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Miscibility of poly(α-methyl styrene-co-methacrylic acid) with alkyl methacrylate-*co*-4-vinylpyridine copolymers

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SUMMARY

The miscibility of blends of poly(α-methyl styrene-*co*-methacrylic acid) (PαMSMA) with various alkyl methacrylate polymers or poly(alkyl methacrylate-*co*-4-vinylpyridine) was studied by differential scanning calorimetry and Fourier transform infra red spectroscopy.PαMSMA is immiscible with poly(methyl methacrylate), poly(ethyl methacrylate) and poly(n-butyl methacrylate) . The introduction of 4-vinylpyridine by random free radical copolymerization within these alkyl methacrylate polymer chains enhanced the miscibility of these copolymers with PαMSMA as a result of specific interactions that occurred between the carboxylic and pyridine groups , evidenced from the significant changes observed by FTIR in the carboxyl and pyridine ring regions. The density of interacting groups required for miscible blends depends on the size of the pendant group.

INTRODUCTION

It is known that poly(α-methyl styrene) is immiscible with high molecular weight polyalkyl methacrylates(1,2). The introduction of groups capable of providing specific interactions between the polymers in a blend is a method for increasing miscibility of polymers (3-9) .

Recently, Cowie et al (10) carried out a study of blends of poly{α-methyl styrene-*co*-[4-(1,1,1 trifluoro-2 hydroxy ethyl methacrylate) α-methyl styrene]} or poly[α-methyl styrene-*co*-4-(2-hydroxy ethyl) α-methyl styrene] with polyalkyl methacrylates and showed that miscible blends were obtained only for the methyl , ethyl and t-butyl derivates.Immiscible blends were however obtained with poly(propyl or butyl methacrylates).

In a previous study (11), we have showed from the polymer-polymer interaction parameter as determined by inverse gas chromatography that poly(styrene-*co*-acrylic acid) containing 20 mol % of acrylic acid was miscible in all proportions with poly(ethyl methacrylate) and poly(ethyl methacrylate-*co*-4-vinylpyridine).Similar results were also reported by Paul et al. (12,13)

In the present study , polyalkyl methacrylates and copolymers of different compositions of α–methyl styrene with methacrylic acid and of alkyl methacrylates with 4-vinylpyridine were prepared by free radical polymerization .Several blends of these copolymers were studied by differential scanning calorimetry and Fourier transform infra red spectroscopy.

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EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) , poly(ethyl methacrylate) (PEMA) and poly(n-butyl methacrylate) were prepared by free radical polymerization using azo-bis isobutyronitrile as initiator.

Random copolymers of different compositions of 1) 4-vinylpyridine with methyl methacrylate (MM4VP) or ethyl methacrylate (EM4VP) or n-butyl methacrylate (BM4VP) and 2) α-methyl styrene with methacrylic acid (PαMSMA) were prepared under similar conditions as the homopolymers, keeping the conversion low as to minimize composition drift.The intrinsic viscosities of the different polymers and copolymers are summarized in Table 1. The 4-vinylpyridine and styrene contents in the MM4VP ,EM4VP ,BM4VP and PαMSMA copolymers were determined by UV spectroscopy and elemental analysis.

Glass transition temperature measurements :

Blends of different ratios PαMSMA/PMMA , PαMSMA/PEMA PαMSMA/PBMA , PαMSMA/MM4VP , PαMSMA/EM4VP and of PαMSMA/BM4VP were prepared by codissolution of the polymers in an appropriate common solvent (THF) and coprecipitation. The blends were then dried in vacuum oven at 60°C for 72 hours. A DSC-7 Perkin Elmer differential scanning calorimeter was used to determine the glass transition temperature of the polymers ,copolymers and of their blends. All measurements were carried out at a heating rate of 20 K/min under a nitrogen blanket.

FTIR spectroscopy :

FTIR spectroscopy was used to analyze the specific interactions in the blends. Dilute solutions of polymers or polymer blends of different ratios of PαMSMA/BM4VP-26 were prepared. Thin films were cast from these solutions on KBr windows.The solvent was evaporated at room temperature . The films were then dried in a vacuum oven . FTIR spectra were recorded using an IBM IR/30 spectrometer at resolution of 1 cm^{-1} and 32 scans.

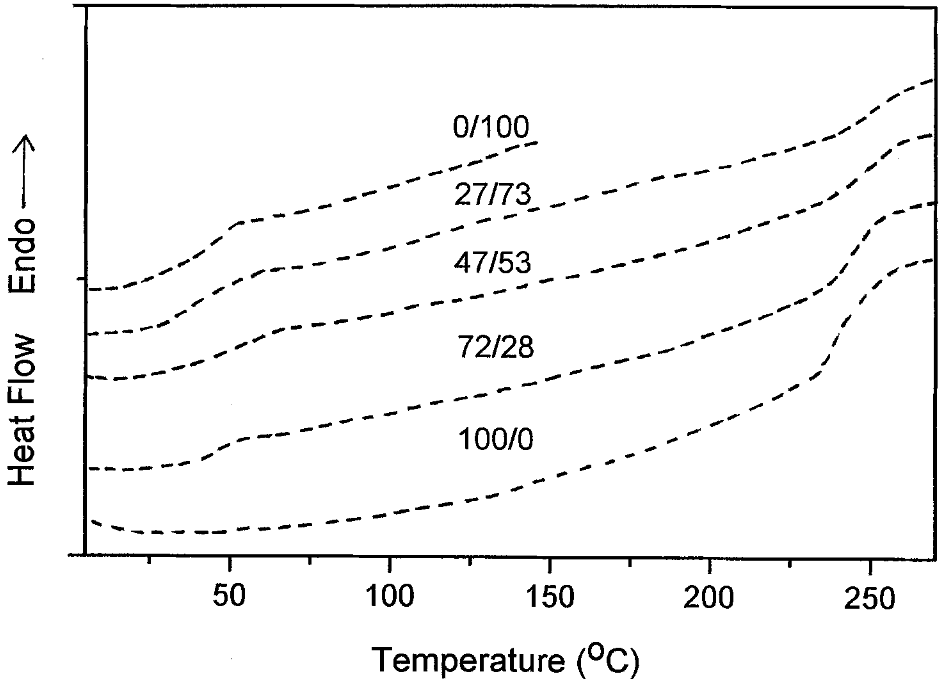
Table 1: Characteristics of polymers and copolymers:

Polymer	Coplymer Composition mol % of AM	 mol % of 4VP	[η] (dL/g)	Tg (°C)
PEMA	0	0	1.56	74.5
PBMA	0	0	2.26	42
MM4VP-08	0	08	1.31	110
EM4VP-08	0	08	1.51	77.5
EM4VP-23	0	23	1.16	86.5
BM4VP-10	0	10.6	1.33	40
BM4VP-18	0	18.9	1.94	41
BM4VP-26	0	26	1.78	46
PαMSMA	50.6	0	0.47	243.6

RESULTS AND DISCUSSION

PαMSMA was found to be immiscible with not only PMMA, PEM, PBMA but also with EM4VP-8 and BM4VP-10. We have carried out qualitative tests and showed that phase separation occurred when PαMSMA is mixed in a common solvent with each of these polymers and opaque films were obtained after solvent evaporation.Two glass transition temperatures (Tg) were observed with all these blends. Figure 1 shows as an example the DSC curves of the PαMSMA /BM4VP-10 blends.

Figure 1 : DSC curves of PαMSMA (100/0) ,BM4VP-10 (0/100) and of their blends of different ratios.



PαMSMA was however found to be miscible in all proportions with MM4VP-8. The miscibility of ethyl or butyl derivatives with the same PαMSMA copolymer required higher amount of 4-vinylpyridine groups within the polymeric chains , in that PαMSMA /EM4VP-23 , PαMSMA /BM4VP-18 and PαMSMA /BM4VP-26 were all miscible. The single glass transition temperature observed with each blend is considered as an evidence of the miscibility of these blends.The miscibility of these blends was first analyzed from the Tg-composition curves , the third power equation and the width of the glass transition temperature versus the blend composition . As shown in Figure 2, the positive deviation of this Tg from the weight average of the Tg's of the pure components is attributed mainly to specific polymer-polymer interactions (carboxylic acid-ester or carboxylic acid-pyridine) that occurred between the components of the blend.These specific interactions were estimated from the constant q obtained from the Kwei equation (14) given by :

$$T_g = w_1.T_{g1} + w_2.T_{g2} + q\, w_1 w_2 \qquad (1)$$

where w_1 and w_2 ,the weight fraction of the components of the blend.

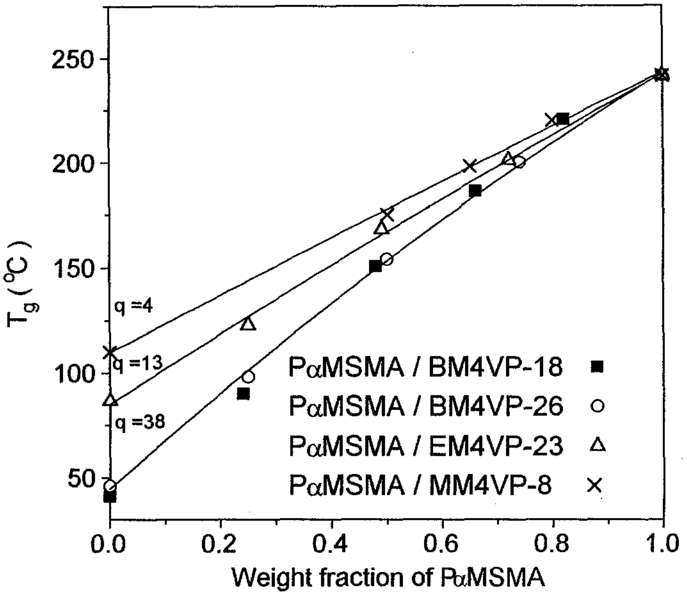


Figure 2 : Glass transition temperature versus weight fraction of PαMSMA.

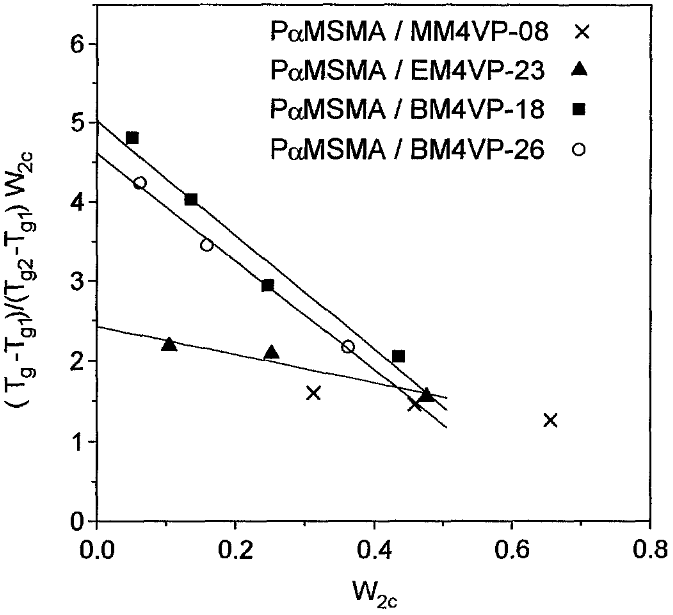


Figure 3 : Tg - Composition behavior of blends according to the third power equation

The glass transition temperature-composition results were also analyzed from the third power equation (15) from :

$$(T_g-T_{g1}) / (T_{g2}-T_{g1}) W_{2c} = (1+K_1) - (K_1 + K_2) W_{2c} + K_2 W_{2c}^2 \qquad (2)$$

where W_{2c} ,the corrected weight fraction of PαMSMA (component of highest T_g) is given by :

$$W_{2c} = KW_2 /(W_1 + KW_2) \quad \text{and} \quad K = \rho_1 T_{g1} / \rho_2 T_{g2} \qquad (3)$$

with W_1 ,W_2 , T_{g1} , T_{g2} , ρ_1 and ρ_2 the weight fractions , glass transition temperatures and densities of the constituents 1 and 2 of the blends.

Accordingly plots of (T_g-T_{g1}) / $((T_{g1}-T_{g2})W_{2c}$ versus W_{2c} for the different miscible blends as shown in Figure 3 confirm that stronger specific interactions are observed with systems of higher densities of interacting species.

Figure 4 displays the glass transition temperature width , determined in a similar way as reported in the literature (16) , versus the the weight fraction of PαMSMA for the different miscible systems. Sharper transitions are observed with PαMSMA /MM4VP-8 system , while broader transitions were obtained with systems of higher alkyl methacrylate groups such as PαMSMA /EM4VP-23 , PαMSMA/BM4VP-18 or PαMSMA /BM4VP-26.

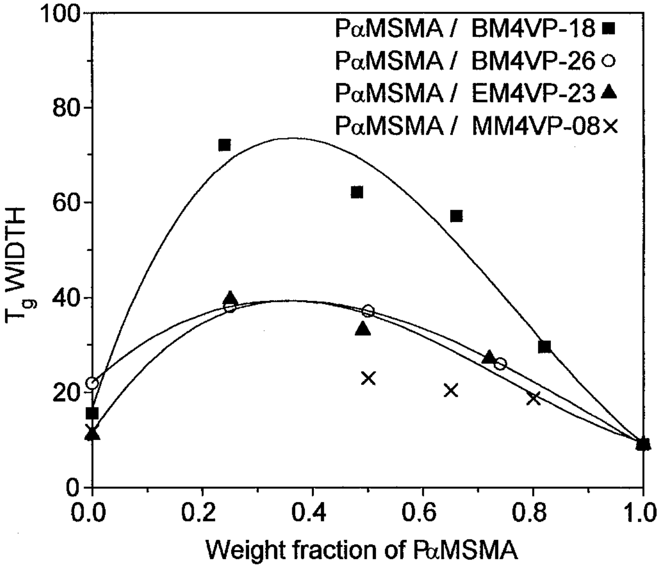


Figure 4 : Glass transition temperature width versus weight fraction of PαMSMA

FTIR spectroscopy was then used to detect the specific interactions between the carboxylic and pyridine groups within the polymer chains, responsible for the miscibility of these blends. Figure 5 shows the expanded scale FTIR spectra of PαMSMA , BM4VP-26 and of their blends of different ratios recorded at room temperature in the 1630-1570 cm^{-1} region. As seen from this figure , the main band observed at 1597 cm^{-1} with the BM4VP-26 copolymer, characteristic of the free pyridine ring , is one of the most affected . In the same region .the

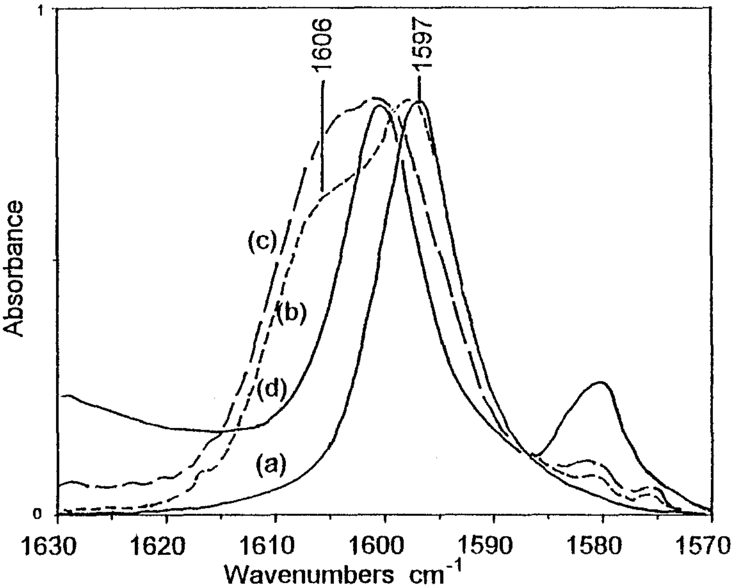


Figure 5 : Scale expanded IR spectra of P α MSMA/BM4VP-26 blends (a) 0/100 ; (b) 25/75 ; (c) 50/50 and (d) 100/0 recorded at room temperature in the 1630-1570 cm $^{-1}$ region.

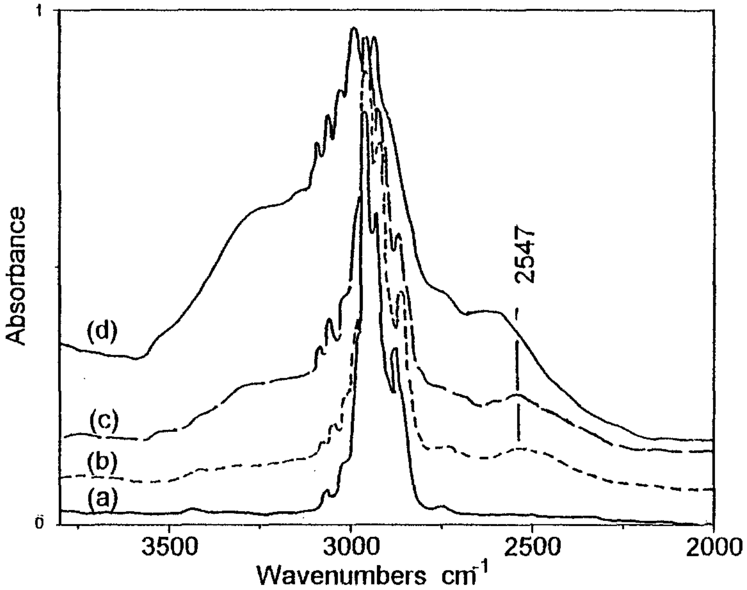


Figure 6: Scale expanded IR spectra of P αMSMA/BM4VP-26 blends (a) 0/100 ; (b) 25/75 ; (c) 50/50 and (d) 100/0 recorded at room temperature in the 3800-2000 cm $^{-1}$ region.

PαMSMA displays a band at 1600. cm^{-1} corresponding to the styrene ring. A Broader band that shifted to higher wavenumbers is observed with the blends. .Although the pyridine ring vibrational modes of the BM4VP-26 interfere witht the styrene groups, an evident shoulder attributed to carboxylic acid-pyridine interactions , is observed at 1606 cm^{-1} with the PαMSMA/BM4VP-26 blends containing 25 and 50 wt % of PαMSMA. Similar interactions as evidenced by a new band corresponding to associated pyridine groups, were in previous studies observed with the miscible blends of butyl methacrylate-*co*-methacrylic acid with styrene-*co*-4vinylpyridine or butyl methacrylate-*co*-4-vinylpyridine (17) and of poly(ethylene-*co*-methacrylic acid) with poly(2-vinylpyridine) (18).

In addition , this type of interactions is detected in the 3800-2000 cm^{-1} region as seen in Figure 6 . As the BM4VP-26 content increases in the blend, the broad band centered at 2627 cm^{-1} which corresponds to carboxylic dimers observed with PαMSMA is shifted to lower wavenumbers up to 2547 cm^{-1} characteristic of the carboxylic acid-pyridine interactions.

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