Elaboration and Characterization of Poly(4-vinylpyridine-*co*-*N*,*N* dimethylacrylamide)/ Poly(styrene-*co*-methacrylic acid) Interpolymer Complexes

*Abdelghani Lassoued, Saïd Djadoun**

Summary: Proton-donor poly(styrene-*co*-methacrylic acid) containing 8 mol % of methacrylic acid (PSMA8) and poly(N,N-dimethylacrylamide-*co*-4vinylpyridine) containing 20 mol % of 4-vinylpyridine (PDMA4VP20) containing two proton accepting sites of different strength were synthesized and characterized by different techniques.By simply mixing appropriate amounts of these copolymers in chloroform, interpolymer complexes were formed, while homogeneous phases were observed when PSMA8 was mixed to poly(N,N-dimethyl acrylamide) or poly(4-vinylpyridine) in the same solvent.Due to the presence of specific interactions that occurred between the copolymers, these interpolymer complexes exhibited a single Tg in the whole composition range, higher than those calculated from the weight average values of the pure copolymers.The Tg-composition curves of these three systems, analyzed using Brostow et al. (BCKV) equation, confirmed from the high a_0 values, obtained with PSMA8/PDMA4VP20 that the presence of 4VP units in PDMA4VP copolymers increased the average strength of intermolecular hydrogen bonding in the PDMA4VP20/PSMA8 systems compared to PDMA/PSMA8 or PSMA8/P4VP blends due to a higher number and stronger efficient specific interactions. Competing specific interactions of different strength carboxyl-pyridine, carboxyl-amide and carboxyl-carboxyl that occurred within these systems were evidenced by FTIR spectroscopy.

Keywords: FTIR; glass transition temperature; interpolymer complexes; poly(*N*,*N*-dimethyl acrylamide-*co*-4-vinylpyridine); poly(styrene-*co*-methacrylic acid); proton-conducting membranes

Introduction

Inter-polymer complexes with “tailored” morphologies and properties may be prepared by mixing two polymers or copolymers and controlling the interactions that occurred between the constituents of the mixtures.[1–5]

Poly (N,N-dimethylacrylamide) (PDMA) and poly(4-vinylpyridine) (P4VP) are well known proton acceptor polymers able to form interpolymer complexes with several proton donor polymers.[6–8] Their proton accepting capacities are however different and depend among other factors on their basicity and their stability with temperature and moisture. Due to the nitrogen atom present in the pyridine ring, P4VP has a stronger proton accepting capacity. Complementary advantages of P4VP and PDMA are desirable. Though blends of these two polymers are immiscible, their random copolymers are expected to have higher miscibility than their blends.

As an extension of our previous work on elaboration and morphology studies of

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Laboratoire des Matériaux Polymères, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediène BP n°32, El-Alia 16111, Algiers, Algeria
E-mail: matpolylab@yahoo.fr

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various interpolymer complexes,[9,10] we have in this contribution attempted to develop systems composed of poly(styrene-co-methacrylic acid) (PSMA) and poly(N,Ndimethylacrylamide-co-4vinylpyridine) (PDMA4VP) inter-polymer complexes with the aim to use them as proton-conducting membranes.

We have characterized these copolymers by FTIR spectroscopy and ^{1}H NMR spectrometry and have investigated their thermal properties and of their interpolymer complexes by differential scanning calorimetry (DSC) and thermogravimetry (TGA).

The Tg-composition curves of these systems were analyzed by the Brostow et al. (BCKV) approach.[11]

The specific interactions that occurred between these copolymers and led to the formation of interpolymer complexes were then investigated by FTIR.

Experimental Part

Materials

Poly(4-vinylpyridine)(P4VP) of a weight average molecular of 60.000, was supplied by Aldrich while poly(N,N-dimethylacrylamide) (PDMA), poly(N,N-dimethylacrylamide-*co*-4-vinylpyridine) containing 20 mol % of 4-vinylpyridine (PDMA4VP20) and poly(styrene-co-methacrylic acid) containing 8 mol % of methacrylic acid were synthesized by bulk free radical polymerization at 60 °C using azo-bis-isobutyronitrile (AIBN) as initiator. The polymer solution was diluted with chloroform and precipitated in n-heptane. The polymers were then purified by dissolution and precipitation and dried in a vacuum oven at 60°C for several days.

Characterizations

These copolymers were in a first step characterized qualitatively by different techniques. The composition of this PDMA4VP20 copolymer shown in Table 1 was determined by ^{1}HNMR from the area ratio of appropriate peaks recorded on a Bruker Advance DPX 300, which corresponds to 75.5 MHz frequencies for ^{1}HNMR using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane as internal standard at room temperature.

Table 1.
Characteristics of polymers and PDMA4VP20 copolymer.

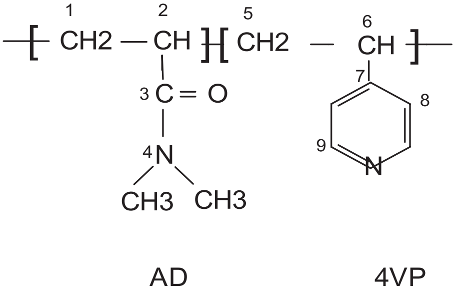
Polymer	4VP (mol %) or SMA in copolymer	Tg (°C)	M_w x10^{-5}	PDI**
PDMA	0	111	3.098	2.336
PDMA4VP20	20	120	2.980	1.508
PSMA8	8	94	1.720	1.960
P4VP*	100	145	0.6	–

* Supplied by Aldrich; ** PDI polydispersity index

The signals of the aromatic protons of the pyridine ring for the PDMA4VP20 copolymer appear as illustrated in Scheme 1 between 8.38 −8.43 ppm for the meta-protons (carbone 9) and between 6.43 −6.76 ppm for the ortho–protons (carbone 8).The signals observed between 3.20 and 2.64 ppm characterize the methyl protons ($N(CH_3)_2$) (carbone 4) of N,N-dimethyl acrylamide moiety. Moreover the signals that appear between 1.2 and 1.64 ppm are due to methylene (CH2-) protons while those appearing between 1.90 and 2.18 are due to methine protons.

The content of styrene within PSMA8 was determined by UV spectroscopy as previously reported.[10]

Prior to DSC analysis, thermogravimetric measurements were carried out under nitrogen from 50°C to 600°C on a TGA-Q500 TA instruments with a heating rate of 10°C/min to investigate the thermal



Scheme 1.

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behaviour of the synthesized polymers and of their different mixtures.

The glass transition temperatures Tg of these polymers and of their various PSMA8/PDMA, PSMA8/P4VP blends or PSMA8/PDMA4VP20 mixtures were measured with a Perkin Elmer DSC PYRIS 1 equipped with an intra-cooler. All Tg measurements were carried out at a heating rate of 20°C/min under nitrogen. The Tg value was taken as the midpoint of the transition from the second scan.

Average molecular weights and polydispersity indices (*PDI*) of these polymers, determined by GPC at 80°C, using PL-GPC 50 chromatograph equipped with a refractive index detector and PLgel columns (from polymer laboratories) and DMF as the solvent are shown in Table 1 which summarizes some characteristics of these polymers.

FTIR spectra of thin films of these copolymers and their blends cast from chloroform solutions onto KBr disks, with a spectral resolution of 2 cm^{-1} and 32 scans were signal averaged on a Perkin-Elmer Spectrum one spectrometer.

Preparation of the Blends and Inter-Polymer Complexes

Blends or interpolymer complexes were prepared by simply mixing appropriate amounts of pairs of these copolymers in chloroform as a common solvent. Polymer blends were prepared by solvent evaporation from the homogeneous phases. The “gel-like” phases were isolated and all samples were dried to constant weight in a vacuum oven at 60°C for several days.

Results and Discussion

The formation of blends or interpolymer complexes depends mainly on the nature of the solvent, the nature and densities of interacting species within the two polymer chains and on the effective specific interactions that occurred between the two constituents of the mixtures.

Qualitative tests showed that homogeneous phases were observed when PSMA8 was mixed to PDMA or P4VP in chloroform while “gel-like” concentrated phases containing mainly the copolymers in equilibrium with a dilute phase are observed when PSMA8 was mixed with PDMA4VP20 in the same solvent.

The evidence and quantification of these specific interactions were then investigated by DSC and FTIR

Differential Scanning Calorimetry Analysis

All PSMA8/PDMA or PSMA8/P4VP blends and PSMA8/PDMA4VP20 interpolymer complexes showed a single Tg in the whole composition range, higher than those calculated from the weight average values of the pure copolymers may indicate in a first step according to the conventional Tg criterion that these blends or inter-polymer complexes are miscible due to the presence of strong specific interactions.

Song et al.[12] have carried out a study of several polymer blends by modulated differential scanning calorimetry and showed the effect of molecular interactions on the glass transition temperature and increment of the heat capacity. They observed a positive Tg-composition and a negative ΔCp-composition for SAN18/PMMA and attributed these observations to a miscible blend. In agreement with such observations the systems considered in this study displayed similar behaviour. Figure 1 illustrates as an example the ΔCp –PSMA8 composition curve for PSMA8/PDMA4VP20.

Since competing interactions of different strength are expected to occur within these systems, we have analyzed the Tg-composition of these systems by the recent approach of BCKV (Brostow et al.)[12] to interpret the observed behaviors expressed by the equation below:

BCKV equation:

$$\begin{aligned}\mathrm{Tg} = {} & \mathrm{w_1 Tg_{,1}} + (1 - \mathrm{w_1})\mathrm{Tg_{,2}} \\ & + \mathrm{w_1}(1 - \mathrm{w_1})[\mathrm{a_0} + \mathrm{a_1}(2\mathrm{w_1} - 1) \\ & + \mathrm{a_2}(2\mathrm{w1} - 1)^2]\end{aligned} \tag{1}$$

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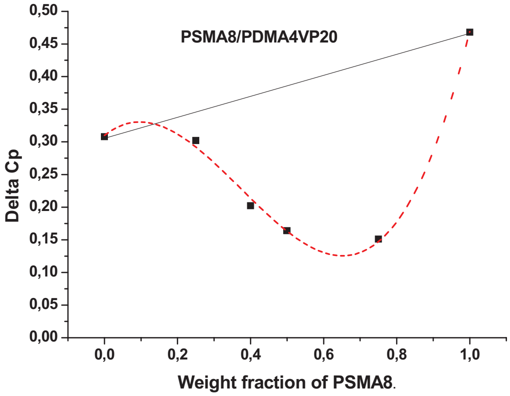

Figure 1.
ΔCp of PSMA8/PDMA4VP20 versus weight fraction of PSMA8.

Where Tg, 1 or 2 and w_1 or 2 are the glass transition temperatures of the pure components and their corresponding weight fractions, respectively**.** a_i are adjustable parameters determined from experimental Tg-composition curves shown in Figure 2–4

Table 2 summarizes the Brostow et al. parameters for the three systems.

The positive $a_0 = 14$ value obtained with PSMA8/PDMA indicates the presence of moderate specific interactions, in agreement with the homogeneous phases observed qualitatively. Higher a_0 values obtained with PSMA8/P4VP system are an evidence of stronger carboxyl-pyridine specific interactions. Much higher a_0 values observed with PSMA8/PDMA4VP20 confirm the formation of interpolymer complexes. The presence of 4VP units in PDMA4VP copolymers increased the average strength of intermolecular hydrogen bonding in the PDMA4VP20/PSMA8 systems compared to PDMA/PSMA8 or PSMA8/P4VP blends due to a higher number and stronger efficient specific interactions.

The relatively low positive $a_1 = 13$ value observed with PSMA8/PDMA system indicates that the maximum of interactions occurred at a volume fraction of PSMA8 close to 0.5. Higher positive a_1 values

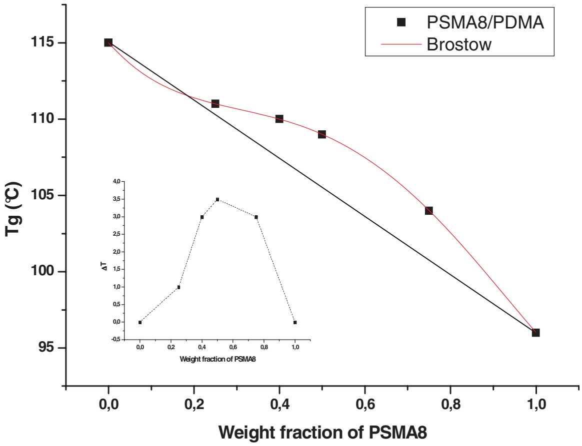

Figure 2.
Tg-composition of PSMA8/PDMA system.

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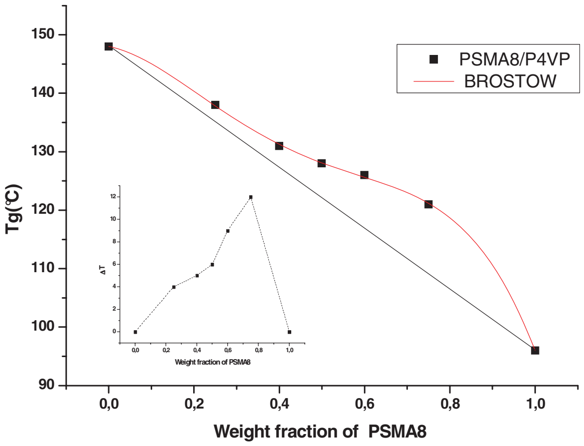

Figure 3.
Tg-composition of PSMA8/P4VP system.

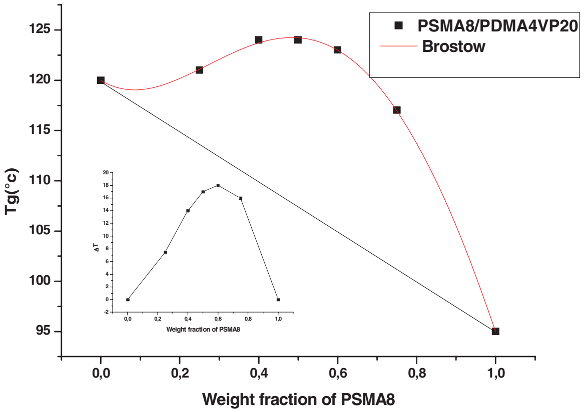

Figure 4.
Tg-composition of PSMA8/PDMA4VP20 system.

obtained with PSMA8/P4VP and PSMA8/PDMA4VP20 explain the occurrence of maximum of specific interactions in presence of an excess of PSMA8, at volume fractions larger than 0.5.A moderate complexity of PSMA8/P4VP system is characterized by the large value of a_2. Competing specific interactions of different strength carboxyl-pyridine, carboxyl-amide and carboxyl-carboxyl occurred within these systems.

Table 2.
Brostow et al. (BCKV) parameters for PSMA8/PDMA, PSMA8/P4VP and PSMA8/PDMA4VP systems cast from chloroform.

	Brostow et al.		
System	a_0	a_1	a_2
PSMA8/PDMA	14	13	−13
PSMA8/P4VP	24	50	63
PSMA8/PDMA4VP20	66	44	−21

Infrared Spectroscopy

PSMA8/P4VP: Evidence of Carboxyl-Pyridine Interactions

We have carried out by FTIR, a qualitative analysis of the specific interactions that

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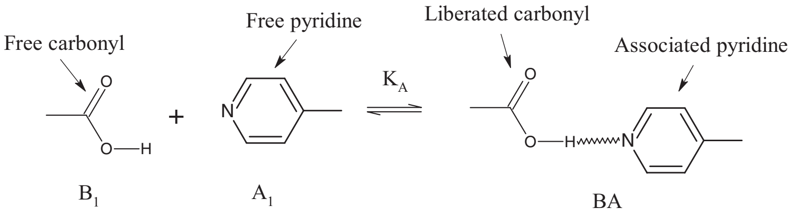
occurred between the carboxylic groups of PSMA8 and the pyridine groups of P4VP in three regions.

Figure 5 shows FTIR spectra of PSMA8, P4VP and their mixtures of different compositions. PSMA8 displays two bands in the 1800-1650 cm^{-1} region at 1698 cm^{-1} and 1740 cm^{-1} characteristic of cyclic carboxylic dimers and free carboxylic groups while P4VP is transparent in this carbonyl 1780-1650 cm^{-1} region. Figure 6 illustrates FTIR spectra of PSMA8, a selected PSMA8/P4VP (40/60) blend and their corresponding curve fitting using a Lorentzian function. The presence of the carboxyl-pyridine interactions within the blends is evidenced in this region from the new redistribution of the carbonyl band in the presence of the second constituent into a broader new band. The presence of carboxyl-pyridine interactions is evidenced from the appearance of a new band at 1725 cm^{-1}.

Figure 7 shows the scale expanded spectra of P4VP and its blends of different ratios with PSMA8 in the 3700–2200 cm^{-1} region. The occurrence of carboxyl-pyridine interactions as P4VP is progressively added in the blend is also evidenced from the shift of the 2630 cm^{-1} satellite band to lower wave numbers up to 2510 cm^{-1}.

PSMA8/PDMA: Evidence of Carboxyl-Amide Interactions

A qualitative analysis of the specific interactions that occurred between the



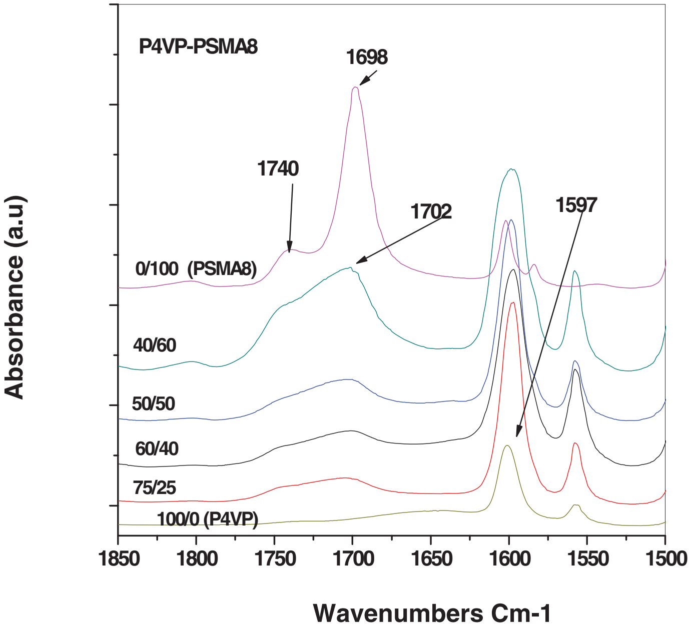


Figure 5.
FTIR spectra of PSMA8, P4VP and their blends of different ratios in the 1850-1500 Cm-1 region.

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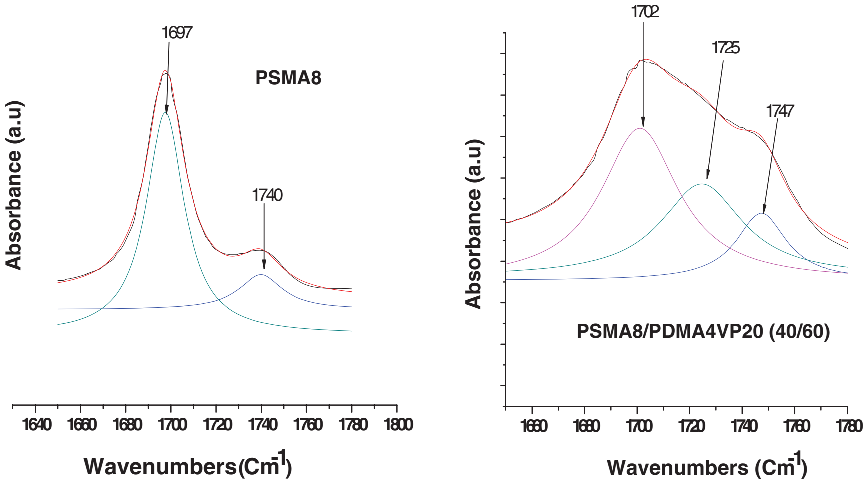

Figure 6.
FTIR spectra of PSMA8 (a) and PSMA8/P4VP (40/60) and their curve fitting.

carboxylic groups of PSMA8 and the amide groups of PDMA, mainly responsible of the formation of the interpolymer complexes, was also carried out in the 1780- 1550 cm^{-1} region. FTIR spectra of PSMA8, PDMA and their mixtures of different compositions are illustrated in Figure 8. PSMA8 displays two bands in the 1800-1650 cm^{-1} region at 1698 cm^{-1} and 1740 cm^{-1} characteristic of cyclic carboxylic dimers and free carboxylic groups while PDMA is transparent in this region. The presence of the carboxyl-amide interactions is evidenced from the appearance of a new band at 1725 cm^{-1} and a

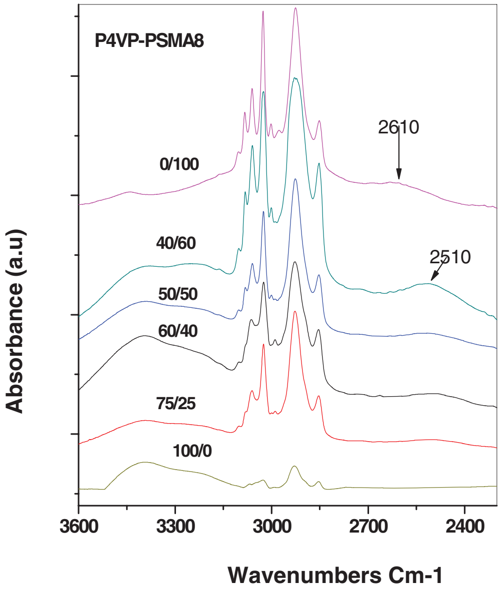

Figure 7.
Scale expanded FTIR spectra of PSMA8, P4VP and their PSMA8/P4VP blends in the 3600-2200 Cm^{-1} region recorded at room temperature.

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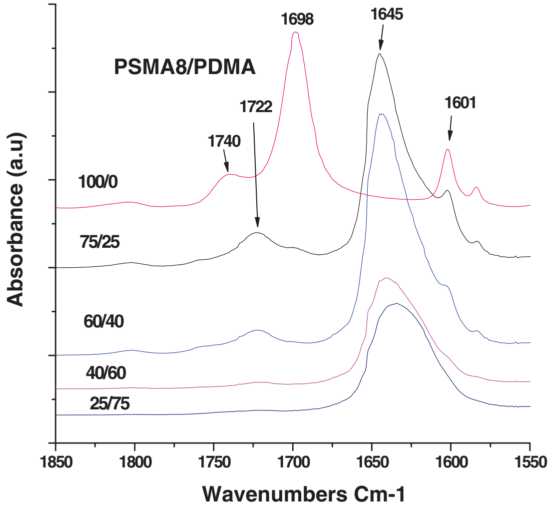


Figure 8.
FTIR spectra of PSMA8 and its blends with PDMA in the 1850-1550 Cm^{-1} region.

decrease of the intensity of the dimers band observed at 1698 cm^{-1}in the 1800-1650 cm^{-1} region. The three bands at 1740 cm^{-1}, 1725 cm^{-1} and 1698 cm^{-1} corresponding to free carbonyl, associated (liberated carbonyl) and cyclic dimer carboxylic groups are illustrated by the Scheme 2 below.

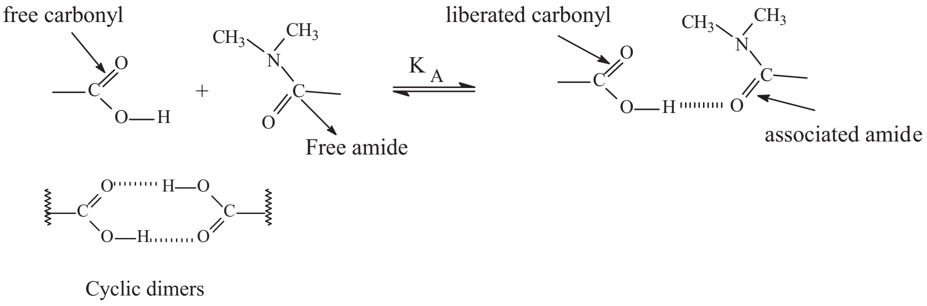
PSMA8/PDMA4VP20 System

FTIR spectra of typical PSMA8/PDMA, PSMA8/P4VP, PSMA8/PDMA4VP20 mixtures, illustrated in Figure 9, confirm the presence of competing specific interactions of different strength carboxyl-pyridine, carboxyl-amide and carboxyl-carboxyl within these systems.

Conclusion

With the aim to elaborate proton-conducting membranes, we have prepared and characterized interpolymer complexes based on poly(styrene-co-methacrylic acid) (PSMA) and poly(N,N-dimethylacrylamide-co-4vinylpyridine) (PDMA4VP) containing two proton accepting sites of different strength, by simply mixing appropriate amounts of pairs of these copolymers in chloroform.

The single Tg observed with each interpolymer complex, higher than those calculated from the weight average values of the pure copolymers indicates that these



Scheme 2.
Free amide carbonyl and carboxylic acid-amide inter-association.

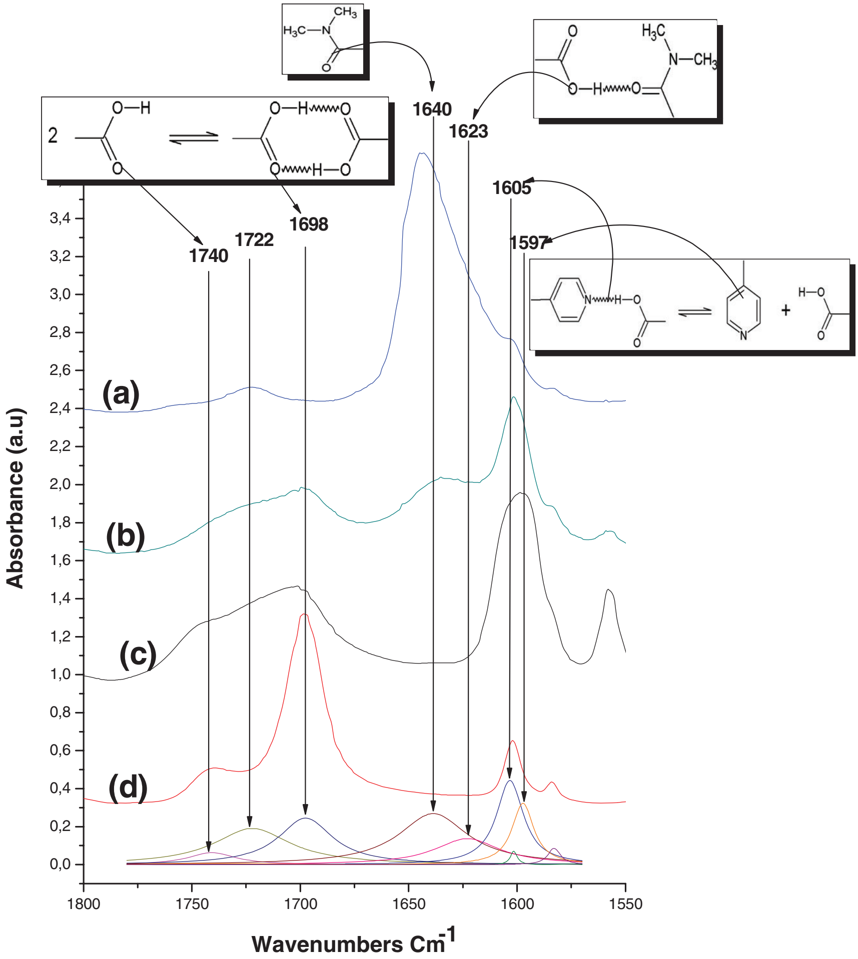


Figure 9.
FTIR spectra of typical PSMA8/PDMA (60/40) (a), PSMA8/PDMA4VP20 (b), PSMA8/P4VP(60/40) (c) PSMA8 (d), and corresponding curve fitting in the 1800-1550 Cm^{-1} region.

interpolymer complexes are miscible due to the presence of strong specific interactions as evidenced by FTIR spectroscopy and DSC.

The Tg-composition of these systems was analyzed using Brostow et al. (BCKV) equation. In agreement with high a_0 values, obtained with PSMA8/PDMA4VP20, the presence of 4VP units in PDMA4VP copolymers increased the average strength of intermolecular hydrogen bonding in the PDMA4VP20/PSMA8 systems compared to PDMA/PSMA8 or PSMA8/P4VP blends due to a higher number and stronger efficient specific interactions.

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