formed precipitate interpolymer complexes, the intensity of the liberated carbonyl groups increases compared to that observed in SAA-27/SAD-17 blends.

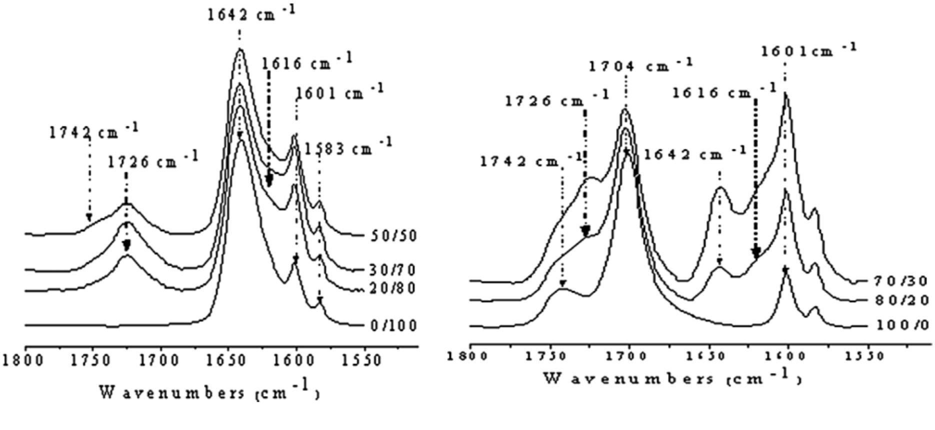


Figure 5.
Scale-expanded infrared spectra of SAA-18/SAD-17 blends in 1800-1550 cm^{-1} region.

Conclusion

This study showed that, due to the presence of specific interpolymer interactions, novel materials of different structures and significant improved thermal stability, were elaborated as precipitates, when poly (styrene-co-acrylic acid) and poly (N,N-dimethylacrylamide) are mixed together in butan-2-one.

Two new bands characterizing the specific interactions, attributed to carbonyl groups that are liberated and associated amide carbonyl groups respectively, appeared at around 1726 cm^{-1} and 1616 cm^{-1} and that led to the formation of such complexes were evidenced qualitatively in the solid state by ATR/FTIR spectroscopy.

The DSC analysis showed a change in the shape of the variation of Tg-composition as the densities of interacting species within the polystyrene matrices increased. Positive deviation is observed with complexes formed from acidic copolymer containing 18 mol% of acrylic acid (SAA18), while a different behavior is observed upon increasing the content of carboxylic groups within the polystyrene matrix as with the SAA32/PDMA system.

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