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Poly[2-(N,N-Dimethylamino) Ethyl Methacrylate] / Poly(Styrene-Co-Methacrylic Acid) Interpolymer Complexes

*Naima Abdellaoui-Arous, Said Djadoun**

Summary: Poly[2-(N,N-dimethylamino)ethyl methacrylate] (PDMAEMA), copolymers of different compositions of styrene with 2-(N,N-dimethylamino)ethyl methacrylate (SDMAEMA) or methacrylic acid (SMA) were synthesized by free radical polymerization and characterized by several techniques. Different ternary mixtures containing proton-acceptors PDMAEMA or SDMAEMA, proton-donor copolymers SMA and a solvent (butan-2-one or THF) were prepared. The present study, that investigated several factors that affected the phase behaviors of the ternary mixtures above, confirmed that, indeed depending on the nature of solvent, densities of interacting species, amounts of efficient specific interactions that occurred between the two copolymers, interpolymer complexes of different structures were elaborated.

The complexation phenomena, observed with these different systems were analyzed in solution by viscometry that confirmed these effects in monitoring the formation of interpolymer complexes. The specific interactions that occurred between pairs of polymers of each system above were qualitatively evidenced by FTIR spectroscopy from the appearance of new bands or their new redistribution. The glass transition temperature Tg of the obtained complexes of different structures determined by DSC varied differently with the weight fraction of one of the copolymers. These various Tg-compositions were analyzed using the Kwei and Brostow et al. approach recently developed. Thermal analysis of some of the elaborated complexes, examined by thermogravimetry, confirmed their improved thermal stability.

Keywords: DSC and thermogravimetry; FTIR; Interpolymer complexes; Poly[2-(N,N-dimethylamino)ethyl methacrylate] poly(styrene-*co*-methacrylic acid); viscometry

Introduction

Several authors reported [1–5] that hydrogen bonding interpolymer complexation in solution occurred when hydrogen bonding polymer-polymer interactions between dissimilar components of a pair of polymers are much stronger than polymer-solvent interactions. This phenomenon is usually accompanied by a collapse of the polymer chains. Depending on the density and strength of interactions and as a result of such interactions, several types of interpolymer complexes of different structures, were reported.[6–9]

In their very recent study, Guo et al.[10] reported the formation of composition-dependent nanostructure complexes based on poly(3-caprolactone)-block-poly(2-vinylpyridine) (PCL-b-P2VP) and poly(4-vinylphenol) (PVPh).

Similarly, Matsushita et al.[11] have also reported that, due to the occurrence of strong selective hydrogen-bonding within blends of poly(styrene-block-2-vinylpyridine) block copolymer and poly(4-hydroxystyrene), various nanophase separated structures were elaborated.

Laboratoire des Matériaux Polymères, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene, BP 32, El Alia, Algiers, Algeria, 1611
E-mail: matpolylab@yahoo.fr

Polymers based on aminomethacrylates as poly(dimethylaminoethyl methacrylate) and their copolymers have been used in various fields such as waste water purification and paper production,[12] elaboration of membranes for nanofiltration and ion-exchange resins[13] and biomedical applications. Moreover, like all tertiary amines, polymers containing amine groups can be easily transformed into quaternary ones to create cationic centers (ammonium salts).[14]

We have in a previous study[15] reported that poly(styrene-*co*-methacrylic acid) containing 22 mol% of methacrylic acid (SMA22) formed interpolymer complexes with PDMAEMA but not with poly(ethyl methacrylate) (PEMA). As an extension of this study,[16] other poly(styrene-*co*-methacrylic acid) (SMA) and poly(styrene-co-2-(N,N-dimethylamino)ethyl methacrylate (SDMAEMA) copolymers of different compositions were prepared with the aim to elaborate new materials with improved properties as miscible blends or interpolymer complexes upon mixing SMA with PDMAEMA or SDMAEMA in THF or butan-2-one.

The effects of solvent, densities of interacting species, self-association and amounts of efficient specific interactions that occurred within these mixtures, on the elaboration of these interpolymer complexes, were then investigated in solution by viscometry and in the solid state by differential scanning calorimetry (DSC), thermogravimetry (TGA) and Fourier transform infra red spectroscopy (FTIR).

Experimental Part

Polymer Synthesis and Characterizations

All monomers were distilled at reduced pressure before use. The azo-bis-isobutyronitrile (AIBN) was purified by recristallisation in methanol.

Poly[2-(N,N-dimethylamino)ethyl methacrylate] (PDMAEMA), copolymers of different compositions of styrene with this latter (SDMAEMA-x) or with methacrylic acidic (SMA-x) proton donors were prepared by free radical polymerization of the corresponding monomers using azo-bis-isobutyronitrile (AIBN) as the initiator at 60 °C under nitrogen atmosphere. The yields of polymers were kept at less than 15% in order to avoid the copolymer composition drift or chains reticulation and also to avoid the formation of homopolymers. The synthesized polymers were purified by repeated dissolution/precipitation and then dried to constant weight in a vacuum oven for several days at 60 °C. These polymers were characterized by several techniques such as viscometry and FTIR spectroscopy, using a Perkin-Elmer 1000 one spectrometer. 60 scans were signal averaged at a spectral resolution of 2 cm^{-1}.

The styrene contents in the copolymers were determined by UV spectroscopy and NMR using a Brucker Advanced spectrometer operating at 200 MHz in THF at 25 °C.

Interpolymer complexes or blends based on proton-acceptors and proton-donors above were prepared in THF or butan-2-one in the usual way as previously reported.[14]

Thermogravimetric experiments were carried out with a TA Q500 analyzer at 10 °C/min under nitrogen atmosphere from 30 °C to 580 °C.

The glass transition temperatures (Tg) were measured with Pyris 1 under nitrogen atmosphere at 10 °C/ min.The samples were first heated from -20 °C to 200 °C, cooled down to -20 °C at 10 °C/min and then heated up to 200 °C at 10 °C/min. The Tg values were determined at the midpoint of the second scan.

Viscosity Measurements

Viscosity measurements of the polymer blend solutions or dilute phases of the various mixtures were conducted with an Ubbelohde viscometer. The intrinsic viscosities of the different polymers and copolymers were determined in butan-2-one and THF in the usual way from the Huggins equation. Table 1 summarizes the intrinsic viscosities of these copolymers.

Table 1.
Intrinsic viscosities of polymers.

Polymères	T (°C)	THF	Butan-2-one
SMA30	30	1.185	0.352
SMA18	30	1.139	0.573
PDMAEMA	25	1.176	0.825
SDMAEMA18	30	1.253	0.664
SDMAEMA9	30	1.246	0.655

FTIR Measurements

Thin films of typical SMA18, SDMAEMA18 and their blends of different ratios were prepared from dilute solutions (3 Wt %) in THF. These films were dried in a vacuum oven for several days at 60 °C. Their FTIR spectra were recorded at room temperature with a resolution of 2 cm^{-1} and 60 scans were signal averaged on a Perkin-Elmer Spectrum one spectrometer.

Results and Discussion

Complexation

Due to methacrylic acid-[2-(N,N-dimethylamino)ethyl methacrylate] specific interactions that occurred upon mixing pairs of these polymers, two kinds of interpolymer complexes, as soluble or precipitate of different structures, were obtained in THF and butan-2-one as common solvents, by monitoring the specific interaction densities within these latter. This qualitative investigation, carried out in the first step, confirmed the major role of the solvent and densities of interacting species within proton-donor copolymers in monitoring the formation of interpolymer complexes. The results showed that 18 mol % of carboxylic groups introduced by copolymerization within polystyrene matrix were sufficient for the formation of interpolymer complexes upon mixing PDMAEMA with SMA18 in THF and in butan-2-one in the whole composition range, giving rise to the formation of a concentrated phase (CP) in equilibrium with a dilute phase (DP) containing most of the solvent. The increase of carboxylic acid content from 18 to 30 mol %, as within SMA30, led to the formation of interpolymer complexes (DP + CP) upon mixing PDMAEMA or SDMAEMA18 and SMA30 in butan-2-one only. Soluble interpolymer complexes characterized by single homogeneous phases were however observed with both systems above in the whole composition range with THF as the common solvent.

The formation of interpolymer complexes also depends on the nature and strength of interacting species between the constituents of a mixture. Indeed, a previous study [14] showed that complexation did not occur in both solvents with poly(ethyl methacrylate) (PEMA) and poly(styrene-co-methacrylic acid) containing 22 mol % of methacrylic acid.

In agreement with Goh et al [15] results on the formation of interpolymer complexes based on poly[2-(N,N-dimethylamino) ethyl methacrylate] and poly(vinyl phenol) (PVPh) in solvents such as methanol, ethanol and butan-2-one, this difference may be explained by the fact that, both the carbonyl oxygen atom and the nitrogen atom of PDMA were involved as proton-accepting sites in the formation of these complexes characterized by stronger specific interactions compared to those occurring between ester groups of PEMA and carboxylic groups of SMA22. Figure 1 shows the complex yield variation with SMA-x composition and Table 2 gathers some tests of miscibility and complexation in THF or Butan-2-one as solvents.

Viscometry

The formation of interpolymer complexes as precipitates is usually accompanied by a collapse of the polymer chains.[17–18] Viscometry remains the simplest technique widely used to study this phenomenon in solution. When such a complexation occurs as caused by an increase of the interpolymer hydrogen bonding density, the viscosity decreases as a result of a contraction of the component polymer chains.

In a similar way as we have previously reported,[14] reduced viscosity measure-

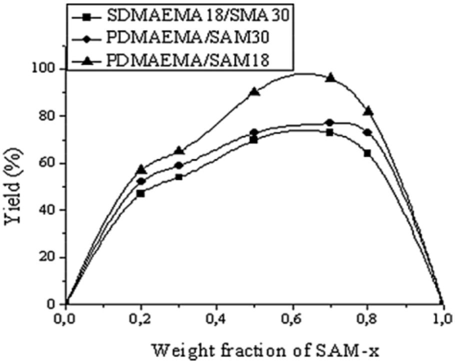

Figure 1.
Complex yield variation with SMA-x Composition in butan-2-one.

ments of polymer blend solutions or apparent reduced viscosities of dilute phases, observed when complexation phenomena occurred, were conducted after filtration of the precipitates, as a function of the initial feed composition, keeping the original concentration of the component polymers at 0.1 g/dL, obviously lower than the critical concentration of each polymer. All measurements were carried out 24 h after the dissolution of the polymers to achieve thermodynamic equilibrium and 10 min after the introduction of the polymer solutions to the viscometer.

In agreement with the qualitative investigation above, viscometry analysis confirmed both effects of solvent and density of interacting species on complexation as illustrated in Figure 2. Figure 2 shows the variation of typical reduced or apparent reduced viscosities of PDMAEMA/SMA-x solutions or of their dilute phases as a function of the feed weight fraction of the SMA-x in THF and butan-2-one, respectively.

Due to the different ability of these solvents to develop hydrogen bonding with the constituents of the mixtures, different behaviours were observed. The reduced viscosity of PDMAEMA/SMA30 solutions prepared in THF varied linearly with the weight fraction of SMA30, while a negative deviation of the apparent reduced viscosity of dilute phases of this system were observed when butan-2-one was the common solvent.

The negative deviation from the linear average viscosity of the two polymers, observed in the whole composition range, with the studied mixtures prepared in butan-2-one or THF is an evidence of the formation of interpolymer complexes as due to the presence of strong interpolymer attractive interactions. Figure 3 illustrates the effect of the density of interacting species within the polymer matrices. Significant differences are observed in THF, known for its strong ability to form hydrogen bonding with proton-donating copolymers, when the content of carboxylic groups increased from 18 to 30 mol%. Self-association effect, evidenced with an increase of carboxylic content within SMA copolymer, was more pronounced with THF, while slight changes only were observed with butan-2-one as solvent.

The minima of these curves correspond to the most stable compositions of the complexes or *fixed mean stoichiometry* (FMS) as illustrated in Figure 4 that shows selected $\Delta\eta$ versus the feed weight fraction of SMA-x in butan-2-one or THF.

Thermogravimetry

There are very few papers related to thermal decomposition of polymethacrylates containing amine groups.[19] In general, thermal degradation behavior of

Table 2.
Tests of miscibility and complexation in Butan-2-one and THF.

Systems	THF	Butan-2-one
SDMAEMA9/SMA18	Miscible (one phase)	Complex (DP + CP)
SDMAEMA9/SMA30	Miscible (one phase)	Complex (DP + CP)
SDMAEMA18/SMA18	Complex (DP + CP)	Complex (DP + CP)
SDMAEMA18/SMA30	Miscible (one phase)	Complex (DP + CP)

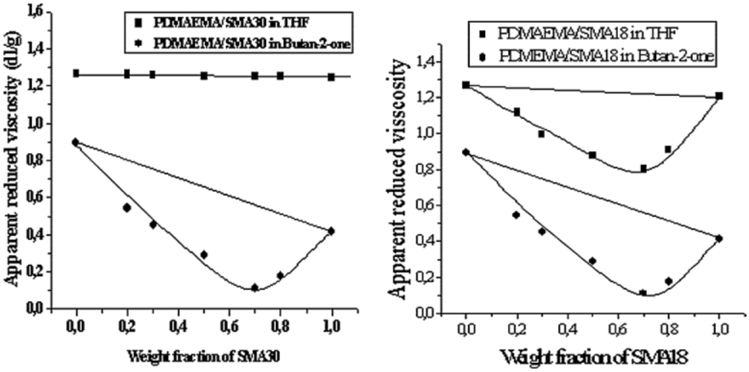

Figure 2.
Reduced and apparent reduced viscosity of PDMAEMA/SMA30 or PDMAEMA/SMA18 in THF and butan-2-one at 25 °C.

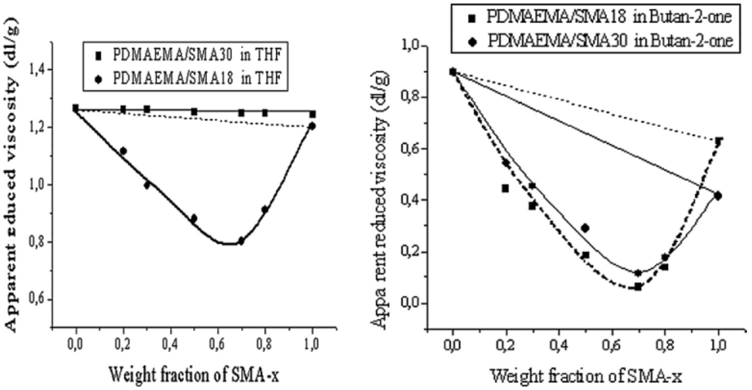

Figure 3.
Reduced and apparent reduced viscosity of PDMAEMA/SMA30 and PDMAEMA/SMA18 in THF or butan-2-one at 25 °C.

polymethacrylates depends on the type of alkyl side chain constituting the ester. Thus, some polymethacrylates degrade relatively easily to monomers on heating, whereas some others undergo ester decomposition without giving the corresponding monomer.

We have previously reported on thermal degradation behavior of poly(styrene-co-methacrylic acid) and their blends or complexes with poly(isobutyl methacrylate-co-4-vinylpyridine)[20] We have in this study, investigated thermal degradation of PDMAEMA or SDMAEMA and some of their selected mixtures as dilute or concentrated phases obtained upon mixing them in butan-2-one with SMAx. We will present for illustration only, thermal analysis of concentrated phases ''interpolymer complexes as precipitates'' and as dilute phases of PDMAEMA/SMA30 system using butan-2-one as solvent.

Figure 5 exhibits TGA and d(TG) thermograms, to indicate the temperatures at which maximum rates of weight loss of PDMAEMA, SMA30 and concentrated phases (CP) of their complexes, obtained from butan-2-one, occurred.

As it can be seen, PDMAEMA appears to have two main degradation stages. This

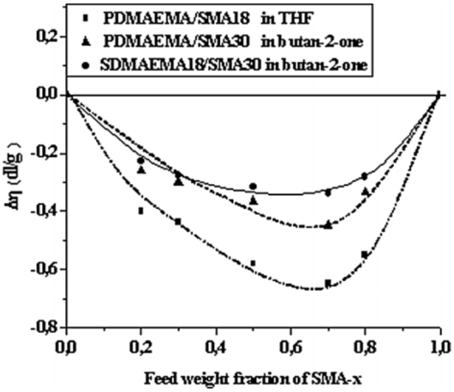

Figure 4.
Selected Δη versus the feed weight fraction of SMA-x in butan-2-one and THF.

polymer lost about 45% of its weight in its first stage between 260 °C and 330 °C with a maximum rate at 322 °C and about 43% in its second stage with a maximum rate at 420 °C. The first degradation stage was attributed to the loss of the dimethyl aminoethyl groups from PDEAEM, released at this stage while the weight loss associated with the second degradation stage was attributed to the elimination of co$_2$ and co groups and to the carbonization processes.

SMA30 degraded in two steps. The first one, in the 80-257 °C region, was ascribed to release of water adsorbed by the hydrophilic polymer and to anhydride ring formation. This copolymer is however stable in the 260-350 °C temperature range. The maximum rate of its second step which occurred at 422 °C is due to the main chain degradation and to the decarboxylation and carbonization processes.

A thermogravimetric analysis of concentrated phases "interpolymer complexes" of PDMAEMA/SMA30 system showed improved thermal stability of these materials, particularly for those containing an excess of SMA30. Three stages of degradation are observed with all these materials. The first stage is due to the presence of SMA30 only since PDMAEMA is stable in this temperature range. The T_{onset} of these materials shifted to higher temperature compared to SMA30, with a maximum rate varying progressively from 176 °C to 185 °C as the content of PDMAEMA in the mixture increased.

The second step of degradation of these interpolymer complexes occurred in the same region than the first step of PDMAEMA degradation, in which SMA30 is stable. Degradation of pure

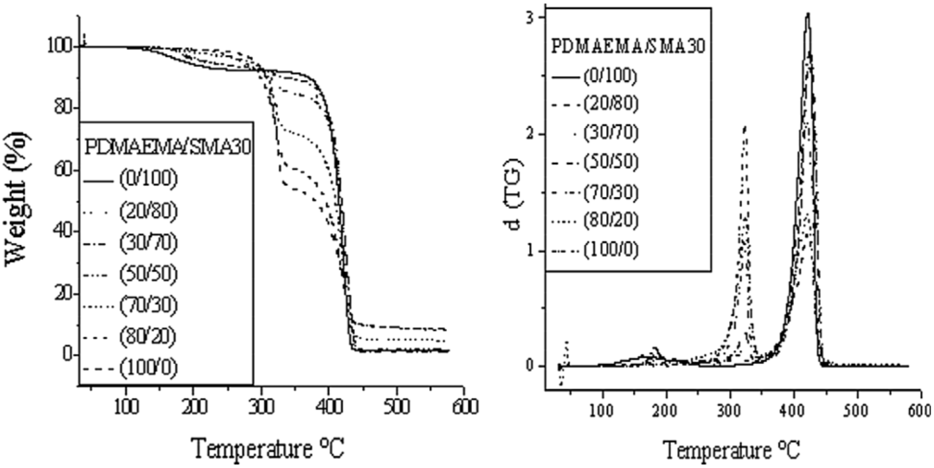

Figure 5.
TGA and d (TG) thermograms of concentrated phases of PDMAEMA/SMA30 system in butan-2-one.

Table 3.
Thermogravimetric data of concentrated phases of PDMAEMA/SMA30 system.

PDMAEMA/SMA30	T 5%	T 50%	T max		
			First stage	Second stage	Third stage
100/0	291.28	379.08	–	322.10	420.58
80/20	273.39	394.72	255.05	322.85	421.78
70/30	283.16	408.55	176.12	321.50	420.58
50/50	224.83	418.17	183.63	322.10	422.33
30/70	218.66	418.17	181.23	320.90	422.98
20/80	228.74	413.96	182.43	312.77	422.98
0/100	187.84	414.56	163.64	–	421.77

PDMAEMA is of 45% by weight at 335 °C whereas the weight losses for these complexes at this temperature are less and decreased progressively with the initial SMA30 feed in the mixtures. This indicates that these materials are thermally more stable than PDMAEMA. In their third stage of degradation, these complexes exhibited only one weight loss with maximum rate decomposition slightly higher than those of their pure constituents for complexes obtained from mixtures containing 50% by weight of SMA30 or more. Table 3 gathers the thermogravimetric data corresponding to concentrated phases "interpolymer complexes as precipitates" using butan-2-one as solvent.

The TGA and d(TG) thermograms of samples of diluted phases observed with PDMAEMA/SMA30, prepared in butan-2-one, are illustrated in Figure 6. Two stages of degradation, practically similar to that of PDMAEMA, were observed with the materials of these phases. This confirmed that these dilute phases are essentially constituted of PDMAEMA. The thermogravimetric data corresponding to diluted phases of PDMAEMA/ SMA30 system using butan-2-one as solvent are mentioned in Table 4.

Differential Scanning Calorimetry (DSC)

A DSC analysis was carried out for selected SDMAEMA18/SMA30 concentrated phases (CP) obtained from butan-2-one and SDMAEMA9/SMA30 homogeneous phases, observed in THF. Table 5 gathers the different values of glass transition temperatures Tg and ΔTg of SDMAEMA18/SMA30 complexes and SDMAEMA9/SAM30 blends cast from butan-2-one and THF respectively, while Figure 7 shows the

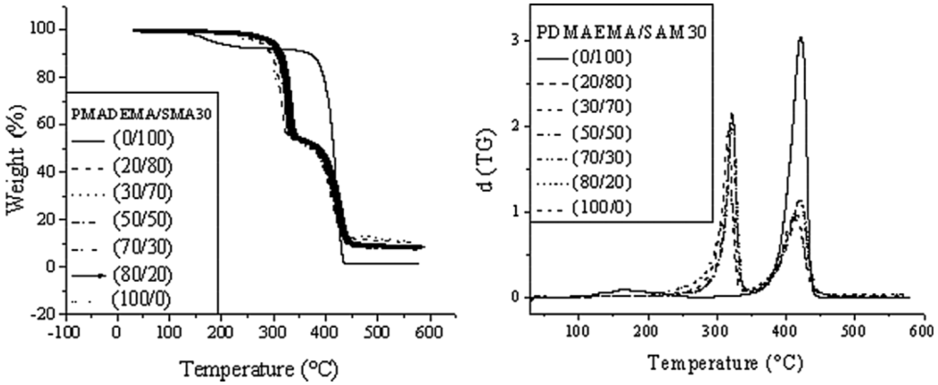

Figure 6.
TGA and d(TG) thermograms of dilute phases of PDMAEMA/SMA30 system.

Table 4.
Thermogravimetric data of diluted phases of PDMAEMA/SMA30 system.

PDMAEMA/SMA30	T 5%	T 50%	T max		
			First stage	Second stage	Third stage
100/0	291.28	379.08	–	322.1	420.58
80/20	288.72	379.38	–	322.1	419.22
70/30	285.57	344.72	–	321.50	418.02
50/50	283.61	376.68	–	321.50	421.03
30/70	255.50	371.56	–	317.74	412.31
20/80	270.53	372.32	–	316.5	414.26
0/100	187.84	414.56	163.64	–	421.77

variation of glass transition temperature versus the composition of SMA-x for these systems.

From the values of **ΔTg**, we note that a better homogeneity is obtained with (20/80) composition for SDMAEMA18/SMA30 system in butan-2-one. This is in good agreement with the viscometry results where the Fixed mean stockiometry (FMS) is obtained for complexes with excess of SMA30 copolymer. In the case of SDMAEMA9/SAM30 blends, a better homogeneity is obtained for (50/50) composition.

A single Tg, much higher than the weight average of the Tg's of the pure constituents, was observed with each of the SDMAEMA18/SMA30 complexes. This is due to the presence of strong specific interactions that occurred between SDMAEMA18 and SMA30. A single glass transition temperature was also depicted, in the whole composition range but with a different Tg-composition behaviour with the SDMAEAM9/SMA30 miscible blends cast from THF and containing a lower density of 2-N,N-dimethylamino ethyl methacrylate moieties.

Table 5.
Values of glass transition temperatures Tg and ΔTg of SDMAEMA18/SMA30 complexes and SDMAEMA9/SAM30 blends.

Polymeric system	Tg	ΔTg	Solvent
SDMAEMA18/SMA30			
100/0	84	12	Butanone
80/20	104.4	33	
50/50	129.3	34	
20/80	137.8	27	
0/100	146	18	
SDMAEMA9/SAM30			
100/0	82.5	12	THF
80/20	119	23	
70/30	119	20	
50/50	113	17	
30/70	105.6	24	
20/80	105	27	
0/100	14	13	

The interactions that occurred within these systems were quantified using DSC and Kwei[21] and Brostow et al.[22] approaches expressed by the following equations:

Kwei equation:

$$T_{g,blend} = \frac{w_1 T_{g,1} + K_{Kwei} w_2 T_{g,2}}{w_1 + K_{Kwei} w_2} + q w_1 w_2 \quad (1)$$

Or

$$T_{g,blend} = w_1 T_{g,1} + w_2 T_{g,2} + q w_1 w_2 \quad (2)$$

When K = 1

Brostow equation:

$$T_{g,blend} = w_1 T_{g,1} + (1-w_1) T_{g,2} + w_1(1-w_1) \times [a_0 + a_1(2w_1-1) + a_2(2w_1-1)^2] \quad (3)$$

$$\Delta_{Tgm} = T_{blend} - w_1 T_{g,1} + (1-w_1) T_{g,2} \quad (4)$$

with $T_{g,i}$ and w_i are the glass transition temperature and the weight fraction of the pure component i, respectively. K_{Kwei}, q,

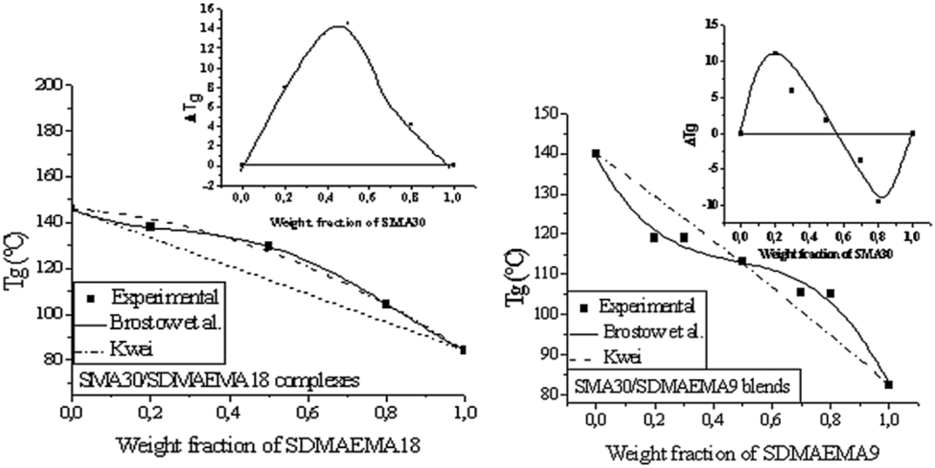

Figure 7.
Tg-composition of SMA30/SDMAEMA18 complexes in butan-2-one or SDMAEMA9/SMA30 blends cast from THF.

and a_i are adjustable parameters, determined from the experimental Tg-composition curves shown in Figure 8. The Kwei and Brostow parameters for SMA30/SDMAEMA18 complexes in butan-2-one or SDMAEMA9/SMA30 blends cast from THF are mentioned in Table 6.

As shown in Table 6, better fits were obtained with both systems, using Brostow et al. approach. The relatively high positive a_0 value, obtained with SMA30/SDMAEMA18 system confirmed, in agreement with viscometry, that strong specific inter-polymer interactions occurred within these inter-polymer complexes. Due to a lower density of inter-polymer specific interactions, this parameter decreased with the SDMAEAM9/SMA30 miscible blends cast from THF and containing a lower density of 2-N, N -dimethylamino ethyl methacrylate moieties.

The positive second parameter a_1 of 19.79 and 83.61, obtained with these SMA30/SDMAEMA18 and SDMAEAM9/SMA30 systems respectively, indicates, as shown in inserts of Figures 7 an enhanced up-shift with respect to the linear mixing rule for mixtures, with the low-Tg SDMAEMA18 or SDMAEMA9 component as the majority.

The highest density of interactions occurred when a high volume fraction of SDMAEMA9 was mixed to SMA30 while the maximum of specific interactions occurred with a lower volume fraction of SDMAEMA18, around 50 mol % with SMA30/SDMAEMA18 system.

This result is in a good agreement with viscometry results and complexation phenomena of Figures 1 and 2.

The a_2 parameter of absolute value of about 53, observed with SMA30/SDMAEMA18 system indicates a moderate complexity of this system mainly due to variations of inter-associations between the copolymers with changes in the mixture composition. It is worth noting that the Kwei constant q estimated for K = 1 is close to a_0 for SMA30/SDMAEMA18 while a very poor fit with very significant error was

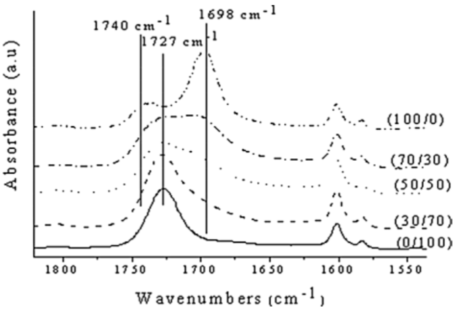

Figure 8.
FTIR spectra of SMA18/SDMAEMA18 system.

Table 6.
Values of Kwei and brostow parameters.

System	Solvent	Brostow et al.				Kwei (K = 1)	
		a_0	a_1	a_2	R^2	q	R^2
SAM30/SMAD9	THF	6.54	83.61	-6.43	0.968	5.53	0.86089
SAM30/SMAD18	Butanone	57.2	19.79	-52.98	1	48.61	0.99333

recorded using Kwei equation for SMA30/SDMAEMA9 blends cast from THF.

FTIR Spectroscopy

Since the formation of miscible blends or interpolymer complexes is mainly due to the occurrence of sufficient specific interactions between carboxylic groups of proton-donor copolymers and 2-(N,N-dimethylamino)ethyl methacrylate groups of PDMAEMA or SDMAEMA copolymers, an FTIR spectroscopy investigation was carried out in the frame of this contribution to identify these interactions within selected SMA18/SDMAEMA18 blends cast from THF in the 1800-1650 cm^{-1} region where changes occurred. Figure 10 shows FTIR spectra of these SMA18, SDMAEMA18 copolymers and their blends of different ratios in this region.

The FTIR spectrum of SMA18 showed two bands at 1740 cm^{-1} and 1698 cm^{-1}, attributed to free and self-associated carboxylic acid groups, respectively while SDMAEMA18 absorbed strongly in the carbonyl region at 1727 cm^{-1}.

As a result of the interactions between these two copolymers, a qualitative analysis confirmed the progressive dissociation of carboxylic dimers of SMA18 upon addition of SDMAEMA18, evidenced by a decrease of intensity of the band at 1698 cm^{-1}, a broadening and a new redistribution of the overall carbonyl band in the 1800-1650 cm^{-1} region, due to the overlap of different contributions. Even though it is difficult to analyse properly these interactions in this region, as illustrated in Figure 10, the deconvolution of a typical blend shows the contributions of the different species and the appearance of a new band at 1715 cm^{-1}, attributed to liberated carbonyl groups of SMA18 due to the interactions that occurred in this blend between the carboxylic groups of

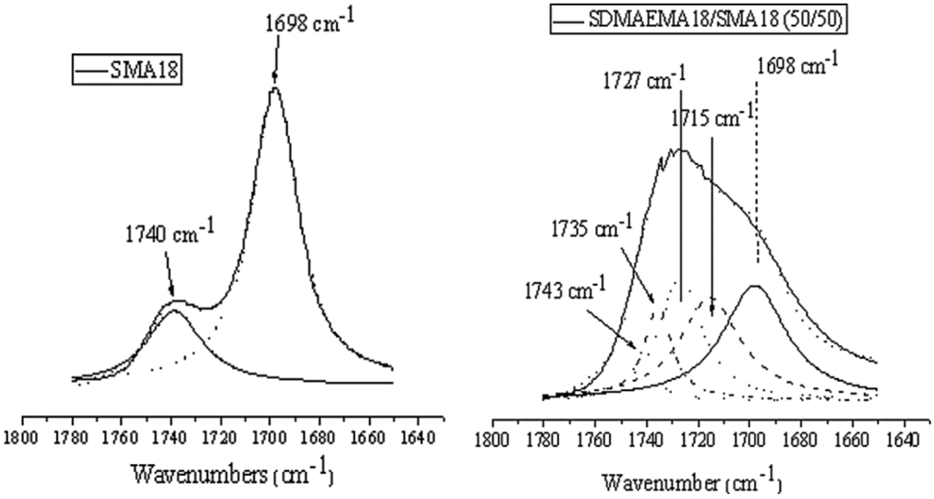

Figure 9.
Déconvolution spectra of SMA18 or SMA18/SDMAEMA18 (50/50) blend.

SMA18 and the basic groups of SDMAEMA18.

Conclusion

This contribution revealed that, due to self-association of carboxylic groups of SMA copolymers and to stronger ability of THF to form hydrogen bonding with proton-donor copolymers than butan-2-one, 30 mol % of methacrylic acid incorporated within polystyrene matrix, led to the formation of PDMAEMA/SMA30 or SDMAEMA18/SMA30 interpolymer complexes in butan-2-one but not in THF while 18 mol % of this latter led to interpolymer complexation in both solvents with PDMAEMA or SDMAEMA18.

The formation of these interpolymer complexes is due to the presence of sufficient interpolymer attractive interactions, qualitatively evidenced by FTIR spectroscopy from the appearance of new bands characterizing these interactions and by viscometry from the negative deviation of the apparent reduced viscosities of their dilute phases from the linear average viscosity of the two polymers of their mixtures.

Moreover, thermal analyses carried out by DSC and TGA, showed that these interpolymer complexes exhibited by a single Tg, much higher than the weight average of the Tg's of their components and improved thermal stability.

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