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Elaboration and Morphology Investigation of Poly(styrene-*co*-acrylic acid)/Poly(styrene-*co*-*N*,*N*-dimethylacrylamide) Interpolymer Complexes

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Summary: Random copolymers of styrene with acrylic acid (SAA) and with N, N-dimethylacrylamide (SAD) of different compositions were prepared and characterized. Depending on the nature of the solvent and the densities of interacting species incorporated within these polystyrene matrices, novel materials as soluble interpolymer complexes in THF or precipitates from butan-2-one were elaborated when SAA and SAD copolymers are mixed together due to the presence of specific interpolymer interactions. These specific intermolecular interactions were evidenced by ATR/FTIR spectroscopy, qualitatively from the appearance of new bands in the 1800–1550 cm^{-1} region and quantitatively using adequate spectral curve fitting for the determination of the fraction of the different species. The DSC analysis showed that all these materials as soluble or precipitate interpolymer complexes exhibited one composition-dependence glass transition temperature T_g, indicating that they are homogenous on a 20–40 nm scale. Information about the mixing at a smaller scale obtained by solid state proton NMR, provided from measurements of proton spin relaxation times T_1 (H) and $T_1\rho$ (H) in the laboratory and rotatory frames carried out for SAA-27, SAD-17 and their (70/30 and 50/50) mixtures as cast from THF or butan-2-one, confirmed similar phase behaviour promoted by a solvatation effect. The single T_1 (H) observed in the pure components and their blends as cast from both THF and butan-2-one confirm that these blends are homogeneous on the scale of 20–40 nm. Furthermore, the $T_1\rho$ (H) recoveries indicate that the blends were homogeneous on the scale of 2–3 nm only when cast from THF, while composite recovery curves $T_1\rho$ (H) were however observed with SAA-27 and its mixtures of different ratios below 120 °C when butan-2-one is the casting medium.

Keywords: complexation; hydrogen bonding; poly(styrene-*co*-acrylic acid); poly(styrene-*co*-*N*, *N*-dimethylacrylamide); solid state ^{1}H NMR

Introduction

The elaboration of polymer materials with improved properties from inter polymer complexes through specific molecular interactions in organic solvent has been over the last decades and is still of a great interest for material scientists. The formation of such interpolymer complexes from binary polymer mixtures is mainly due to the nature of the solvent and the presence, density and strength of interactions that occurred between the two components in the mixture.[1–3]

Different types of interpolymer complexes are reported in the literature[4,5] as

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soluble with a loose structure or as precipitates with a stable structure when the polymer-polymer interactions that occurred between the dissimilar components of the mixture are much stronger than polymer-solvent interactions

We have previously reported on the interpolymer complex formation upon mixing copolymers containing various densities of interacting species of different nature[6–8] in solution by viscometry choosing in most cases THF and butan-2-one as the common solvent. Indeed due the strong ability of THF to form hydrogen bonding with the different proton-donating copolymers that we have used, most binary mixtures formed homogeneous phase in THF even for relatively high densities of interacting species while gel-like or precipitates materials were obtained from mixtures prepared in butan-2-one when sufficient interactions occurred between the complementary groups.

In the solid state, the observation of a single glass transition temperature T_g with each of these binary systems, determined by DSC, is an indication of the formation of homogeneous phases on a scale of 20–40 nm due to the presence of hydrogen bonding interactions that occurred between the complementary groups in these complexes as evidenced by FTIR.

In a very recent study,[9] we have synthesized poly(styrene-*co*-acrylic acid) and poly(styrene-*co*-*N*,*N*-dimethylacrylamide) of various densities of interacting species and investigated the complexation behaviour of mixtures of these copolymers in THF and butan-2-one.The results showed that while one homogeneous phase is observed in THF with each composition of poly(styrene-*co*-acrylic acid) containing 27 mol % of acrylic acid (SAA-27) and poly(styrene-*co*-N,N-dimethylacrylamide) containing 17 mol % of *N*,*N*-dimethylacrylamide (SAD-17) mixture, turbid solutions observed when butan-2-one solutions of these copolymers are mixed together indicates their phase transition.

Since some specific properties of these materials depend strongly on their levels of mixing and as an extension of this work, we have in this contribution investigated the morphology and the phase behaviour of interpolymer complexes based on SAA-27 and SAD-17 in the solid state at different scales of mixing as-cast from THF and butan-2-one by DSC, FTIR/ATR and by solid state proton NMR from measurements of the proton spin relaxation times T_1 (H) and $T_1\rho$ (H) in the laboratory and rotatory frames carried out for SAA-27, SAD-17 and their (70/30 and 50/50) mixtures.

Experimental Part

Polymer Synthesis and Characterizations

Random copolymers of styrene a) with acrylic acid SAA-27 containing 27 mol % of acrylic acid and b) with *N*,*N*-dimethylacrylamide containing 17 or 32 mol % of N,N-dimethylacrylamide (SAD-17, SAD-32) 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 then dried to constant weight in a vacuum oven for several days at 60 °C. They were characterized as previously described[9] 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). The characteristics of these copolymers are listed in Table 1.

ATR/FTIR Measurements

Mixtures of different ratios of SAA-27 and SAD-17 or SAD-32 were prepared by co-dissolution of the copolymers in a common solvent (THF or butan-2-one). Films were generated from THF solutions with evaporation of the solvent with pure polymers or their blends. In the case of SAA-27/SAD-32 mixtures in butan-2-one, interpolymer complexes as precipitates were

Table 1.
Characteristics of the copolymers.

Polymer	M_n 10^{-4} (g/mol.)	M_w 10^{-4} (g/mol.)	I
SAD-17	6.08	12.7	2.09
SAD-32	6.04	12.8	2.12
SAA-27	10.00	14.6	1.46

M_n = number-average molecular weight, M_w = weight-average molecular Weight, I = molecular weight distribution.

formed, isolated, and dried in a vacuum oven for several days at 60 °C. ATR/FTIR spectra of these two types of 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 (T_g) 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. T_g was taken as the average value of the midpoint of the heat capacity change of several scans.

Solid State ^{1}H NMR Measurements

Proton NMR measurements were carried out on a Bruker SXP spectrometer operating at 60 Mhz (a home build set up at Laboratory of Prof. Weill's group at institut Charles Sadron).[10,11]

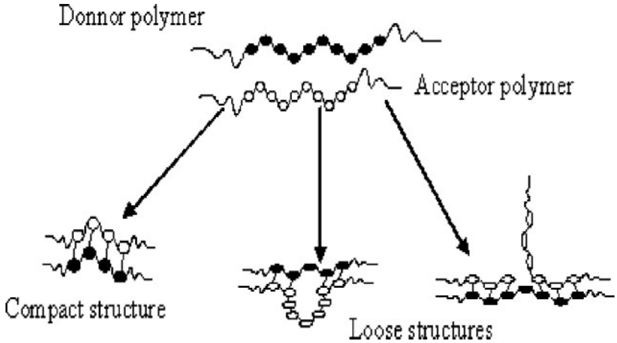
Measurements of the spin-lattice relaxation time in the laboratory frame T_1 (H) at 60 MHz were performed by the inversion recovery sequence.

For the spin-lattice relaxation time in the rotating frame $T_1\rho$ (H) was obtained in standard spin locking decay.

Results and Discussion

The results of this study showed, that depending on the nature of the solvent and the densities of interacting species introduced within the (SAA or SAD) copolymers, when pairs of these copolymers are mixed together in a common solvent, two kinds of materials were obtained from homogeneous phases (as soluble interpolymer complexes of loose structure) or as precipitate interpolymer complexes (of compact structure). Indeed, the competition between polymer-solvent and polymer-polymer interactions governs the complex formation processes (Scheme 1).

SAA-27/SAD-17 and SAA-27/SAD-32 mixtures of different ratios in THF or butan-2-one were prepared. Homogeneous and cloudy solutions were obtained with SAA-27 and SAD-17 when THF or butan-2-one solvents were respectively used. SAA-27 formed, however, soluble interpolymer complexes in THF and precipitate interpolymer complexes with SAD-32 over the entire feed composition in butan-2-one. These latter interpolymer complexes, as precipitates, were isolated and then dried in a vacuum oven at 60 °C for several days to a



Scheme 1.
Some structures which can be adopted by the complexes.[12]

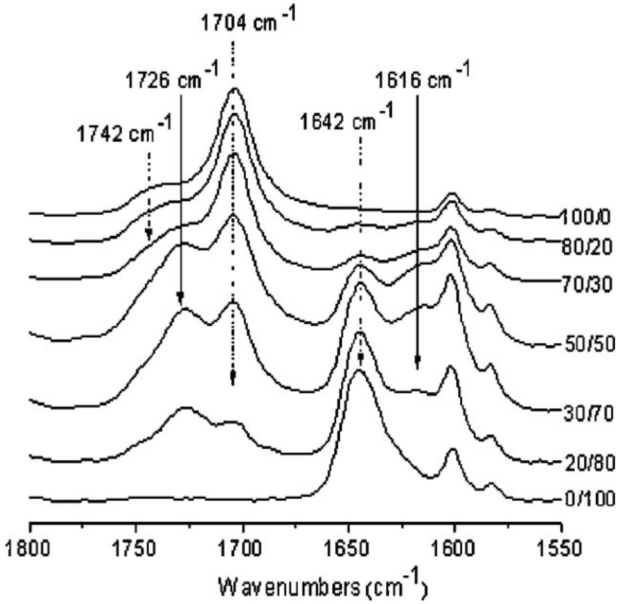


Figure 1.
Scale expanded ATR spectra of SAA-27/SAD-17 blends in the 1800–1550 cm^{-1} region.

constant weight. The nitrogen content in the SAA-27/SAD-32 interpolymer complexes was determined in a similar way as previously described[9] by elemental analysis. The compositions of the SAA-27/SAD-32 complexes, in the range 55–82 centered at 53 mol % of SAA-27, suggest that SAA-27 prefers to form in butan-2-one 1:1 ratio complexes with SAD-32.

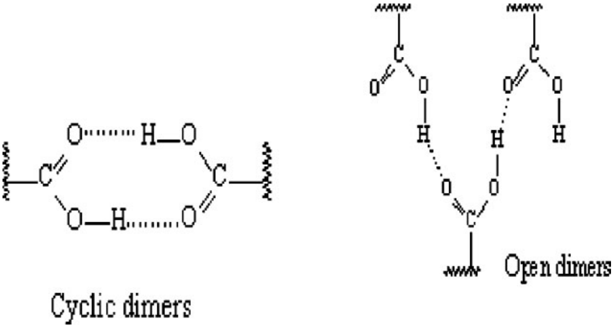
ATR/FTIR Analysis

The formation of interpolymer complexes is due to the density and strength of the hydrogen bonding interactions that occurred between these two components (involving carboxyl and amide groups). We have used FTIR/ATR, one of the most powerful technique, to identify and quantify such specific interactions. According to the chemical structures of the copolymers, the interactions involved between the carboxyl and amide groups may be described by the schemes below:

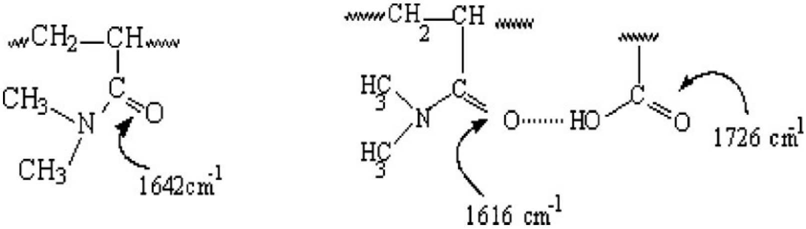
We have in a first step carried out a qualitative analysis of these specific interactions arising from hydrogen bonding between the carboxylic groups of the SAA and the amide groups of the SAD in the carbonyl-stretching 1800–1550 cm^{-1} region. Figure 1 illustrates as an example the ATR/FTIR spectra of pure SAA-27, SAD-17 and of their as-cast blends of different ratios from butan-2-one recorded at room temperature.

The acidic SAA-27 copolymer showed two peaks at 1742 cm^{-1} and 1704 cm^{-1}, attributed to free and associated carboxylic groups, respectively while the SAD-17 or SAD-32 copolymers displayed a strong absorption at about 1642 cm^{-1} attributed to the free amide carbonyl groups. As SAD is added to SAA, the intensities of these bands are affected and two new bands of increasing intensity appeared at around 1726 cm^{-1} and 1616 cm^{-1}. These latter bands are attributed to carbonyl groups that are liberated and associated amide carbonyl groups respectively as a result of carboxyl–amide associations.

As shown in Figure 2 as the content of amide groups within the SAD increases, as in the SAA-27/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.



Scheme 2.
Possibilities for carbonyl groups in relation to hydrogen bonding.[9]



Scheme 3.
Free amide carbonyl and carboxylic acid-amide interassociation.[9]

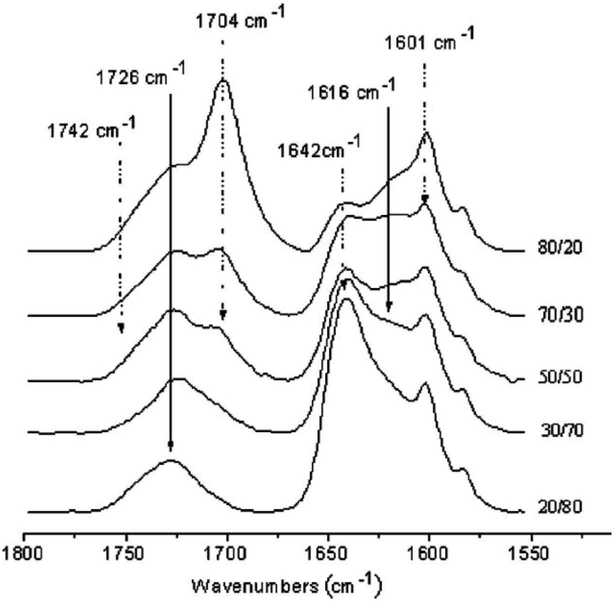


Figure 2.
Scale expanded ATR spectra of SAA-27/SAD-32 complexes in the 1800–1550 cm^{-1} region.

Table 2.
Curve-fitting data from ATR spectra of SAA-27/SAD-17 and SAA-27/SAD-32 systems in the 1670–1550 cm^{-1} amide region at room temperature.

	SAA-27/SAD-17 (THF)			**SAA-27/SAD-17** (Butan-2-one)			**SAA-27/SAD-32** (Butan-2-one)		
	ν cm^{-1}	W cm^{-1}	f	ν cm^{-1}	W cm^{-1}	f	ν cm^{-1}	W cm^{-1}	f
80/20	1645	19	0.260	–	–	–	1645	15	0.097
	1614	38	0.740	–	–	–	1615	52	0.903
70/30	1646	19	0.270	–	–	–	1643	18	0.114
	1613	38	0.730	–	–	–	1617	52	0.886
50/50	1644	18	0.297	1646	18	0.181	1643	18	0.123
	1615	39	0.703	1616	42	0.819	1617	52	0.877
30/70	–	–	–	1644	16	0.268	1643	20	0.203
	–	–	–	1618	42	0.732	1618	48	0.797
20/80	1646	20	0.324	1643	18	0.291	1643	20	0.236
	1613	40	0.676	1617	43	0.709	1622	44	0.764

ν = Wavenumber, W = Width at ½ height, f = Mole fraction.

Figure 1 and 2 show that the intensity of the associated amide band increases with an increase of the SAA-27 content in the blend.

In a second step, a quantitative analysis of these interactions was carried out in the 1670–1550 cm^{-1} 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 from the spectra of the blends with Gaussian and Lorentzian spectral curve-fitting procedures, respectively, for the amide and styrene bands with the following relation:

$$f_{\mathrm{ass}}^{\mathrm{amide}} = 1 - \frac{\mathrm{A}_{1642}}{\mathrm{A}_{1642} + \frac{\mathrm{a}_{1642}}{\mathrm{a}_{1616}}\mathrm{A}_{1616}} \qquad (1)$$

where A_{1642} and A_{1616} are the areas of the bands at 1642 cm^{-1} and 1616 cm^{-1}, respectively, a_{1642} and a_{1616} are the absorptivities of the two bands, assuming an absorptivity ratio of 1.[13] Table 2 summarizes the curve-fitting data that confirm the solvent effect, in agreement with the qualitative observations. Broader bands are observed with the associated amide groups for SAA-27/SAD-32 complexes.

DSC Analysis

DSC is one of the most widely used techniques for evaluating the phase behaviour of binary mixtures of polymers.[14,15] One T_g intermediate between the glass transition temperatures of the two pure SAA-27 and SAD-17 copolymers, was observed from the DSC thermograms of the materials cast from the homogeneous mixtures of the different compositions prepared in THF or the cloudy solutions observed when SAA-27 is mixed with SAD-17 in butan-2-one. As shown from Figure 3, the different behavior of T_g-composition observed with these as cast SAA-27/SAD-17 mixtures is attributed to the solvent effect characterized by $\Delta\chi$.[16–18] This solvent effect on the T_g of the mixtures is confirmed with these SAA-27/SAD-17 systems that led to a more pronounced $\Delta\chi$ effect with significant difference between the T_g of the mixtures cast from butan-2-one and those obtained from THF.[9]

As the density of the interacting species is increased, a single phase as with blends is observed with SAA-27/SAD-32 interpolymer complexes. As can be seen from Figure 4, the T_g of the complexes are higher than those calculated from the additivity rule, resulting from higher number of interpolymer interactions that occurred between the carboxylic acid groups of SAA-27 and the carbonyl amide groups of SAD-32.

The quantitative analysis using the Kwei equation confirms the presence of specific interactions between the two con-

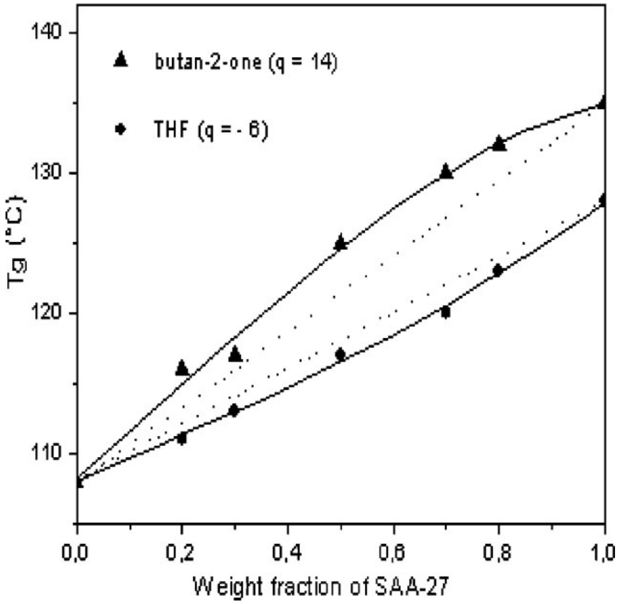


Figure 3.
Variation of the T_g of SAA-27/SAD-17 mixtures with SAA-27 composition as cast from THF or butan-2-one.

stituents of the different binary systems in the solid state.

$$T_g = w_1 T_{g_1} + w_2 T_{g_2} + q\, w_1 w_2 \qquad (2)$$

Where T_{g_1}, T_{g_2}, w_1, and w_2 are the glass-transition temperatures and weight fractions of components 1 and 2, respectively, and q a fitting constant.

The obtained q values confirmed that indeed stronger interpolymer interactions occurred for the SAA-27/SAD-17 systems cast from butan-2-one than the one from

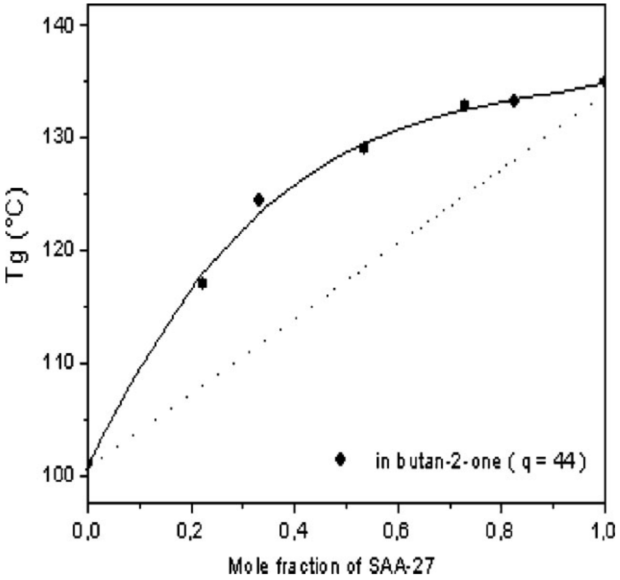


Figure 4.
Variation of the T_g of SAA-27/SAD-32 mixtures with SAA-27 composition as cast from butan-2-one.

THF. A higher q value (of 44) obtained with SAA-27/SAD-32 is due to stronger and more important favourable interpolymer interactions that led to highly interassociated polymer complexes.

Solid State ^{1}H NMR

A single T_g based on DSC analysis implies that the mixing of two blending components is in a scale of about 20–40 nm. Solid-state NMR spectroscopy is a technique that can characterize the phase structure of polymer mixtures at much smaller scale. The spin-lattice relaxation times in the laboratory and rotating frames are very sensitive to the size of the domains through the process of spin-diffusion. When the domain size of a blend is below 30 nm, a single spin-lattice relaxation time T_1 (H) in the laboratory frame is observed whereas a single $T_1\rho$ (H) reveals an intimate mixing below the scale of 2–3 nm. When the domains are greater than 50 nm, multiple T_1 (H) are observed and phase separation occurs.

T_1(H) and $T_1\rho$ (H) were determined for SAA-27, SAD-17 and their (70/30 and 50/50) mixtures as cast from THF or butanone, using a home build set up at laboratory of Prof. Weill's group (Institut Charles Sadron) in the 25–180 °C temperature range.

As shown from Figure 5, the single T_1 (H) values observed with the pure components and their blends as cast from both THF and butanone in the studied temperature range, confirms that these blends are homogeneous on the scale of 20–40 nm. The spin-lattice relaxation times of the pure components and of their blends cast from butan-2-one were higher than those cast from THF. These results confirm the solvent effect, in agreement with the thermal analysis carried out by DSC. The gap with T_1 (H) values determined for both types of materials obtained from THF and butan-2-one, confirms the gap of the values of T_g observed by DSC.

This effect is also confirmed from the $T_1\rho$ (H) measurements as shown in Figure 6.

The $T_1\rho$ (H) recoveries indicate that the blends were homogeneous on the scale of 2–3 nm only when cast from THF. Composite recovery curves $T_1\rho$ (H) were however observed with SAA-27 and its mixtures of different ratios below 120 °C when butan-2-one is the casting medium.

It is necessary to note also that the $T_1\rho$ (H) values of the mixtures SAA-27/SAD-17 (70/30) or (50/50) are higher than those obtained for the pure constituents. This may be due to the presence of attractive interactions between both constituents of the mixture.[19–21]

The quasi monoexponetial behaviour of $T_1\rho$ (H) confirms the solvent effect in

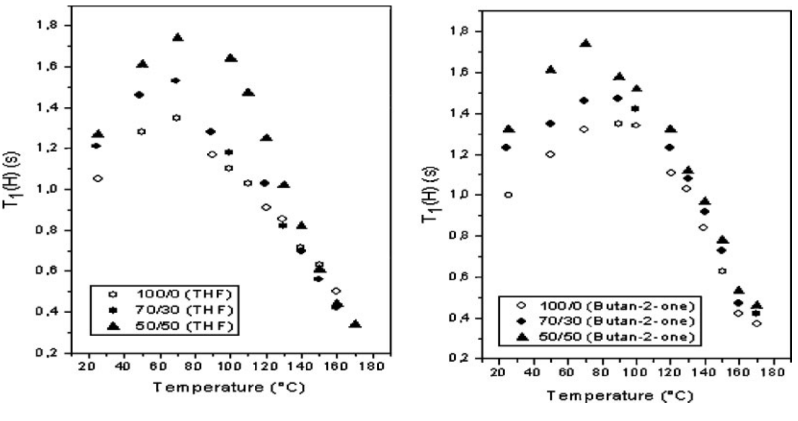


Figure 5.
Variation of the spin-lattice relaxation time in the laboratory T_1 (H) with temperature for SAA-27/SAD-17 mixture.

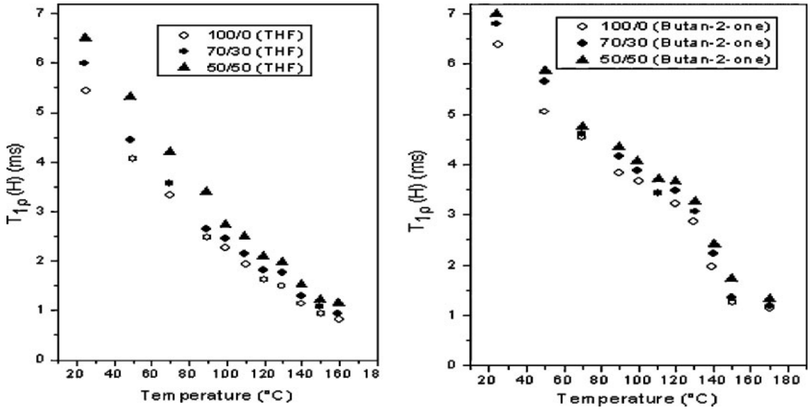


Figure 6.
Variation of the spin-lattice relaxation time in the rotating frame $T_1\rho$ (H) with temperature.

agreement with the other techniques. These observations point to differences in local contacts promoted by different distributions of the hydrogen bonding in the copolymer complexes, on a distance scale probed by $T_1\rho$ (H). The strong self association tendency of SAA-27 in butan-2-one is the main reason that it does not mix intimately with SAD-17 but does mix at a scale of 2–3 nm when THF is the casting solvent. Such morphological changes should modify the polymer compatibility in blends and ion binding by these membranes.

Conclusion

This study showed that, due to the presence of specific interpolymer interactions, novel materials, based on polystyrene matrices, as soluble interpolymer complexes in THF or precipitates from butan-2-one were elaborated when poly(styrene-*co*-acrylic acid) and poly(styrene-*co*-*N*,*N*-dimethylacrylamide) are mixed together.

The carboxylic-amide hydrogen bonding interactions that occurred between these copolymers and that led to the formation of such complexes were evidenced in the solid state by ATR/FTIR spectroscopy qualitatively and quantitatively.

The DSC analysis showed that all these materials are homogeneous on a 20–40 nm scale and that the T_g values of the complexes as "precipitates" from butanone were higher than those as-cast from THF.

The solid state proton NMR, confirmed from the observations of single proton spin relaxation times T_1 (H) and $T_1\rho$ (H) in the laboratory and rotatory frames for SAA27, SAD17 and their (70/30 and 50/50) mixtures as cast from THF the formation of homogeneous phases on the scale of 2–3 nm. Composite recovery curves $T_1\rho$ (H) observed with SAA-27 and its mixtures of different ratios below 120 °C when butan-2-one is the casting medium confirms the solvent effect.

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