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Ternary Systems of Two Interacting Copolymers and a Solvent

Said Djadoun

Laboratoire de Chimie Macromoleculaire, Université des Sciences et de la Technologie
H. Boumediene, BP No 9, Dar El Beida, Alger, Algeria

SUMMARY

Closed loop diagrams were obtained with ternary systems containing two interacting copolymers (styrene-4-vinylpyridine / styrene-methacrylic acid or methyl methacrylate-4-vinylpyridine / methyl methacrylate-methacrylic acid) and a solvent (dioxane or chloroform). Viscosimetric interaction parameters were determined in both solvents. Higher interactions in chloroform than in dioxane were evidenced from greater positive Δb_{23}.

A single glass transition temperature obtained with the pair of copolymers of styrene-methacrylic acid / butyl methacrylate-4-vinylpyridine confirmed the compatibility of these copolymers in the solid state.

INTRODUCTION

The phenomenon of phase separation into two dilute phases, each containing mainly one of the polymeric species, observed on mixing two polymers in a common solvent in which they are separetely soluble has been recognized for more than three decades (DOBRY and BOYER-KAWENOKI. 1947, KERN 1956, KRAUSE 1972). In previous papers (DJADOUN et al. 1977, DJADOUN 1979), we have showed that depending on the solvent used, the introduction of relatively small amounts of methacrylic acid and 4-vinylpyridine into the poly(methyl methacrylate) (PMMA) and polystyrene (PS) respectively, by random copolymerization led to a homogenous phase with the two polymers compatible with each other. We have also reported that the obtained phase diagrams for systems of higher contents of interacting groups were closed loops.

In this paper we report a study of ternary systems of copolymers of styrene-4-vinylpyridine (SB) with styrene-methacrylic acid (SA) and of methyl methacrylate-4-vinylpyridine (MB) with methyl methacrylate-methacrylic acid (MA) in two solvents, dioxane and chloroform.

A number of authors (KONIGSVELD et al. 1974, PETERSEN et al. 1969, ALESKSEYENKO 1960) pointed out that compatibility of two polymers in solution does not necessarily imply compatibility after removal of solvent. Differential scanning calorimetry (DSC) is a technique extensively used to study the compatibility of polymers (TING et al. 1980, STOELTING et al. 1970 ,FRIED et al. 1978). Two glass transition temperatures are observed when the two polymers are incompatible with each other, while a single glass transition temperature is observed when they are compatible. This technique has limitations especially when the polymers have very close glass transition temperatures. To show whether compatible pairs of polymers in solution are also compatible in bulk, we prepared copolymers of butyl methacrylate-4vinylpyridine and styrene-methacrylic acid, and films of pairs of these copolymers were cast and characterized by DSC.

EXPERIMENTAL

Homopolymers and copolymers of styrene, methyl methacrylate and of butyl methacrylate were prepared by free radical polymerization at 60°C with azo-bis isobutyronitrile as the initiator. Copolymers SA,SB, MA,MB and butyl methacrylate-4-vinylpyridine (BMB) were characterized as previously described (DJADOUN 1979). Depending on the solvent, the two copolymers led to the formation of two phases: one dilute phase (DP) containing almost pure solvent in equilibrium with the other phase rich in both polymers (CP). For such systems, points on the phase diagrams were obtained (DJADOUN et al. 1977). Solution viscosity measurements were carried out with a cannon Ubbelohde capillary viscosimeter at 25°C.

The polymer blends were prepared by the method of solution casting. Equal amounts of PS and PBMA or copolymers of SA and BMB were disolved in butanone Films were cast on a Teflon plate at room temperature with the initial concentration of 1g/100 ml. The films were dried in a vacuo at 60°C for four days after the butanone was slowly evaporated. The Dupont model 900 differential scanning calorimeter was used to determine the glass transition temperatures T_g of the blends of polymers. Samples were punched from the cast films and sealed into aluminium DSC pans. An empty pan was used as reference. The thermograms were obtained under nitrogen from -50°C to 150°C at a heating rate of 10°C/minute.

RESULTS AND DISCUSSION

Similar phenomena as obtained previously were observed even for systems where the major constituent is the same (SA and SB) or (MA and MB) in dioxane and in chloroform. At low contents of interacting groups, homogenous phase is observed, while on increasing the density of these groups within the main polymeric chain a dilute phase containing mostly solvent is in equilibrium with a concentrated phase in which are collected the two copolymers. The formation of these two phases was found to depend on the solvent as listed in Tables (1,2).

TABLE 1

Dependence of the Phase Relations on the Density of Interacting Groups and the Solvent for the System SA / SB /Solvent.

SA / SB	Chloroform	Dioxane
SA-10.5/SB-1.62	C	C
SA-10.5/SB-5.80	C	C
SA-10.5/SB-8.85	C	C
SA-10.5/SB-16.10	DP+CP	C
SA-15.0/SB-16.10	DP+CP	C
SA-22.82/SB-16.10	(a)	C
SA-31.30/SB-22.60	(a)	DP+CP

TABLE 2

Dependence of the Phase Relations on the Density of Interacting Groups and the Solvent for the System MA / MB / Solvent.

MA / MB	Chloroform	Dioxane
MA-5.10/MB-10.57	C	C
MA-8.52/MB-10.57	C	C
MA-8.52/MB-14.00	C	C
MA-8.52/MB-19.08	DP+CP	C
MA-15.7/MB-19.08	(a)	C
MA-22.30/MB-19.08	(a)	DP+CP

(a) Since the acid copolymer is insoluble in chloroform, the system could not be studied.

C stands for a compatible polymer pair.

The ternary phase diagrams for these systems are shown in Figures (1,2). In ternary systems of two polymers and a solvent, repulsive interactions cause shrinkage of the polymeric coils and the viscosity of the mixture decreases with respect to the viscosity of the binary systems of either component in the same solvent,however, the viscosity of the mixture increases in the case of attractive interactions between the polymeric species. Intrinsic viscosities of MA-8.52 (copolymer of methyl methacrylate-methacrylic acid containing 8.52 mole % of methacrylic acid) and MB-10.57

(copolymer of methyl methacrylate-4-vinylpyridine containing 10.57 mole % of 4-vinylpyridine) and their 1:1 mixture were determined in dioxane and chloroform.

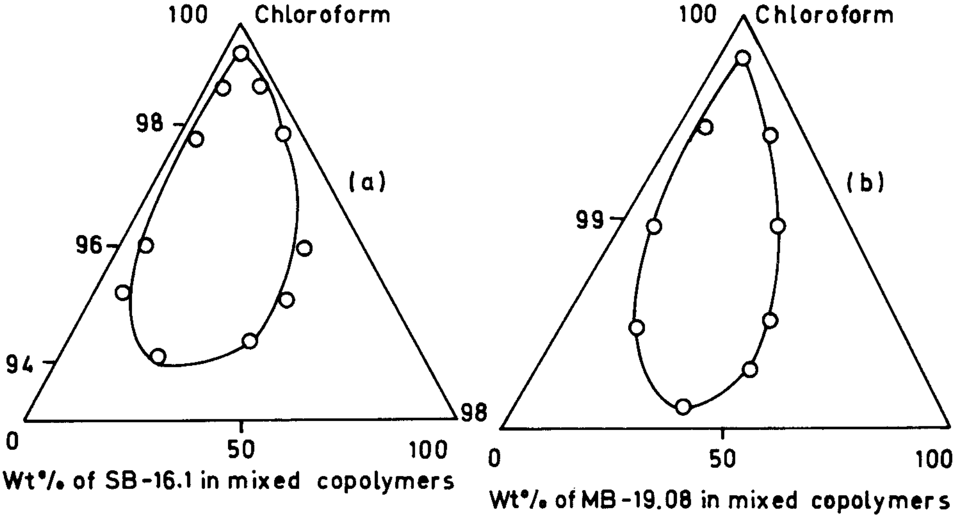

Figure (1) : Phase Diagrams of Ternary Systems in Which a concentrated phase contains both copolymers in chloroform:(a) SA-10.5/SB-16.1 ; (b) MA-8.52/MB-19.08.

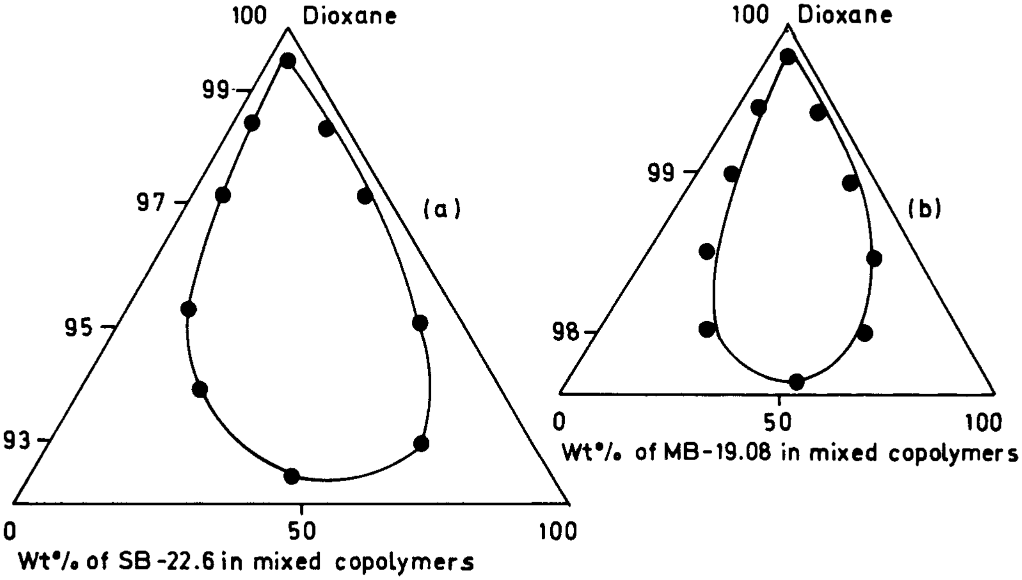

Figure (2) : Phase Diagrams of Ternary Systems in which a concentrated Phase contains both copolymers in dioxane (a) SA-31.3/SA-22.6 ; (b) MA-22.3/MB-19.08.

From the plots of their reduced viscosities versus concentration shown in Figures (3,4), we can see that in chloroform the slope of the 1:1 mixture of these copolymers was steeper than the one of either component, while in dioxane the slope of the same mixture was intermediate between those of its components.

Information on the interactions between the polymeric species was obtained using the approximate method of (KRIGBAUM and WALL,1950). The difference between the experimental $b_{23}^{exp.}$ and the theoretical $b_{23}^{the.}$ interaction parameters was used to determine the compatibility of polymers.

Figure (3)

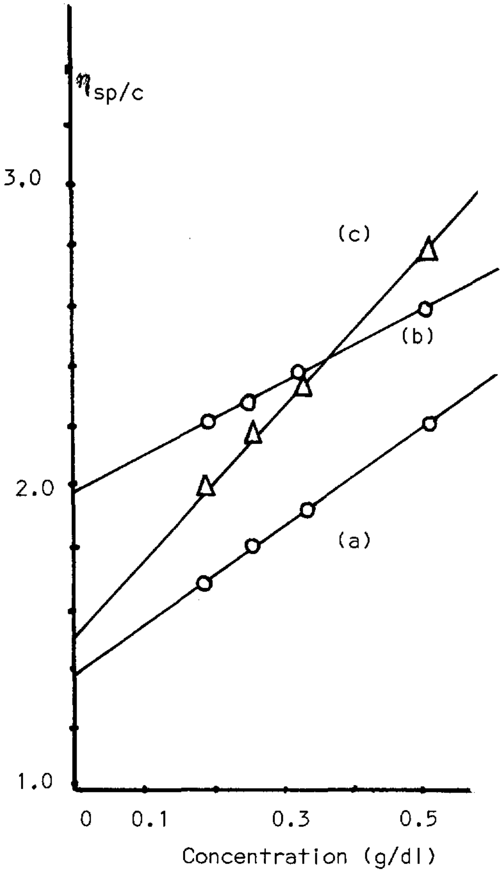

Figure (4)

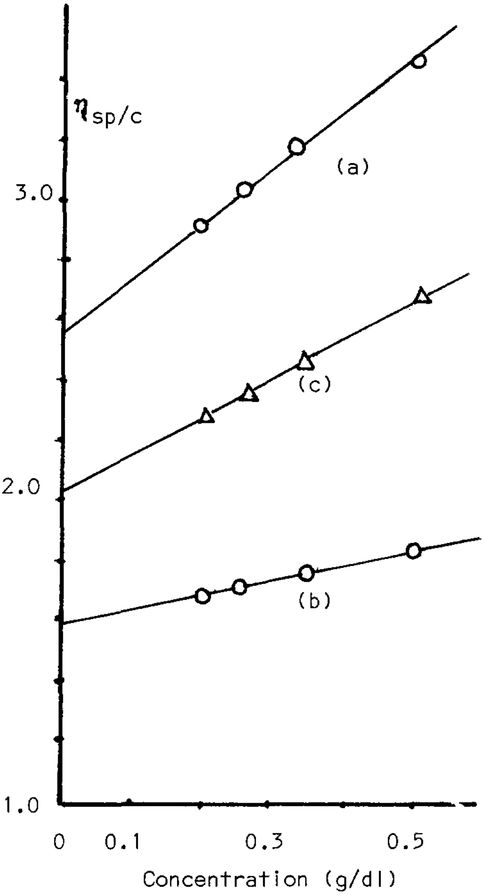

Figure (3) : Reduced viscosity plots of chloroform solutions of MA-8.52 (a) MB-10.57 (b) and their 1:1 mixture (c).

Figure (4) : Reduced viscosity plots of dioxane solutions of MA-8.52 (a) MB-10.57 (b) and their 1:1 mixture (c).

The experimental viscosimetric interaction parameter between the polymeric species (2) and (3) in a solvent (1) was obtained from

$$b_m = x_2^2\, b_{22} + 2\, x_2 x_3\, b_{23} + x_3^2\, b_{33} \qquad (1)$$

where b_m is the global interaction between all the polymeric species; x_i standing for the weight fraction of polymer i , and the b_{ii} interaction parameters are expressed as

$$b_{ii} = k_i [\eta]_i^2 \qquad (2)$$

k_i is the Huggins constant of the component i.

The theoretical interaction parameter was calculated as

$$b_{23}^{the.} = (b_{22} . b_{33})^{0.5} \qquad (3)$$

According to this model, positive Δb_{23} values indicate attractive interactions and therefore polymer compatibility; however the polymers will be incompatible with negative values. Table (3) displays the interaction parameter data.

TABLE 3

Viscosimetric Interaction Parameters of MA-8.52 / MB-10.57 Pairs in Chloroform and Dioxane at 25°C.

		Chloroform	Dioxane
MA-8.52	b_{22}	1.71	1.70
MB-10.57	b_{33}	1.33	0.60
MIXTURE	b_m	2.57	1.20
	$b_{23}^{exp.}$	3.62	1.25
	$\Delta b_{23}^{the.}$	1.52	1.00
	Δb_{23}	2.10	0.25

Positive Δb_{23} values were found for the 1:1 mixture with both solvents, with much higher positive Δb_{23} value for the system in chloroform than in dioxane. This is an evidence of stronger acid-base interactions in chloroform than in dioxane and supports the observed phase diagrams, in that, higher concentrations of interacting groups are needed to lead to the formation of a concentrated phase when dioxane is the solvent used . This seems to agree with our calorimetric data of low molecular weight analogs : the enthalpy of mixing of isobutyric acid and 4-ethylpyridine depended strongly on the solvent. The interactions between the carboxyl and pyridine groups were found to be more exothermic in chloroform than in dioxane.

The film cast from PS-PBMA mixture was opaque and the DSC thermogram showed two distinct glass transition temperatures at 22°C and 98°C which corresponded to the values of the parent homopolymers; however one intermediate glass transition temperature was observed with the transparent film of the SA-10.50 / BMB-6.50 mixture as shown in Figure (5).

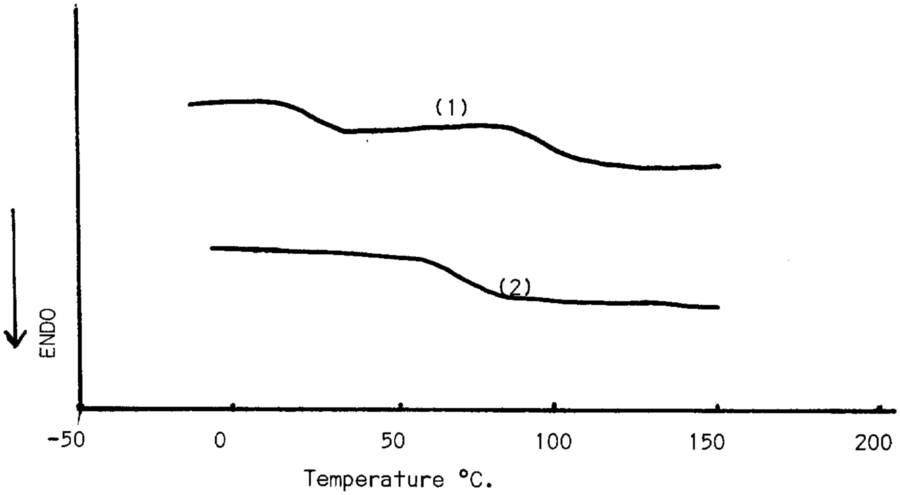

Figure (5) : DSC Thermograms of 1) Homopolymer blend (PS/PBMA) and 2) blend of copolymers (SA-10.5/BMB-6.54).

The experimental glass transition temperature for the compatible mixture of copolymers was of 52°C; since these copolymers contained only small amounts of acid or base, we assumed that their T_g's would not differ much from those of the homopolymers. Applying the FOX equation (FOX 1956) to our system, the calculated T_g was of 55.6°C, in good agreement with the experimental one.

In conclusion, compatibility of two polymers is favored by the acid-base interactions in both solid and solution phases. We have also found that similar phenomena occurred with other interacting groups (LASSOUED and DJADOUN) and depended strongly on the temperature. Evidence for hydrogen-bonding interaction is to be carried out by infra-red spectroscopy.

REFERENCES

ALESKSEYENKO V.I., Vysokomol.Soedin., 2 , 1449 (1960).

DJADOUN S.; GOLDBERG R.N. and MORAWETZ H., Macromolecules 10, 1015 (1977).

DJADOUN S., PhD Dissertation Polytechnic Institute of New York, Diss. Abst. Int. B, Volume 40, Part 6, 2696 (1979).

DOBRY A. and BOYER-KAWENOKI F., J. Polym. Sci., 2 , 90 (1947).

FRIED J.R., KARASZ F.E. and MACKNIGHT W.J.,Macromolecules, 11, (1978).

FOX T.G.,Bull. Am. Phys. Soc., 1 , 123 (1956).

KERN R.J. J. Polym. Sci., 21 , 19 (1956).

KONIGSVELD,R., L.A. KLEINTJENS and SCHOFFELLERS H.M., Pure Appl. Chem., 39, 1 (1974).

KRAUSE S.,J. Macromol. Sci., Revs. Macromol. Chem., C 7 ,251 (1972).

KRIGBAUM W.R. and WALL F.W. , J.Polym. Sci.,5 , 505 (1950).

LASSOUED A. and DJADOUN S. (to be submitted).

PETERSEN R. J. ,CORNELIUSSON R. D.and ROZELLE L.T. Polymer Prepr.,Am. Chem. Soc., Div. Polym. Chem., 10 , 385 (1969).

STOELTING J. KARASZ F.E. and MACKNIGHT W. J. ,Polym. Eng. and Sci., 10, 133 (1970).

TING S.P., KWEI T.K. and PEARCE E. M. , J.Polym. Sci., Polymer Letters, 18 , 201 (1980).

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