DOI: 10.1002/masy.201150504

Investigation of Hydrogen Bonded Interpolymer Complexes Based on Poly (n-butyl methacrylate–*co*-methacrylic acid) and Poly (n-butyl methacrylate -*co*-4-vinyl pyridine). Temperature Effect

*Farid Metref, Said Djadoun**

Summary: Two kinds of interpolymer complexes as soluble or precipitate of different structures were obtained in both THF and butan-2-one as common solvents by monitoring the hydrogen-bonding density within homoblends of poly(n-butyl methacrylate-*co*-4-vinylpyridine) (BM4VP) and poly(n-butyl methacrylate-*co*-methacrylic acid) (BMMA). A viscometry study confirmed such differences between these two types of interpolymer complexes from the behavior of the reduced viscosity of their blend solutions with feed blend composition. Qualitative and quantitative analyses of the interactions that occurred between these copolymers of relatively bulky side chain length containing various amounts of methacrylic acid and 4-vinylpyridine were carried out by FTIR. The fraction of associated pyridine groups to the carboxylic groups of the BMMA increases as the content of these latter increases in the BMMA/BM4VP blends. The obtained results also showed that the fractions of associated pyridine within the BMMA25/BM4VP26 blends are higher than those within BMMA18/BM4VP19 or BMMA8/BM4VP10. The FTIR analysis of a selected BMMA18/BM4VP19 1:1 ratio, carried out from 80 °C to 160 °C, above the glass transition temperatures of the two constituents of the blend, confirms the presence of strong hydrogen bonding interactions between the pyridine and the carboxylic groups within these blends even at 160 °C. A LCST is expected to occur at higher temperature as shown from the progressive decrease of the fraction of the associated pyridine.

Keywords: FTIR; Hydrogen bonding; interpolymer complexes; poly (butyl methacrylate-*co*-methacrylic acid); poly (butylmethacrylate-*co*-4-vinyl pyridine); viscometry

Introduction

Several studies on the methacrylic acid-vinyl pyridine interactions as introduced within polymer chains of the same or different nature are reported in the literature.[1–4] Depending on the nature of the solvent used, poly (methacrylic acid) and poly (vinypyridine) formed polymer blends and interpolymer complexes through strong hydrogen bonding.[5] This latter study confirmed by high-resolution solid state ^{13}C Nuclear magnetic resonance spectroscopy that both polymer blends and interpolymer complexes are homogeneous on a scale of about 1-3 nm. Similarly, I.Katime et al.[6] also reported that polymer blends and complexes are formed due to the interactions that occurred between poly (monoethyl itaconate) and poly (vinylpyridine). Their FTIR study evidenced that these interactions are of hydrogen bonding

---

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

type with partial pyridine protonation. Coleman et al[7] carried out a study of blends of poly (styrene-*co*-methacrylic acid) containing 9 mol % of methacrylic acid and poly (styrene-*co*-2-vinylpyridine) containing 17 mol % of 2-vinylpyridine and showed that the carboxylic acid–2-vinylpyridine interactions are of moderate strength and of hydrogen bonding nature. A relatively recent FTIR study confirmed the presence of both hydrogen bonding and ionic species when poly (4-vinylpyridine) is mixed with maleic acid-*alt*-ethylene copolymer.[8]

We have in previous studies already reported[9–10] that depending on the amounts of carboxylic and 4-vinylpyridine groups introduced within two polymer chains of different or same nature, miscible blends in all proportions or interpolymer complexes are formed via hydrogen bonding interactions.

Extensive research has been carried out on the formation of interpolymer complexes and their properties in solution and solid states as frequently published in regular and review papers.[11–15]

The temperature, the nature of the solvent and the hydrophobicity of the interacting polymers are among the most important factors that influence the formation and stability of hydrogen bonded interpolymer complexes.[16–18]

Proton donor poly (n-butyl methacrylate-*co*-methacrylic acid) and proton-acceptor poly (n-butyl methacrylate-*co*-4-vinylpyridine) copolymers containing various amounts of methacrylic acid and 4-vinylpyridine respectively were in this contribution prepared by free radical polymerization and characterized. Due to the methacrylic acid-4-vinylpyridine hydrogen bonding interactions that may occur upon mixing these two kinds of copolymers, interpolymer complexes are expected to be formed in THF and butan-2-one as common solvents. These specific interactions will be in a first step analyzed by viscometry, one of the simplest and widely used techniques.

This contribution will also investigate by FTIR qualitatively and quantitatively the interactions developed in homoblends of different compositions of poly (n-butyl methacrylate-*co*-methacrylic acid) containing 8, 18 or 25 mol % of methacrylic acid with poly (n-butyl methacrylate-*co*-4-vinylpyridine) containing 10, 19 or 26 mol % of 4-vinylpyridine, particularly in the 1650–1580 cm^{-1} region characteristic of pyridine rings. In this region, the acidic copolymer is transparent. The effects of the amount of interacting species introduced within the same polymer matrix and the side chain butyl groups on interpolymer interactions were investigated.

A study of the effect of temperature on the stability of these interactions was carried out by FTIR above the glass transition temperature of each constituent of the blend in the 80–160 °C temperature range.

Experimental Part

All monomers were distilled at reduced pressure before use. The azo-bis-isobutyronitrile (AIBN) or benzoyl peroxide (PBO) were purified by recristallization in methanol.

Poly (n-butyl methacrylate-*co*-methacrylic acid) (BMMA8, BMMA18 or BMMA25) copolymers containing 8, 18 or 25 mol % of methacrylic acid and poly (n-butyl methacrylate-*co*-4-vinylpyridine) (BM4VP10, BM4VP19 or BM4VP26) copolymers containing 10, 19 or 26 mol % of 4-vinylpyridine were prepared by free radical polymerization, using as initiator azobisisobutyronitrile (AIBN) at 60 °C or benzoyl peroxide at 65 °C for BM4VP-19. The yields of copolymers were kept at less than 15% in order to avoid the copolymer composition drift and chains reticulation and also to avoid the formation of homopolymers.

The methacrylic acid content in the BMMA copolymers was determined by a standard titration technique in a mixture of benzene/methanol. The 4-vinylpyridine content in the BM4VP copolymers was analyzed by UV spectroscopy and elemental analysis.

Films of these copolymers were cast from THF solutions and dried in a vacuum oven at 60 °C for several days. The glass transition temperatures of these copolymers (Tg) were measured by DSC using a Perkin Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 K/min under a nitrogen blanket. The Tg of these copolymers taken from the second scan and their intrinsic viscosities, determined in the usual way in butan-2-one or THF, are summarized in Table 1.

Thin films of these copolymers and of their blends were cast from THF solutions with a concentration of 2% w/v onto KBr disks and then dried in a vacuum oven at 70 °C for several days. FTIR spectra were recorded on a Nicolet 550 Fourier Transform infrared spectrometer with a resolution of 2 cm^{-1} and were averaged over 60 scans. In a similar way, FTIR spectra of the 1:1 ratio BMMA18/BM4VP19 blend were recorded in the 80 °C-160 °C temperature range.

All the viscosities of the polymer blend solutions were measured with an Ubbelohde viscometer at 25 °C. Intrinsic viscosities of these blends in THF or butan-2-one are determined in the usual way from the Huggins equation.

Blend solutions of the BMMA8/ BM4VP10 and BMMA25/BM4VP10 systems in butan-2-one of a total concentration of 0.1g/dl were prepared and their reduced viscosities as a function of the blend composition were measured at 25 °C when the solution was homogeneous and clear. When the solutions were turbid because of precipitation, apparent viscosities are measured after filtration of the precipitates.

Table 1.
Characteristics of copolymers

copolymers	[η] (dl/g)	Tg (°C)
BMMA8	1.668 a)	56
BMMA18	1.467 a)	78
BMMA25	1.372 a)	110
BMV4P10	1.330 b)	40
BMV4P19	1.940 b*)	41
BMV4P26	1.780 b)	46

a)in butan-2-one, b*)in THF using BPO as initiator

Results and Discussion

Complexation Behavior

Qualitative tests showed that homogeneous phases are observed in THF only for BMMA8/ BM4VP10, BMMA8/BM4VP19 and BMMA18/BM4VP10 solutions and for BMAM8/ BM4VP10 when butan-2-one is the common solvent. Cloudy solutions and gel-like or precipitates are obtained in both solvents when the proton-donor and proton-acceptor densities within the poly (n-butyl methacrylate) are increased, although complexation in THF requires higher hydrogen bonding density. Similar phenomena in the same solvents are reported in the literature for poly (methyl methacrylate-*co*-4-vinylpyridine)/poly(methyl methacrylate-*co*-methacrylic acid),[19] poly(styrene-*co*-meth acrylic acid)/poly(styrene-*co*-4-vinyl-pyridine)[3] and poly(styrene-*co*-4-vinyl benzoic acid)/poly(n-butyl methacrylate-*co*-4-vinylpyridine).[20]

Figure 1 shows the complexation maps of BMMA/BM4VP in both THF and butan-2-one as obtained from the qualitative tests.

Viscometry

The Hydrogen-bonding complexation has been reviewed by Jiang et al.[11] Several authors have also reported that such interpolymer complexation in solution, due to strong hydrogen bonding interactions, is usually accompagnied by a collapse of the polymer chains and interpolymer complexes as precipitates are formed. Soluble graft-like complexes are also reported in the literature.[21–22]

Among the techniques usually used to study these types of complexation in solution or bulk such as laser light scattering, nonradiative energy transfer fluorospectroscopy and DSC, viscometry remains the simplest one.

The interpolymer hydrogen bonding interactions in these systems were in a first step analyzed by viscometry using both THF and butan-2-one as solvents. The specific interactions that occurred between the two constituents of the mixture were

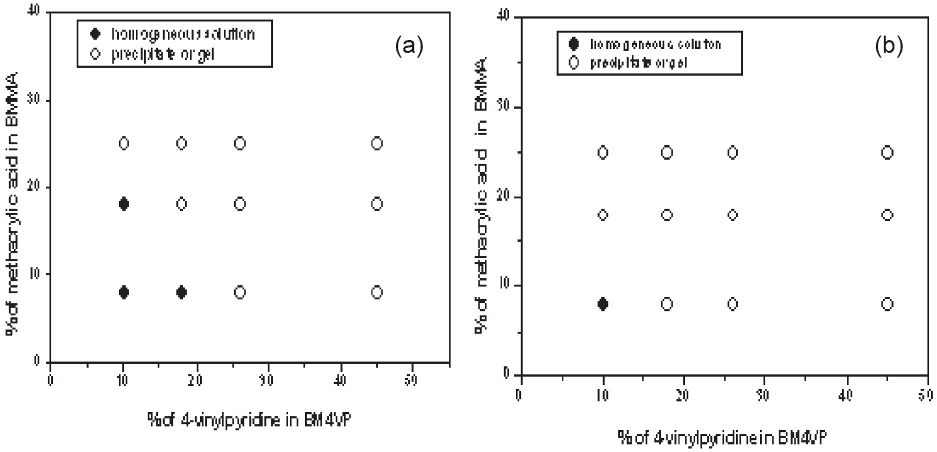

Figure 1.

Complexation maps of BMAM/BMV4P systems at different % of acidic and basic groups (1:1 ratio) (a) in THF and (b) in Butan-2-one at 25 °C.

evidenced qualitatively and analyzed quantitatively by FTIR.

The reduced viscosity of blend solutions of BMMA8/BM4VP10 and BMMA25/BM4VP10 of various ratios (w/w) in THF, varied linearly with the concentration for a total concentration higher than 0.212 g/dl. In agreement with results reported by S.Liu et al.,[20] this similar behavior indicates the presence of weak specific interactions since THF is a proton acceptor able to compete with BM4VP10 for interactions with the carboxylic groups of BMMA8 or BMMA25. The positive deviation of the reduced viscosity of BMMA25/BM4VP10 blend solutions of total concentrations of 0.212 g/dl in THF from the additivity law shown in Figure 2 confirms the presence of sufficient interactions that formed an interpolymer complexe. A shown in Figure 1, polymer concentration of 0.1 g/dl of this system led to the formation of interpolymer complexes of different nature and interpolymer com-

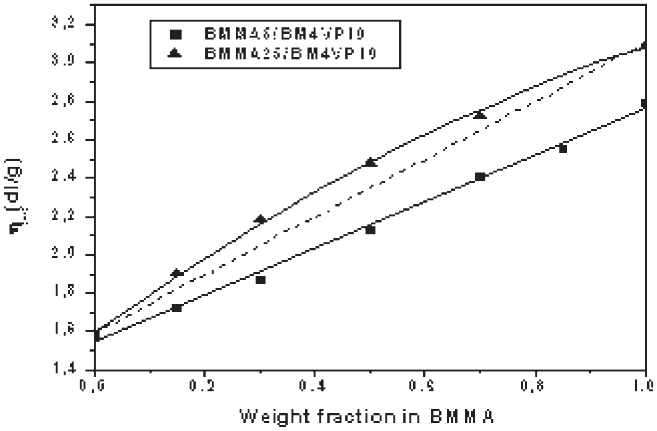

Figure 2.

Reduced viscosity of the 0.212 g/dl blend solutions of the BMMA/BM4VP10 system in THF as a function of the blend composition.

Table 2.
Viscosimetric interaction parameters of BMMA8/ BM4VP10 system calculated from Krigbaum and Wall method in THF at 25 °C.

Polymers	b_{ii} a)	b_m	b_{23}^{exp}	b_{23}^{the}	Δb_{23}	$[\eta]^{exp}$	$[\eta]^{the}$ b)	K_H c)
BMAM8	0.208					2.752		0.027
BMV4P10	0.188					1.521		0.018
15/85		0.176	0.137	0.198	−0.061	1.645	1.705	0.064
30/70		0.191	0.190	0.198	−0.008	1.790	1.890	0.060
50/50		0.280	0.361	0.198	+0.163	2.063	2.136	0.066
70/30		0.298	0.426	0.198	+0.228	2.343	2.383	0.054
85/15		0.190	0.141	0.198	–	2.569	2.567	0.029

a): $b_{ii} = Ki\ [\eta]_i^2$, b): $[\eta]_m^{th} = [\eta]_2\ X_2 + [\eta]_3\ X_3$, c): Huggins constant

Table 3.
Viscosimetric interaction parameters of BMMA8/ BM4VP10 system calculated from K.K.Chee method in THF at 25 °C.

Polymers	$[\eta]^{the}$	Δb
BMAM8		—
BMV4P10		
15/85	1.705	−0.060
30/70	1.890	−0.083
50/50	2.136	+0.163
70/30	2.383	+0.228
85/15	2.567	−0.057

plexes as precipitates are formed in THF with systems of higher densities of hydrogen bonding interacting species.

Krigbaum and Wall[23] and K.K.Chee[24] well known empirical approaches were used to analyze the viscosity behavior of these two systems in THF previously described and briefly summarized by the equations below:

According to Krigbaum and Wall Δb_{23} is given by:

$$\Delta b_{23} = b_{23}^{exp} - b_{23}^{th} \qquad (1)$$

Where b_{23}^{th} is the theoretical parameter defined as $b_{23}^{th} = (b_{22}\ b_{33})^{1/2}$ and b_{23}^{exp} the experimental viscosimetric interaction parameter obtained from:

$$b_m = X_2^2\, b_{22} + X_3^3\, b_{33} + 2\, X_2 X_3\, b_{23}^{exp} \qquad (2)$$

In a similar way Δb_{23} was also calculated using the K. K. Chee approach.[24] Tables 2–5 summarize the data of these different systems in THF.

The weak positive Δb_{23} values slightly higher with the BMMA25/BM4VP10 confirm the presence of weak specific interactions. Such weak specific interactions are still sufficient to induce the miscibility of these homoblends. The experimental intrinsic viscosities of these blend solutions are compared to those calculated from their weighted average values and found to be slightly lower. Since the intrinsic viscosity of a polymer blend is affected by several factors particularly molecular weight, structure and shape, both positive and negative deviations from the additivity law are reported in the literature.[25]

Table 4.
Viscosimetric interaction parameters of BMMA25/ BM4VP10 system calculated from Krigbaum and Wall method in THF at 25 °C.

Polymers	b_{ii} a)	b_m	b_{23}^{exp}	b_{23}^{the}	Δb_{23}	$[\eta]^{exp}$	$[\eta]^{the}$ b)	K_H c)
BMAM25	0.182					3.471		0.015
BMV4P10	0.188					1.521		0.0180
15/85		0.233	0.362	0.185	0.177	1.786	1.813	0.0730
30/70		0.207	0.235	0.185	0.051	2.094	2.106	0.0473
50/50		0.173	0.162	0.185	−0.023	2.485	2.500	0.0280
70/30		0.227	0.288	0.185	+0.103	2.896	2.886	0.0270
85/15		0.222	0.341	0.185	+0.156	3.120	3.179	0.0228

a): $b_{ii} = Ki\ [\eta]_i^2$, b): $[\eta]_m^{th} = [\eta]_2\ X_2 + [\eta]_3\ X_3$, c): Huggins constant

Table 5.
Viscosimetric interaction parameters of BMMA25/ BM4VP10 system calculated from K.K.Chee method in THF at 25 °C.

Polymers	$[\eta]^{the}$	$\overline{\Delta}b$
BMAM25		
BMV4P10		
15/85	1.815	+0.180
30/70	2.105	+0.050
50/50	2.494	−0.023
70/30	2.883	+0.103
85/15	3.177	+0.156

Figure 3 displays the reduced viscosity of the 0.1g/dl (below C* defined as the reciprocal of the intrinsic viscosity) blend solutions of these BMMA8/BM4VP10 and BMMA25/ BM4VP10 systems in butan-2-one as a function of the blend composition. The two systems behaved differently in this solvent. The BMMA8/BM4VP10 blend solution shows a positive deviation of the reduced viscosity from the additivity law. Such a positive deviation may be attributed to the formation of soluble interpolymer complexes of loose structure of sufficiently large hydrodynamic volume resulting from a combination of low density of interacting sites and relatively bulky butyl side groups. Indeed the two copolymers containing low content of hydrogen bonding interacting species sufficiently spaced within the same poly (n-butyl methacrylate) matrix mix randomly.

S. Liu et al.[22] observed similar positive deviation and the formation of soluble graft-like complexes based on carboxy terminated polystyrene oligomers and poly (4-vinylpyridine). Increasing by copolymerization the carboxylic acid content within the poly (n-butyl methacrylate) matrix from 8 mol% to 25 mol % showed a different behavior of the apparent reduced viscosity of BMMA25/BM4VP10 butan-2-one solutions. A negative deviation from the additivity law is observed with this solvent of a weaker ability to compete with the proton acceptor copolymer. This is due to the presence of more intense hydrogen bonding interactions expected to occur between the two copolymers as the carboxylic acid content of BMMA25 becomes higher with tendency to form interpolymer complexes with more compact structure. As discussed in the previous section of this contribution, interpolymer complexes as precipitates were obtained in both solvents upon increasing both amounts of interacting species.

Infrared Spectroscopy

We have in the first step of this investigation by FTIR, carried out a qualitative analysis of the specific interactions that occurred

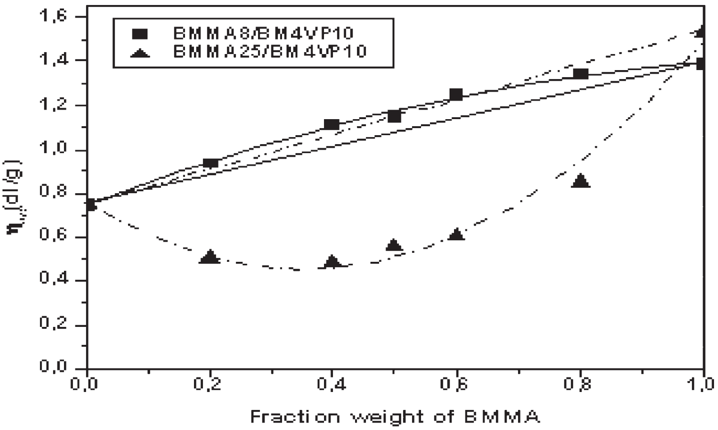

Figure 3.
Reduced viscosity of the 0.1g/dl (below C*) blend solutions of the BMMA/ BM4VP10 system in butan-2-one as a function of the feed blend composition.

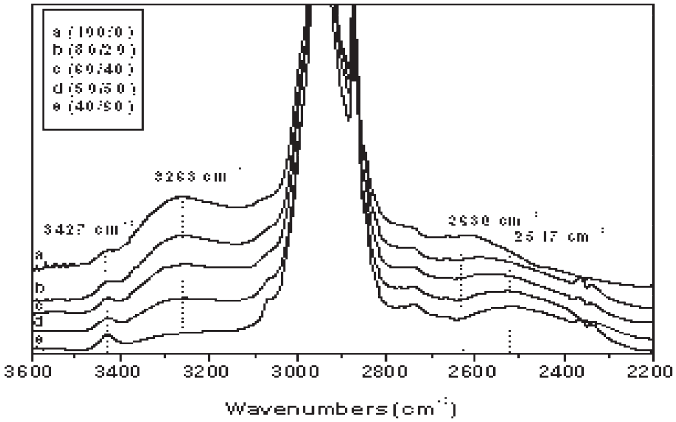

Figure 4.
Scale expanded FTIR spectra of BMMA25/BM4VP26 blends in the 3600–2200 cm^{-1} region recorded at room temperature.

between the carboxylic groups of the BMMA and the pyridine groups of the BM4VP, mainly responsible of the formation of the interpolymer complexes in the two regions of interest: the hydroxyl stretching 3700–2200 cm^{-1} region, and the 1650–1580 cm^{-1} pyridine region.

Figure 4 shows as an example the scale expanded infrared spectra of the BMMA25 and its blends of different ratios with BM4VP26 in the 3600–2200 cm^{-1} region. The BMMA25 displays a broad band with a maximum at 3263 cm^{-1} and a satellite band at 2630 cm^{-1}. Due to the presence of bulky butyl groups in each copolymer, the carboxyl-ester interactions are considered as weak. As the basic BM4VP26 copolymer is progressively added in the blend, the intensity of the band at 3263 cm^{-1}decreases while the maximum of the 2630 cm^{-1} satellite band shifts to lower wave numbers up to 2517cm^{-1}. This is characteristic of the carboxyl-pyridine interactions.

Figure 5 illustrates the scale expanded FTIR spectra of the BM4VP26 and the BMMA25/ BM4VP26 blends recorded at room temperature in the 1630–1580 cm^{-1}.

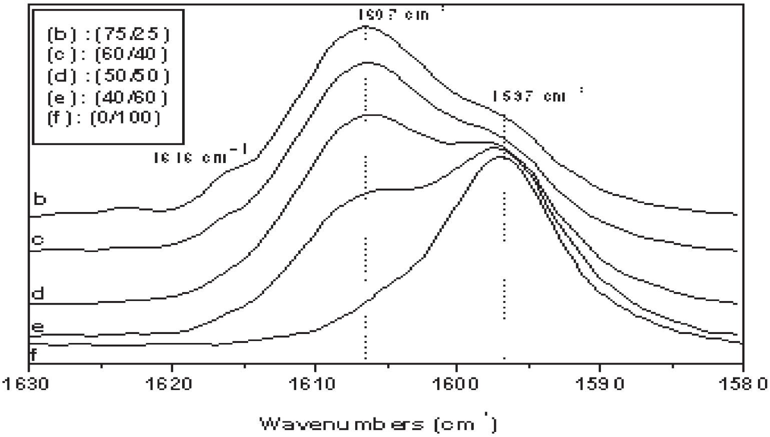

Figure 5.
Scale expanded FTIR spectra of BMMA25/BM4VP26 blends in the 1630–1580 cm^{-1} region recorded at room temperature.

The BM4VP26 exhibits a band centered at 1597 cm^{-1} due to free pyridine ring. Qualitatively, when BMMA25 is added to BM4VP26, a new band of increasing intensity appears at around 1607 cm^{-1}. This band characterizes the associated pyridine groups. As the amount of the acidic copolymer is increased in the blends, a broadening of this band towards higher wave numbers is observed. A small negligible band appeared around 1616 cm^{-1} with the 75:25 BMMA25/BM4VP26 blend. This is attributed to a partial pyridine protonation.

The intensity of hydroxyl-pyridine interactions increases within the BMMA25/BM4VP10 blends as compared to BMMA8/BM4VP10 blends. Similar variations were observed when BMMA25/BM4VP26 blends were compared to BMMA18/BM4VP26 blends.

Due to the bulky butyl groups of the polymer matrix, the main interactions that occurred within the homoblends are those between the carboxyl and pyridine groups.

In the second step a quantitative analysis of the main specific interactions that occurred between the BMMA and BM4VP was carried out in the 1650–1580 cm^{-1} region. The fractions of the relative areas related to the two bands at 1597 cm^{-1} and 1607 cm^{-1} characteristic of free and associated pyridine groups were determined using a Lorentzian spectral curve fitting procedure. The BMMA copolymer is transparent in this region.

The fraction of free pyridine groups was calculated from the following relation:[26]

$$F_F^N = \frac{A_{1597}}{A_{1597} + \frac{a_{1597}}{a_{1607}} A_{1607}} \tag{3}$$

Where A_{1597} and A_{1607} are the areas of the bands at 1597 and 1607 cm^{-1}, respectively, a_{1597} and a_{1607} are the absorptivities of the two bands, assuming an absorptivity ratio of unity.

The obtained results are summarized in Table 6.

Fraction of associated pyridine groups to the hydroxyl groups of the BMMA increases as the BMMA content increases in the blend. As it is shown in Table 6 and in a good agreement with the viscometry results, the fractions of associated pyridine within the BMMA25/BM4VP26 blends are higher than those of BMMA8/BM4VP10 blends due to higher number of interacting sites.

Table 6.
Curve-fitting data from infrared spectra of BMMA/BM4VP blends in the pyridine region.

Weight %	Free pyridine			Associated pyridine		
	ν (cm^{-1})	$W_{1/2}$(cm^{-1})	Fract	ν (cm^{-1})	$W_{1/2}$(cm^{-1})	Fract
BMMA8/BM4VP10						
80/20	1597.4	10.3	0.317	1606.9	11.6	0.683
60/40	1597.3	10.0	0.394	1607.0	12.1	0.606
50/50	1597.3	10.0	0.510	1607.0	11.0	0.490
40/60	1597.3	10.0	0.595	1607.0	11.2	0.405
20/80	1597.3	10.8	0.775	1607.3	10.2	0.225
BMMA25/BM4VP10						
75/25	1597.3	10.0	0.169	1607.1	13.1	0.831
60/40	1597.2	10.4	0.206	1606.8	12.5	0.794
50/50	1597.2	10.6	0.265	1607.1	13.8	0.735
40/60	1597.0	10.8	0.393	1606.8	12.4	0.607
25/75	1597.0	10.0	0.454	1606.8	12.8	0.546
BMMA18/BM4VP26						
75/25	1597.0	10.0	0.276	1606.9	13.3	0.724
60/40	1597.2	10.7	0.355	1607.0	12.5	0.645
50/50	1597.1	10.4	0.512	1606.9	12.0	0.488
40/60	1597.2	11.0	0.672	1607.1	11.9	0.328
BMMA25/BM4VP26						
75/25	1596.9	10.1	0.195	1606.7	13.3	0.805
60/40	1597.1	10.8	0.257	1606.7	13.2	0.743
50/50	1569.7	11.0	0.359	1606.8	13.0	0.641
40/60	1596.7	11.0	0.554	1606.8	12.9	0.446

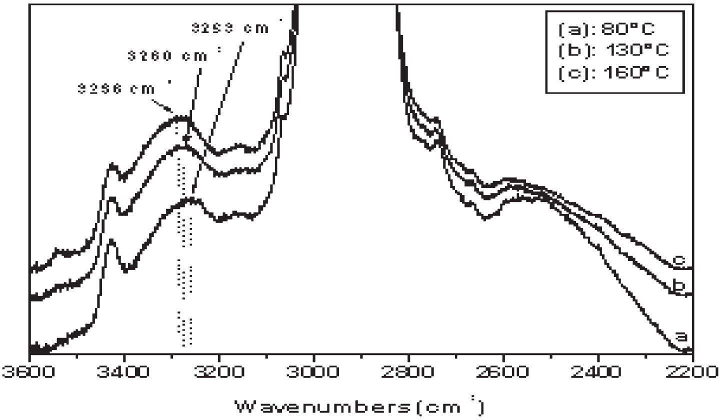

Figure 6.
Scale expanded FTIR spectra of BMMA18/BM4VP19 (50/50) blends in the 3600–2200 cm^{-1} region at different temperatures.

For the same acidic copolymer BMMA25, the fraction of associated pyridine groups decreases as the density of the 4-vinylpyridine within the polymer matrix increases. The fraction of associated pyridine also increased with an increase of the proton donor density for a given basic copolymer.

Temperature Effect

A study of the effect of temperature on the stability of the intensity of hydroxyl-pyridine interactions within a selected 1:1 ratio BMMA18/BM4VP19 blend was carried out by FTIR spectroscopy above the glass transition temperatures of the two copolymers in the temperature range of 80–160 °C. As shown in Figure 6, the band observed at 3272 cm^{-1} shifted to higher wave numbers as the temperature is increased. This is an evidence of the dissociation of a fraction of the hydrogen bonding interactions occurring within the blends. A weak shoulder characteristic of free hydroxyl groups appeared at 3550 cm^{-1}.

Figure 7 displays the infrared spectra at different temperatures for the 1:1 ratio

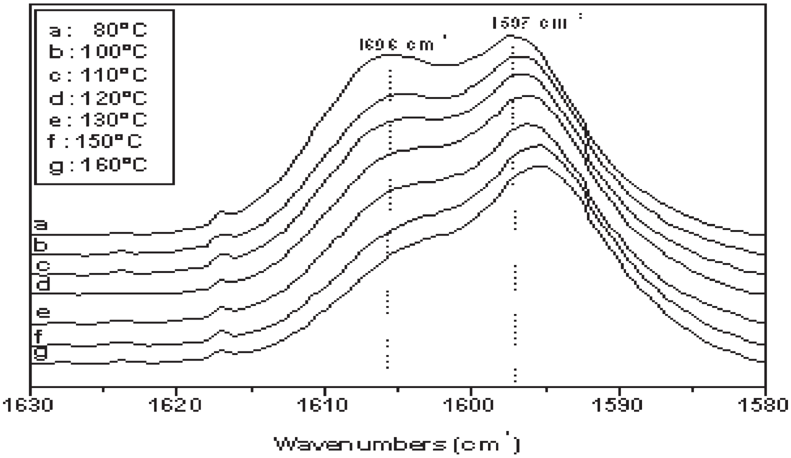

Figure 7.
Scale expanded FTIR spectra of BMMA18/BM4VP19 (50/50) blends in the 1630–1580 cm^{-1} region at different temperatures.

Table 7.
Curve-fitting data from infrared spectra of BMMA18/BM4VP19 (50/50) blends in the pyridine region at different temperatures.

T(°C)	Free pyridine			Associated pyridine		
	ν (cm^{-1})	W$_{1/2}$(cm^{-1})	Fract	ν (cm^{-1})	W$_{1/2}$(cm^{-1})	Fract
80 °C	1596.6	10.2	0.511	1606.3	11.0	0.489
100 °C	1596.3	10.6	0.570	1606.0	11.0	0.430
110 °C	1596.2	10.9	0.600	1605.9	10.8	0.400
120 °C	1595.9	11.1	0.635	1605.7	10.8	0.365
130 °C	1595.7	11.3	0.661	1605.5	10.7	0.339
150 °C	1595.3	11.7	0.720	1605.1	10.4	0.280
160 °C	1595.1	11.9	0.742	1604.9	10.4	0.258

BMMA18/BM4VP19 blend in the 1650–1580 cm^{-1}. Similarly, a decrease of the band intensity at 1606 cm^{-1} corresponding to the hydrogen bonded pyridine-carboxylic groups is observed as the temperature is raised from 80 °C to 160 °C. However, this band still appears as an observable shoulder even at 160 °C, suggesting the considerable stability of these interactions.

Similarly, a quantitative analysis was carried out using equation (3) above. The fraction of free pyridine groups was calculated for this blend at different temperatures and the results are gathered in Table 7.

Indeed the fraction of the associated pyridine decreases progressively and leveled off as temperature increases as displayed in Figure 8.

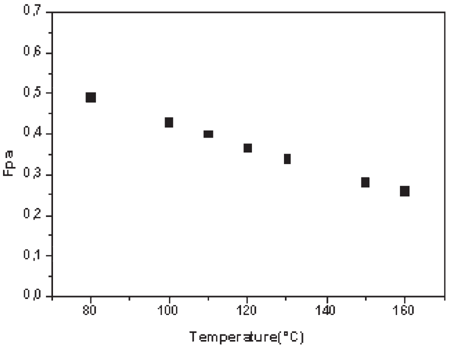

Figure 8.
Fraction of associated pyridine groups (Fpa) of BMMA18/BM4VP19 (50/50) blends versus the temperature.

Conclusion

This study showed that different interpolymer complexes were obtained in both THF and butan-2-one by monitoring the hydrogen-bonding density only within homoblends of poly(n-butyl methacrylate-*co*-4-vinylpyridine) (BM4VP) and poly(n-butyl methacrylate-*co*-methacrylic acid) (BMMA).The differences between these types of interpolymer complexes are confirmed by viscometry from the behavior of the reduced viscosity of their blend solutions with feed blend composition.

The quantitative analysis of the interactions that occurred within homoblends of poly (butyl methacrylate-*co*-methacrylic acid) and poly (butyl methacrylate-*co*-4-vinylpyridine) containing different amounts of interacting species, carried out by Fourier Transform infrared spectroscopy (FTIR) in the 1650–1580 cm^{-1} region characteristic of the pyridine groups, showed that due to the butyl groups of the polymer matrix, the main interactions that occurred within these homoblends are those between the carboxyl and pyridine groups. The results also showed that the fractions of associated pyridine within homoblends of BMMA25/BM4VP26 are higher than those within BMMA18/BM4VP19 or BMMA8/ BM4VP10.

The temperature effect carried out by FTIR analysis qualitatively and quantitatively for the 1:1 ratio BMMA18/BM4VP19 from 80 °C to 160 °C, above the glass transition temperatures of the two constituents of the blend, confirmed the presence of hydrogen bonding interactions between the pyridine and the carboxylic groups within these blends even at 160 °C. A LCST is expected to occur at higher temperature as shown from the progressive decrease of the fraction of the associated pyridine.

[1] J. Y. Lee, P. C. Painter, M. M. Coleman, *Macromolecules* **1988**, *21*, 954.
[2] Y. Wang, G. Qi, H. Peng, S. Yang, *Polymer* **2002**, *43*, 2811.
[3] S. Bennour, F. Metref, S. Djadoun, *J.Appl. Polym.Sci.* **2005**, *98*, 806.
[4] A. Habi, S. Djadoun, *Thermochimica Acta* **2008**, *469*, 1.
[5] J. Z. Yi, S. H. Goh, *Polymer* **2001**, *42*, 9313.
[6] J. L. Velada, L. C. Cesteros, E. Meaurio, I. Katime, *Polymer* **1995**, *36*, 2765.
[7] H. R. Motzer, P. C. Painter, M. M. Coleman, *Macromolecules* **2001**, *34*, 8390.
[8] V. Villar, L. Trusta, M. L. Fernàndez-Berridi, J. J. Iruin, M. Iriarte, L. Gargallo, D. Radic, *Thermochimica Acta* **2003**, *402*, 209.
[9] S. Djadoun, F. E. Karasz, F. Metref, *Macromol. Symp.* **1994**, *78*, 155.
[10] K. ElMiloudi, M. Benygzer, S. Djadoun, N. Sbirrazzuoli, S. Geribaldi, *Macromol Symp.* **2005**, *230*, 39.
[11] M. Jiang, M. Li, M. Xiang, H. Zhou, *Adv. Polym.Sci.* **1999**, *46*, 121.
[12] V. V. Khutoryanskiy, *Int. J. Pharm.* **2007**, *334*, 15.
[13] V. V. Khutoryanskiy, Z. S. Nurkeeva, G. A. Mun, A. V. Dubolazov, *J.Appl. Polym.Sci.* **2004**, *93*, 1946.
[14] N. P. Bayramgil, *Polym. Degrad. Stab.* **2008**, *93*, 1504.
[15] M. Pinteala, T. Budtova, V. Epure, N. Belnikevich, V. Harabagiu, B. C. Simionescu, *Polymer* **2005**, *46*, 7047.
[16] G. A. Mun, Z. S. Nurkeeva, V. V. Khutoryanskiy, A. B. Biketenova, *Macromol. Rapid Commun.* **2000**, *21*, 381.
[17] G. A. Mun, Z. S. Nurkeeva, V. V. Khutoryanskiy, V. A. Kan, A. D. Sergaziev, E. M. Shaikhutdinov, *Polymer Science series B.* **2001**, *43*, 289.
[18] P. W. Labuschagne, W. A. Germishuizen, S. M. C. Verryn, F. S. Moolman, *Eur. Polym. J.* **2008**, *44*, 2146.
[19] S. Djadoun, *Polymer Bulletin* **1983**, *9*, 6–7 313.
[20] L. Zhu, M. Jiang, L. Liu, H. Zhou, L. Pan, Y. Zhang, *J. Macromol. Sci. - Phys. B* **1998**, *37*(6), 827.
[21] S. Liu, G. Zhang, M. Jiang, *Polymer* **1999**, *40*, 5449.
[22] S. Liu, Q. Pan, J. Xie, M. Jiang, *Polymer* **2000**, *41*, 6919.
[23] W. R. Krigbaum, F. T. Wall, *J. Polym. Sci.*, **1950**, *5*, 505.
[24] K. K. Chee, *Eur. Polym. J.* **1990**, *26*, 423.
[25] Y. Wang, G. Qi, H. Peng, S. Yang, *Polymer* **2002**, *43*, 2811.
[26] L. Jose, L. C. Cesteros, I. Katime, *J. Appl Spectrosc.* **1996**, *50*, 893.