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Hydrogen Bonding Complexes of Poly (styrene-*co*-2-hydroxyethyl acrylate) and Poly (styrene-*co*-4-vinylpyridine)

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Summary: Random copolymers of poly(styrene-*co*-4-vinylpyridine) (S4VP) and poly (styrene-*co*-2-hydroxyethyl acrylate) (SHEA) of different compositions were prepared and characterized. An investigation of the effects of solvent and densities of the interacting species incorporated within these copolymers showed that novel and various hydrogen bonding interpolymer complexes of different structures were elaborated when these copolymers are mixed together. The specific interactions that occurred within the SHEA copolymers and the elaborated complexes were evidenced by FTIR qualitatively from the appearance of a new band at 1604 cm^{-1} and quantitatively using appropriate spectral curve fitting in the carbonyl and pyridine regions. The intermolecular hydrogen bonding interactions that occurred between the hydroxyl groups of the SHEA and the nitrogen atom of the pyridine groups in the S4VP are stronger than the self-associations within the SHEA. In the solid state, a DSC analysis showed that the variation of the glass transition temperatures of these materials with the composition behaved differently with the densities of interacting species and were analyzed quantitatively. A thermal stability study of the synthesized copolymers and of their different mixtures carried by thermogravimetry confirmed a similar behaviour.

Keywords: complexes; DSC; FTIR; hydrogen bond; miscibility; poly(styrene-*co*-2-hydroxyethyl acrylate)

Introduction

It is reported that the formation of interpolymer complexes in organic solvents via hydrogen bonding from binary polymers containing interacting species depends strongly on the nature of the solvent, the densities and the strength of these species.[1–5] Different types of interpolymer complexes may be formed as soluble with a loose structure when the specific interactions are relatively weak and not dense or as precipitates with a stable and compact structure only when polymer-polymer interactions that occurred between the components of the mixture are stronger than polymer-solvent interactions and exceed a certain level. Such strong hydrogen bonding interactions between polymers are expected to increase the thermal stability of the resulting material.

The literature reports that due to the presence of strong interpolymer specific interactions of hydrogen bonding or ionic types, miscible blends or interpolymer complexes are formed when poly(carboxylic acid) are mixed with poly(vinyl pyridine).[6,7]

Katime et al.[8] studied the miscibility and specific interactions that occurred in blends of poly(vinyl pyridines) with poly (hydroxy methacrylate). Their results showed that all blends exhibit a single glass transition temperature higher than the glass

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transition of the blends calculated from the additivity rule. These authors did not however observe any formation of interpolymer complexes, as precipates in methanol.

We have previously studied mixtures of poly(styrene-*co*-methacrylic acid) with poly(styrene-*co*-4-vinylpyridine) and showed that interpolymer complexes as precipitates were formed in butan-2-one[9,10] when sufficient densities of interacting groups were incorporated within polystyrene matrices.

It is of interest to investigate whether poly(4-vinylpyridine) and these basic copolymers can form interpolymer complexes with poly(styrene-*co*-2-hydroxyethyl acrylate) because of its tendency to replace poly(2-hydroxylethyl methacrylate) in many instances in biomedical applications. We therefore have in this contribution synthesized and characterized copolymers of different compositions of styrene with 2-hydroxyethyl acrylate (SHEA) and with 4-vinylpyridine (S4VP). We have then carried out a study of the effects of the nature of solvent used (chloroform or butan-2-one) and the densities of 2-hydroxyethyl acrylate and 4-vinylpyridine incorporated within polystyrene matrices on the elaboration of novel materials as blends or interpolymer complexes of different structures when copolymers of poly(styrene-*co*-2-hydroxyethyl acrylate) (SHEA) are mixed together with poly(styrene-*co*-4-vinylpyridine) (S4VP).

The specific interactions that occurred between the SHEA and the S4VP copolymers and the complexation behaviours in solution and solid state of the elaborated materials from mixtures of these copolymers were investigated by differential scanning calorimeter (DSC) and Fourier Transform Infra Red spectroscopy (FTIR) qualitatively and quantitatively. A thermal stability study of the synthesized copolymers and of their different mixtures was carried by TGA. The dilution effect and optimization of the densities of interacting species required for complexation were also investigated.

Experimental Part

Synthesis and Characterizations

Poly(styrene-*co*-2-hydroxyethyl acrylate) containing 16 and 33 mol % of 2-hydroxyethyl acrylate (SHEA-16 and SHEA-33) were prepared by solution free radical polymerization at 60 °C in dioxan. Poly (styrene-*co*-4-vinylpyridine) containing 13, 30 and 40 mol % of 4-vinylpyridine (S4VP-13, S4VP-30 and S4VP-40) were prepared by bulk free radical polymerization at 60 °C, using azoisobutyronitrile (AIBN) as the initiator keeping the conversion low.

The copolymers were isolated by precipitation in a non solvent then purified by repeated dissolution/reprecipitation in choloroform/heptane and dried in a vacuum oven at 60 °C for several days. The content of styrene and 4-vinylpyridine within these copolymers was determined by UV spectroscopy and RMN spectroscopy for S4VP copolymers.

The average molecular weights of these copolymers were determined by size exclusion chromatography using a Waters 2414 chromatograph equipped with a refractive index detector. The comonomer compositions, average molecular weights and other characteristics of the synthesized copolymers are listed in Table 1.

Thermal Analyses

Films of the various copolymers and of their blends of different ratios were prepared from chloroform solutions. These films were dried to constant weight in a vacuum oven at 60 °C during several days to remove traces of solvent and used in the thermal analyses.

A Q100 TA instruments was used to measure the glass transition temperatures T_g of these copolymers and of their blends under a nitrogen atmosphere in the 0 °C to 180 °C temperature range. The scanning rate was of 20 °C/min. The T_g is taken from the second scan as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

Table 1.
The different characteristics of the synthesised copolymers.

	UV		RMN	GPC			DSC	TGA
	HEA (mol%)	4VP (mol%)	4VP (mol %)	Mw (g/mol)	Mn (g/mol)	I = Mw/Mn	Tg (°C)	T_{max} (°C)
SHEA-16	16			554841	251620	2.21	92	434
SHEA-33	33			2100884	587302	3.58	74	440
S4VP-13		13		435929	223311	2.78	113	425
S4VP-30			30	98 500	63961	1.54	114	418
S4VP-40			40	143 000	80791	1.77	117	416

Thermogravimetric analysis was carried out prior to DSC on a TA instruments TGA-Q500 under nitrogen atmosphere from 40 °C to 600 °C at a heating rate of 10 °C/min.

FTIR Measurements

Thin films of these copolymers and of their blends of different ratios were prepared by casting from a 3% w/v solution in chloroform onto KBr disks. The films were kept in a vacuum oven for several days at 60 °C until the solvent was removed. The FTIR spectra were recorded at room temperature with PERKIN ELMER spectrometer using 60 scans at a resolution of 2 cm^{-1}.

Results and Discussion

We have carried out qualitative tests and showed that depending on the nature of the solvent (chloroform or butan-2-one) and the densities of interacting species, two types of interpolymer complexes are formed. Soluble interpolymer complexes were obtained through mixing appropriate amounts of SHEA (SHEA-16 or SHEA-33) and S4VP (S4VP-13 or S4VP-30) chloroform or butan-2-one solutions, while SHEA-33 formed precipitate interpolymer complexes with S4VP-40 in butan-2-one. The formation of these interpolymer complexes is due to the specific interactions of hydrogen bonding type that occurred between the constituents of the different complexes which are analyzed in their solid state by FTIR and DSC.

Thermogravimetric Analysis

The thermogravimetric traces (TGA) of SHEA-33, S4VP-13 and their blends of different ratios and of their corresponding derivative thermogravimetric d(TGA) are shown in Figure 1 while Table 2 summarizes their thermogravimetric parameters that also includes among others the temperatures at which 5% and 50% degradation

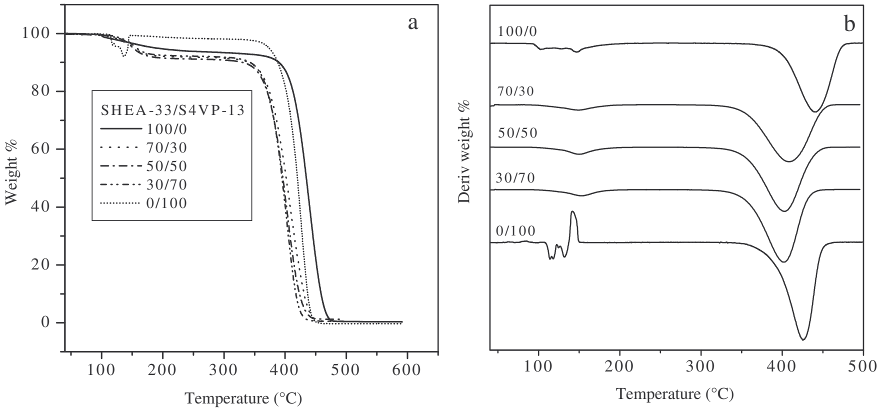

Figure 1.
TGA (a) and d(TGA) (b) curves of SHEA-33, S4VP-13 and of their blends of different ratios.

Table 2.
Thermogravimetric parameters of SHEA-33, S4VP-13 and their blends.

Wt. %	ΔT(°C) (Step 1)	ΔT(°C) (Step 2)	T_{max1} (°C)	T_{max2} (°C)	T5% (°C)	T50% (°C)	% Δm (H_2O)
100/0	94–197	350–487	102–145	440	124	435	13
70/30	98–194	299–454	149	408	149	402	8
50/50	105–198	297–451	150	403	151	395	9
30/70	106–200	298–450	153	402	155	395	8
0/100	172–217	332–461	–	425	373	418	2

occurs. It is evident from these figures that the thermal degradation of SHEA-33/S4VP-13 blends proceeds by two steps represented by two peaks in the corresponding d(TGA) curves. The first step, located between 94 °C and 217 °C is attributed to loss of adsorbed water (The HEA and 4VP comonomers have hydrophilic characters), the second step corresponds to the degradation of the blend, whose temperature of maximum degradation increases with SHEA-33 composition increase in the SHEA-33/S4VP-13 blends.

This analysis shows that these as-cast materials absorb an amount of water varying from 13% for SHEA-33 to 9% for complexes. This will affect the interpolymer interactions and explain the enhanced thermal degradation observed with these materials as evidenced from the negative deviation of the temperature of degradation of these materials with the composition.

Thermal Analyses

The single glass transition temperature observed with each blend is an evidence of the formation of homogeneous phases. All other systems displayed a single T_g. The T_g-composition curves shown in Figure 2 can be fitted by the Kwei equation given by:

$$T_g = w_1 T_{g_1} + w_2 T_{g_2} + q w_1 w_2 \qquad (1)$$

Where wi are the weight fractions of the components and T_gi their corresponding glass transition temperature.

The values of q, which have been taken as adjustable parameters, are -63, -37 and -19 for SHEA-16/S4VP-13, SHEA-33/S4VP-13 and SHEA-16/S4VP-30, respectively. Indeed as reported in the literature,[11] the Kwei constant depends on both processes of self-association and inter-association in the mixture. The negative deviation more pronounced with SHEA-16/S4VP-13, due mainly to intramolecular hydrogen bonding dissociation within

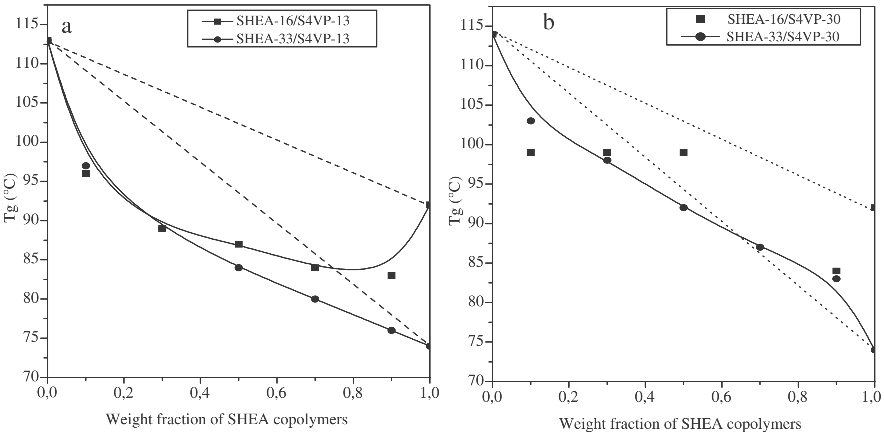

Figure 2.
Glass transition temperature dependence with blend compositions of SHEA-16/S4VP-13 and SHEA-33/S4VP-13 (a); SHEA-16/S4VP-30 and SHEA-33/S4VP-30 (b) blends.

SHEA-16, decreases with increasing hydroxyl group density in the copolymer. Similar observations were reported by Katime et al.[12] for blends of poly(vinyl acetate-*co*-vinyl alcohol) with poly(N,N-dimethylacrylamide) and by Chang and co-workers in poly(vinylpyridines with phenolic resin).[13]

As the content of 4-vinylpyridine increases from 13 to 30 mol % as within S4VP-30, the number of interacting sites increases when this latter is mixed with SHEA-33.

When the number of interacting sites in the proton-donating polymer is low as in SHEA-16 and the Hydrogen-bonding interactions that occurred between this latter and the proton-accepting relatively weak, a negative T_g-composition with a greater q value (-19) is still observed with the SHEA-16/S4VP-30 mixtures.

An S-shaped curve of T_g-composition is however observed with the SHEA-33/S4VP-30 mixtures. The T_g of the blend is lower than the additive T_g for SHEA-33 content less than 70% by but above the additive T_g for higher proton-donor SHEA-33 content.

These results confirm that different types of interpolymer complexes of different structures may be obtained by controlling the number of specific interactions.

FTIR Analysis of SHEA-33/S4VP-13 and SHEA-33/S4VP-30 Blends

Figure 3 shows for illustration the scale expanded infrared spectrum of SHEA-33 copolymer and of its blends of different ratios with S4VP-30 recorded at room temperature in the hydroxyl region. As already reported in a previous study.[14] and displayed in Figure (3), SHEA-33 exhibits in this 3750–3130 cm^{-1} region, a shoulder at 3580 cm^{-1} attributed to free hydroxyl groups and a broad band centred at 3478 cm^{-1}, due to the overlapped hydrogen bonded hydroxyl groups with carbonyl groups and with other hydroxyl groups. When the content of the basic copolymer is added to SHEA copolymer, the centre of the band at 3478 cm^{-1} broadens and shifts gradually to lower wavenumbers, reflecting a new redistribution of hydrogen bonded hydroxyl groups within the SHEA-33 and with pyridine groups.

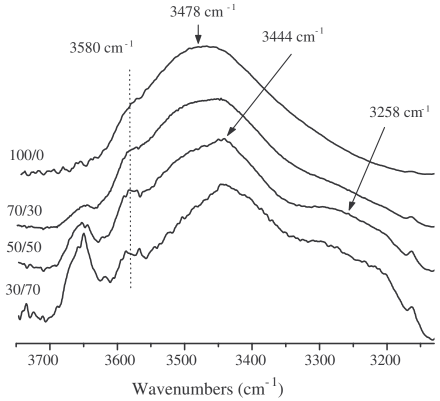

Figure 3.
Scale-expanded infrared spectra of SHEA-33/S4VP-30 blendes in the hydroxyl region.

Due to the relatively higher fraction of hydroxyl groups within SHEA-33 compared to the pyridine fraction within the basic copolymer S4VP-13, the intensity of intra and intermolecular interactions hydroxyl-carbonyl remains non negligible even in the presence of an excess of S4VP-13 within the SHEA-33/S4VP-13 mixtures as evidenced by a broad band. This may be

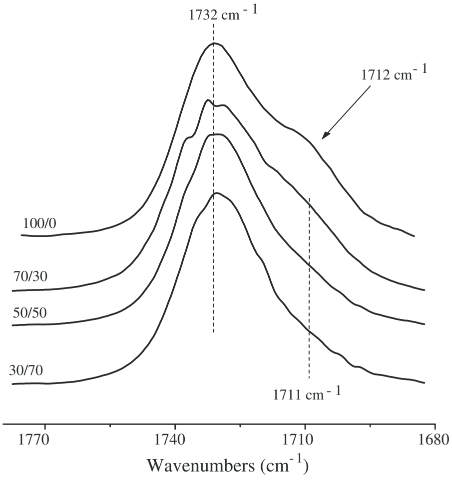

Figure 4.
Scale-expanded infrared spectra of SHEA-33/S4VP-30 blendes in the carbonyl region.

explained by a non densification of the interpolymer interactions of rather stronger hydroxyl-pyridine interactions in agreement with the negative deviation of T_g-composition. As the S4VP content in the blend increases, the main peak at 3478 cm^{-1} broadens and shifts gradually to 3444 cm^{-1}. The frequency shift of the maximum of the 50/50 blend is 136 cm^{-1} for SHEA-33/S4VP-30 higher than the one corresponding to the interactions within the pure SHEA-33 of about 102 cm^{-1}.

Besides a new band of intermediate intensity, increasing with the S4VP content in the mixture, attributed to hydroxyl associated to pyridine groups, appears as a shoulder at 3258 cm^{-1}. This confirms the occurrence of stronger specific interactions than those of self-associated ones within the SHEA copolymers. A more apparent peak was observed for PHEMA/P4VP as reported by Katime et al.[8]

The occurrence of these hydroxyl-pyridine interactions is also evidenced qualitatively in the carbonyl stretching region. As it can be seen from Figure 4, the SHEA-33 shows two bands in this region at 1732 cm^{-1} and 1712 cm^{-1} attributed to the free and hydrogen bonded carbonyl groups respectively. The amount of the hydroxyl-carbonyl interactions characterized by the shoulder at 1712 cm^{-1} decreases as the S4VP-30 content increases in the blend. Similar results were observed with SHEA-33/S4VP-13 systems. These observations are in agreement with those depicted in the hydroxyl region.

A quantitative analysis using an adequate curve fitting procedure was carried in this carbonyl stretching region to determine the fraction of free and associated carbonyl groups as the S4VP-13 or S4VP-30 amount is added within the blends using a Gaussian function. The fraction of free carbonyl F_f was determined from:

$$F_f = \frac{A_F}{A_F + A_A/a} \qquad (2)$$

Where A_f and A_a are the areas under the peaks of free and associated carbonyl groups respectively and ***a*** the ratio of the molar absorption coefficients taken as 1.23.[15] The results summarized in Table 3 show that the fraction of free carbonyl groups increases with the basic copolymer content in the blends.

Table 3.
Curve-fitting results of the carbonyl-ester bands in the SHEA-16/S4VP-13, SHEA-16/S4VP-30, SHEA-33/S4VP-13, SHEA-33/S4VP-30 mixtures.

	Free carbonyl ester band			H-Bonded carbonyl ester band		
	Wavenumber (cm^{-1})	Width (cm^{-1})	F_F	Wavenumber (cm^{-1})	Width (cm^{-1})	F_A
SHEA-16/S4VP-13						
100/0	1732	19	0.73	1711	20	0.27
70/30	1731	20	0.83	1711	18	0.17
50/50	1731	20	0.88	1710	16	0.12
30/70	1730	21	0.91	1709	15	0.09
SHEA-16/S4VP-30						
100/0	1732	19	0.73	1711	20	0.27
70/30	1731	20	0.84	1711	19	0.16
50/50	1730	20	0.89	1710	19	0.10
30/70	1730	21	0.92	1709	17	0.08
SHEA-33/S4VP-13						
100/0	1732	19	0.67	1712	22	0.33
70/30	1731	22	0.72	1712	23	0.28
50/50	1731	22	0.78	1711	23	0.22
30/70	1730	23	0.88	1709	18	0.12
SHEA-33/S4VP-30						
100/0	1732	22	0.67	1712	22	0.33
70/30	1732	22	0.73	1712	23	0.27
50/50	1731	20	0.81	1711	21	0.19
30/70	1730	21	0.86	1710	21	0.14

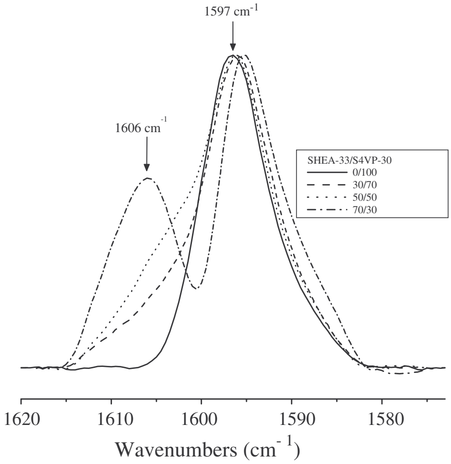

Figure 5.
Scale-expanded infrared subtracted spectra of SHEA-33/S4VP-30 in the pyridine region.

Figure 5 displays as an example the subtracted spectra of SHEA-33/S4VP-30 blends in the 1620–1575 cm^{-1} region that also confirm qualitatively the presence of these specific interactions from the appearance of a new band at 1604 cm^{-1} corresponding to hydrogen-bonded pyridine rings.

A quantitative analysis is performed in this region. Using a Lorentzian function and an absorptivity ratio of 1,[8] the results of the curve fitting shown in Table 4 confirm the decrease of the fraction of free pyridine as the amount of SHEA-33 increases in the blend.

Conclusion

This study showed that though relatively strong hydrogen bonding interactions occurred between the hydroxyl groups of moderate proton-donating SHEA copolymers and pyridine groups of S4VP, Hydrogen bonding interpolymer complexes as precipitates are formed only when the densities of the interacting species reached certain amounts as for SHEA-33 mixed in butan-2-one with S4VP containing 40 mol % of 4-vinylpyridine or more.

These specific hydroxyl-pyridine interactions were evidenced by FTIR qualitatively from the appearance of a new band at 1604 cm^{-1} and quantitatively using appropriate spectral curve fitting in the carbonyl and pyridine regions. In the solid state, the

Table 4.
Curve-fitting results of the carbonyl-pyridine bands in SHEA-16/S4VP-13, SHEA-16/S4VP-30, SHEA-33/S4VP-13 and SHEA-33/S4VP-30 blends.

	Free pyridine band			H-Bonded pyridine band		
	Wavenumber (cm^{-1})	Width (cm^{-1})	F_F	Wavenumber (cm^{-1})	Width (cm^{-1})	F_A
SHEA-16/S4VP-13						
0/100	1597	11	1			
30/70	1597	11	0.78	1604	7	0.22
50/50	1597	10	0.75	1604	7	0.25
70/30	1597	11	0.59	1604	8	0.41
SHEA-33/S4VP-13						
0/100	1597	11	1			
30/70	1597	12	0.75	1604	9	0.25
50/50	1597	11	0.67	1604	9	0.33
70/30	1597	11	0.47	1604	10	0.53
SHEA-33/S4VP-30						
0/100	1597	11	1			
30/70	1597	11	0.81	1604	8	0.19
50/50	1597	10	0.72	1604	8	0.28
70/30	1597	10	0.59	1604	8	0.41
SHEA-16/S4VP-30						
0/100	1597	11	1			
30/70	1597	12	0.88	1604	6	0.12
50/50	1597	11	0.83	1604	7	0.17
70/30	1597	10	0.70	1604	7	0.30

DSC analysis showed a change in the shape of the variation of T_g-composition as the densities of interacting species within the polystyrene matrices increased. Negative deviations are observed with complexes formed from copolymers containing relatively low densities of interacting species. Increasing the number of interacting sites led to a positive deviation as for SHEA-33/S4VP-30 containing an excess of SHEA-33. These results are in agreement with those revealed by the quantitative FTIR analysis that indeed confirmed the presence of significant fractions of inter associated hydroxyl-pyridine and self-associated hydroxyl-carbonyl species withinthese particular complexes. The thermal stability study carried by TGA confirmed a similar behaviour.

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