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Study of the miscibility of poly(ethyl methacrylate-*co*-4-vinylpyridine)/poly(styrene-*co*-cinnamic acid) blends

Naïma Bouslah, Nabila Haddadine, Djamel Bendiabdallah, Farouk Amrani[*]

Chemistry Institute, University of Sciences and Technology Houari Boumediene,
B.P. 32, El Alia, Algiers 16111, Algeria

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Summary

The miscibility of a series of poly(ethyl methacrylate-*co*-4-vinylpyridine) with poly(styrene-*co*-cinnamic acid), is investigated by differential scanning calorimetry. The results show that each blend is miscible as ascertained by a single composition dependent glass transition temperature. The Tg's of the blends exhibit positive deviations from the weight average Tg's of the blend components. The thermograms data exploited according to the Kwei and Schneider approaches suggest the occurrence of strong specific intermolecular attractive interactions within the binary systems. The strength of these interactions, as estimated from the Kwei q-values, increases with the proton donor and proton acceptor contents in the copolymers.

Introduction

It is well known that the miscibility of polymeric blends requires a favorable heat of mixing since the contribution of the combinatorial entropy of mixing of high molecular weigth polymers to the Gibbs free energy is negligible. Therefore miscibility of binary (co)polymer systems has been brought about by introducing within the components chains of initially immiscible blends, antagonist functional groups capable of developing interactions that result in an exothermic mixing. These interactions have been classified into two different kinds. A so-called repulsion effect (1) generated by intramolecular interactions between dissimilar comonomeric units of copolymeric chains and intermolecular attractive interactions which can be the result of electrostatic forces, dipole-dipole resonance, proton transfer and hydrogen bonding (2-4).

A wide variety of antagonist functional groups has been used to induce polymer miscibility(5). Strong interactions have been achieved upon mixing on the one side, a proton accepting fanctionalized polymer with, on the other side, a proton donating modified polymer, such as pyridyl and 2-[*N*,*N*-dimethylamino] ethyl methacrylate radicals

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[*] Corresponding author

for the former and carboxylic acid and hydroxyl groups for the latter.

Among the numerous binary polymer blends investigated, much attention has been paid to systems with proton donating modified poly(styrene)/proton accepting modified poly(methacrylate)s. In this context, Landry and Teegarden (6) studied the effect of introducing acid groups of various strength such as vinyl phenol, styrene-4-carboxylic acid and styrene-4-sulfonic acid in enhancing miscibility of modified polystyrene with poly(methyl methacrylate) or poly(*N*,*N* -dimethylacrylamide). Wu and *co*-workers(7), in a study on miscibility improvement, via introducing hydrogen bonding interactions into a polystyrene/poly(ethyl methacrylate) system, found that the modification of polystyrene chains by 9 mol. % of vinylphenol induced the complexation between poly(styrene-*co*-vinylphenol) and poly(ethyl methacrylate). Paul et al (8) reported that the modification of polystyrene chains with relatively low acrylic acid levels, 8 mol.%, has led to miscible blends with poly(methyl, ethyl and n-propyl) methacrylates.

In a recent publication (9) we presented results of FTIR and DSC studies of miscible binary system poly(styrene-*co*-cinnamic acid)/poly(ethyl methacrylate-*co*-2-[*N*,*N*-dimethylamino]ethyl methacrylate. In this paper, the previous study is extended by examining the effect of the exchange of the basic comonomer 2-[*N*,*N*-dimethylamino] ethyl methacrylate in the poly(ethyl methacrylate) chains by 4-vinylpyridine units on the miscibility of modified poly(styrene)/poly(ethyl methacrylate) system. The study is performed as a function of blend composition and ionic groups content in both polymer chains.

Experimental

Materials

Styrene (S), ethyl methacrylate (EMA) and 4-vinylpyridine (4VP) were vacuum distilled prior to use. Cinnamic acid (CA) was recrystallized from chloroform solutions. Poly (styrene-*co*-cinnamic acid), PSCA, and poly(ethyl methacrylate-*co*-4-vinylpyridine), PEMAVP, were prepared by 2,2'azo-bis-isobutyronitrile induced free radical solution copolymerization in dioxane and butanone respectively at 60°C, under N_2 blanket. The yields were maintained below 15% in order to avoid any drift in copolymer composition. The synthesized copolymers were purified by several dissolution followed by precipitation into a large excess of non-solvent, isolated and vacuum dried at 40'C for several days.

Polymer Characterization

The chromophore content in the PEMAVP copolymers was determined by UV spectroscopy analysis from copolymer solutions in chloroform using poly(4-vinylpyridine) as a standard. The molar content of the cinnamic acid in the PSCA copolymers was obtained by titration of the acid residues of copolymer solutions in benzene/methanol (80/20 vol. %) using previously standardized sodium hydroxide solution. The weight-average (M_w) and number-average (M_n) molecular weights of PSCA and PEMAVP copolymers were determined by size exclusion chromatography using respectively polystyrene and poly(methyl methacrylate) as standards. The intrinsic viscosities measured at 25°C in dilute THF solutions, by extrapolation to zero concentra tion were 1.57 and 0.68 for PEMAVP23 and PSCA21 respectively. The most important characteristics of the synthesized polymers are summarized in Table 1.

DSC Measurements

The polymer blends with different compositions were prepared by codissolution of the required weighted amount of each component in a common good solvent (THF). After stirring the solutions for 1 day to ensure thorough mixing, the blends were coprecipitated in petroleum ether. The powder samples were isolated and dried until constant weight in a vacuum oven at 50°C for several days. DSC thermograms were recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter, previously calibrated with Indium. The samples weighing from 10 to 15 mg were scanned at a rate of 20 K/min under nitrogen purging. All samples were preheated to 200°C and kept at that temperature for 10 min to ensure complete removal of any trace of residual solvent. Thermograms were recorded on the second or subsequent scans and the Tg determined at midpoint were reproducible.

Table 1. Composition and Molecular weight of the copolymers.

Polymer	Composition ionic content (mol. %)	M_n	M_w
PEMAVP13	12.50	99900	313100
PEMAVP23	22.96	-	-
PSCA5	4.66	97100	163300
PSCA8	8.00	90300	147100
PSCA21	21.57	-	-

Results and discussion

DSC measurement of glass transition temperature is widely used to investigate the miscibility of blends, provided that the glass transition temperatures of the pure components are clearly distinguishable. It is expected that a miscible polymer blend should present a single glass-transition. The value of such Tg is generally located between those of the parent polymers and depends on the blend composition. Since the Tg's of the blend components in the systems studied in the present work are at least 30°C far apart, the single composition dependent glass transition temperature criterion can be used unambiguously. The recorded thermograms of PEMAVP13/PSCA5, PEMAVP13/PSCA8 and PEMAVP23/PSCA21 blends, in the 2/1, 1/1 and 1/2 weight fractions, exhibit a single Tg intermediate between those of the pure components, indicating that these systems are miscible in the tested compositions. In each case, the Tg value is affected by the blend composition; it gradually shifts to higher temperatures with increasing PSCA content. The Tg values are listed in Table 2. Furthermore, the experimental Tg values of the blends are higher than those calculated from the additivity rule, Fig. 1. Similar deviations have been already reported (10-12) in blends where the two components develop strong specific interactions. Among several equations commonly used to follow the dependence of Tg on the composition of the polymer blend, the Kwei (13) and the Schneider et al. (14) equations are able to describe positive deviations

Table 2. Glass transition temperature of PEMAVP/PSCA blends

Sample		Tg (°C)
PEMAVP13		85.2
PEMAVP23		86.0
PSCA5		115.7
PSCA8		125.7
PSCA21		163.9
PEMAVP13/PSCA5	(2 : 1)	97.7
PEMAVP13/PSCA5	(1 : 1)	102.9
PEMAVP13/PSCA5	(1 : 2)	111.1
PEMAVP13/PSCA8	(2 : 1)	106.7
PEMAVP13/PSCA8	(1 : 1)	114.1
PEMAVP13/PSCA8	(1 : 2)	121.7
PEMAVP23/PSCA21	(2 : 1)	125.5
PEMAVP23/PSCA21	(1 : 1)	141.0
PEMAVP23/PSCA21	(1 : 2)	149.0

The Kwei equation contains in addition to the classical Gordon-Taylor expression (15), an extra term that reflects the specific interactions occurring within the blends

$$Tg = \frac{W_1Tg_1 + KW_2Tg_2}{W_1 + KW_2} + qW_1W_2 \qquad (1)$$

where Tg, Tg_1 and Tg_2 are the glass transition temperatures of the blend and pure components 1 and 2 respectively; W_1 and W_2 are the weight fractions of the pure components, K and q are adjustable parameters. For systems which present strong interactions between the two polymers, such as those studied in this work, K is set equal to unity and a reduced version of the Kwei equation can be used $Tg = W_1Tg_1 + W_2Tg_2 + qW_1W_2$.The parameter q has been considered to be a measure of the strength of the specific interactions that are taking place between the blend components; larger q values indicate stronger interactions. The values of the adjustable parameter q, determined by fitting the experimental Tg data to the Kwei equation, Fig 1, were found to be 14, 37 and 59 for PEMAVP13/PSCA5, PEMAVP13/PSCA8 and PEMAVP23/PSCA21 respectively. These values suggest an increasing excess stabilization energy and show clearly that the extent of the intermolecular interactions follows the order PEMAVP13/PSCA5 <PEMAVP13/PSCA8 <PEMAVP23/PSCA21.

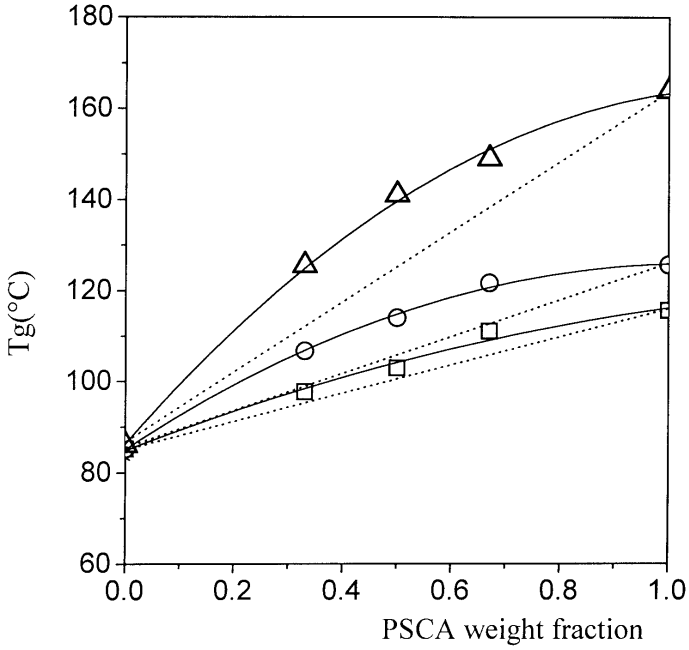

Fig.1. Glass transition temperature as a function of blend composition:
(□) PEMAVP13/ PSCA5, (O) PEMAVP13/PSCA8, (Δ) PEMAVP23/PSCA21.

In the previous study(9) we have shown that binary systems of poly(ethyl methacrylate-*co*-2-[*N,N*-dimethylamino] ethyl methacrylate, PEMADAE containing 13 mol.% of basic units were miscible with the PSCA copolymers. The strength of the intermolecular interactions within the PEMADAE/PSCA blends, as estimated from the Kwei q-values, was found to follow a similar trend to that of PEMAVP/PSCA system. Furthermore, the PEMADAE/ PSCA blends present larger q-values than PEMAVP/PSCA systems as shown through a typical example in Fig.2. The 2-[*N,N*-dimethylamino] ethyl methacrylate units seem to have a greater ability to hydrogen bond with carboxylic acid groups of the PSCA copolymers than 4-vinylpyridine units.

We have also used the Schneider et al. third power equation to follow the Tg composition curves:

$$(Tg - Tg_1)/[(Tg_2 - Tg_1)W_{2c}] = (1 + K_1) - (K_1 + K_2)W_{2c} + K_2 W_{2c}^2 \qquad (2)$$

where W_{2c}, the corrected weight fraction of component of highest glass transition temperature is given by $W_{2c}=KW_2/(W_1+KW_2)$with $K = \rho_1, Tg_1/\rho_2\ Tg_2= K'\ Tg_1/Tg_2$ and ρ_1, ρ_2 are the densities of the pure components 1 and 2 respectively, the other terms are identical to those of equation (1). Schneider et al. approach assumes that the free volume reduction resulting from the directional specific interchain interactions between the constituents of a binary system leads to a positive deviation in the Tg composition curve.

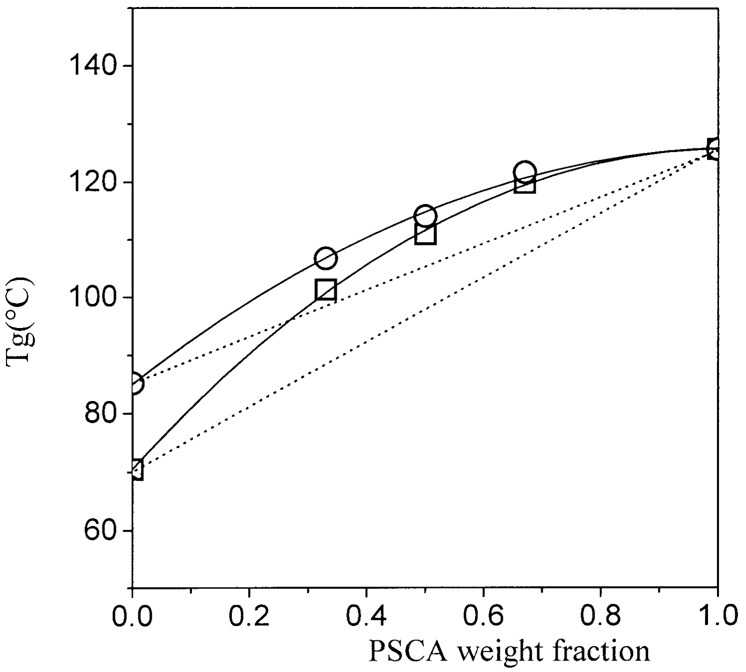

Fig.2. Glass transition temperature as a function of blend composition (□) PEMADAE13/PSCA8 q=54 ,(O) PEMAVP13/PSCA8 q=37.

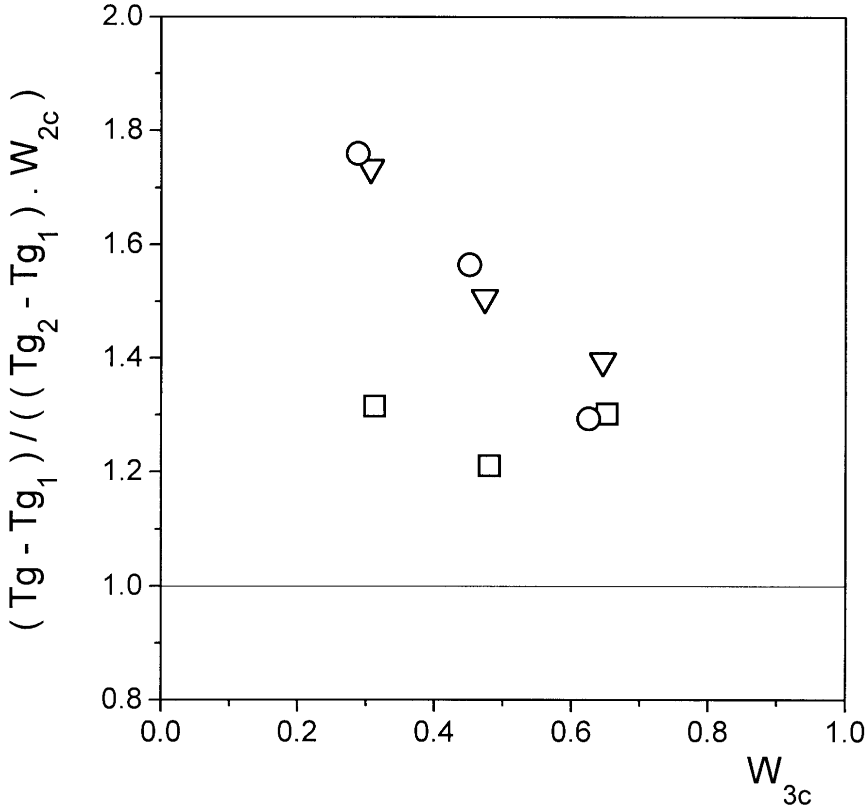

Fig.3. $(Tg - Tg_1) / ((Tg_2 - Tg_1) W_{2c})$ versus W_{2c} of PSCA in blends of (□) PEMAVP13/ PSCA5, (∇) PEMAVP13/PSCA8, (O) PEMAVP23/PSCA21.

For volume additivity the parameters K_1, = K_2 = 0 and equation (2) is reduced to:

$(Tg - Tg_1) / ((Tg_2 - Tg_1) W_{2c} = 1$, therefore the plot of $(Tg - Tg_1) / ((Tg_2 - Tg_1) W_{2c})$ versus W_{2c} will be an horizontal line about the value of 1.

The positive deviations from unity observed for the various blends in Fig.3 indicate the occurrence of strong specific intermolecular interactions within the components of the PEMAVP/PSCA systems. The order of the strength of interactions corroborates the results obtained by the Kwei approach.

Conclusion

Thermal analysis indicated that the PEMAVP/PSCA blends were miscible over the three blend compositions studied and regardless of the substitution level in the antagonist polymer chains, as ascertained by the observation of a single composition dependent glass transition temperature. The Tg's of the blends exhibited large positive deviations from the simple rule of additivity suggesting the occurrence of strong intermolecular interactions. Furthermore, the Kwei approach indicated that the strength of these interactions increases with the number of the interaction sites on both PEMAVP and PSCA chains. The formation of hydrogen bonds between carboxylic acid groups of PSCA copolymers and both carbonyl and pyridyl ones in PEMAVP is the driving force in the miscibility of the system. Finally, a comparison of the present results with a previous study of a PEMADAE/PSCA system, shows that the 2-[*N*,*N*-dimethylamino]ethyl methacrylate units seem to have a greater ability to hydrogen bond with carboxylic acid groups of the PSCA than 4-vinylpyridine units.

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