Ternary Systems Containing an Acidic Copolymer, a Basic Copolymer, and a Solvent. 1. Phase Equilibria[1]

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ABSTRACT: Ternary phase diagrams were determined for systems consisting of polystyrene or a styrene–4-vinylpyridine copolymer, poly(methyl methacrylate) or a methyl metacrylate–methacrylic acid copolymer, and a solvent (dioxane, butanone, or chloroform). While the polystyrene–poly(methyl methacrylate)–solvent systems all exhibit two coexisting dilute phases, each containing predominantly one of the polymeric species, introduction of a small concentration of the acidic and basic comonomer leads to solutions containing both polymers. At higher concentrations of strongly interacting comonomers, a different type of phase separation is observed where a concentrated phase containing both copolymers is in equilibrium with a highly dilute solution. The solvent dependence of the phase diagrams is discussed in relation to polymer–solvent interaction parameters (derived from intrinsic viscosities) and in the light of calorimetric data of the enthalpy of mixing of low molecular weight analogues of the monomer residues in the copolymers.

In 1910, Beijerinck[3] made the surprising observation that dilute aqueous solutions of gelatin and agar do not mix but form two coexisting phases, each containing almost exclusively one of the macromolecular solutes. Similar observations were later made on a large number of ternary systems containing two synthetic polymers in the same solvent[4–7] and it may, in fact, be said that it is relatively rare to find two polymers which form mutually miscible solutions.[8] These phenomena are related to the observation that most polymers are incompatible with each other.[9]

We know of no case where two low molecular weight solutes, dissolved in the same solvent, would form two immiscible solutions. This contrast in the behavior of polymers and their low molecular weight analogues has been convincingly interpreted by Gee:[10] In ternary systems containing two low molecular weight solutes, an unfavorable energy of mixing of the solute species will be more than compensated by the entropy of mixing; however, with two polymeric solutes the entropy of mixing per unit weight is negligible, so that even a small positive value of ΔH of mixing will ensure the coexistence of two liquid phases.

Negative values of the ΔH of mixing of polymeric species may result in another type of phase separation when solutions of two polymers will be in equilibrium with an extremely dilute solution. This phenomenon which has been termed "complex coacervation" [11] is best known in the mutual precipitation of acidic and basic macromolecules in aqueous solution. Even relatively weak acid–base interaction, as that between poly(acrylic acid) and poly(ethylene oxide), may lead to polymer complex formation because of the cooperativity of the interacting groups.[12]

In the present study we have attempted to show how the phase equilibrium of ternary systems containing two incompatible polymers is modified as we introduce into the polymeric chains increasing densities of strongly interacting groups. This was accomplished by introducing 4-vinylpyridine residues into polystyrene and methacrylic acid residues into poly(methyl methacrylate) by random copolymerization. Mixtures of these polymeric species were studied in dioxane, butanone, and chloroform and the information on phase equilibria was supplemented by calorimetric data.

Experimental Section

Polymer Preparation and Characterization. Homopolymers and copolymers of styrene and of methyl methacrylate were prepared by free-radical polymerization at 60 °C using azo-bis(isobutyronitrile) initiator. The copolymerizations were stopped at conversions below 15% to minimize any drift in the copolymer composition. The compositions of styrene–4-vinylpyridine copolymers were obtained from the absorption at 256 nm (the maximum in the absorption spectrum of polyvinylpyridine), where the extinction coefficients of vinylpyridine and styrene residues were found to be 15 700 and 1 870 $\text{cm}^2\ \text{g}^{-1}$, respectively. The composition of methyl methacrylate–methacrylic acid copolymers was determined by titration of a solution in benzene–ethanol (20 vol % ethanol) with sodium ethoxide in the same mixed solvents using phenolphthalein as end point indicator. The degree of polymerization was characterized by intrinsic viscosity measurements at 25 °C in chloroform (dL g^{-1}). Table I summarizes the data for the polymers and copolymers used in this study. The Mark–Houwink constants for polystyrene[13] and for poly(methyl methacrylate)[14] were taken as $K = 7.16 \times 10^{-5}$ dL g^{-1} and $a = 0.76$ and $K = 4.8 \times 10^{-5}$ dL g^{-1} and $a = 0.80$, respectively, yielding viscosity-average molecular weights of 4.22×10^5 for the polystyrene and 9.35×10^5 for the poly(methyl methacrylate). Since the copolymers (containing relatively low comonomer concentrations) were prepared under similar conditions as the homopolymers and since the comonomers had similar reactivities, it may be assumed that homopolymers and copolymers had similar molecular weights.

Determination of Phase Equilibria. Two types of phase equilibria were analyzed. (1) In systems containing two dilute phases, each containing mostly one of the polymers, the phases were separated, weighed, and dried. The polymer residue of each phase was weighed and dissolved in chloroform and the content of the styrene homopolymer or copolymer was determined spectroscopically at its absorption maximum using an appropriate calibration curve. The weight of the methyl methacrylate homopolymer or copolymer was obtained by difference. Alternatively, a point on the phase diagram was obtained by adding solvent to a two-phase system until the turbidity disappeared. (2) In systems in which both copolymers were concentrated in one of the phases, points on the phase diagrams were obtained by three procedures: (a) Solutions of one of the copolymers were titrated with a solution of the other copolymer, noting the composition at which the system became turbid. (b) A relatively concentrated solution containing a mixture of the acidic and basic copolymers was titrated with solvent, noting the composition of the system at which a dilute phase separated. After adding additional solvent, the two phases were separated and weighed and the composition of the dilute phase was calculated from the composition of the concentrated phase and the material balance. (c) In the case of the concentrated phase formed in butanone containing S-8.85 and M-8.52, the solution was dried, and the mixed acidic and basic copolymers were weighed and dissolved in dioxane for spectroscopic determination of the styrene copolymer. It should be noted that the investigation of phase equilibria was limited to systems containing less than 10% polymer, since the high viscosity of more concentrated systems did not permit the use of our experimental methods.

Calorimetry. Enthalpies of mixing were determined in a heat conduction microcalorimeter similar to one described previously,[15] in which two solutions separated by a partition were mixed by rotation of the calorimetric heat sink. The heat sink accommodates a reaction cell constructed of high density polyethylene with a total volume of about 2.5 mL. The half-response times of the instruments are in the range of 60 to 90 s. The amplified thermopile voltages were recorded

Table I
Preparation and Characterization of Polymers and Copolymers

(a) Styrene Polymer and Copolymers

Mol % 4-vinylpyridine		$[\eta]$,[a]
Monomer mixture	Copolymer	dL g^{-1}
0	0	1.35
1.24	1.62	1.53
3.25	5.80	1.73
4.95	8.85	1.78
10.0	16.1	
15.0	22.6	

(b) Methyl Methacrylate Polymer and Copolymers

Mol % methacrylic acid		$[\eta]$,[a]
Monomer mixture	Copolymer	dL g^{-1}
0	0	2.87
1.45	2.24	2.66
3.61	5.10	2.32
5.76	8.52	1.50
11.4	15.7	
17.0	22.3	

[a] In chloroform at 25 °C.

Table II
Dependence of the Phase Relations on the Density of Interacting Groups and the Solvent

	Phases		
System	Dioxane	Butanone	Chloroform
S/M	2DP	2DP	2DP
S-1.62/M-2.24	2DP	2DP	C
S-5.80/M-5.10	C	C	C
S-8.85/M-8.52	C	DP + CP	DP + CP
S-16.11/M-15.7	C	DP + CP	*a*
S-22.6/M-15.7	DP + CP	*b*	*a*
S-16.1/M-22.3	DP + CP	*b*	*a*
S-22.6/M-22.3	DP + CP	*b*	*a*

[a] Since the acidic copolymer is insoluble in chloroform, this system could not be studied.

[b] The concentrated phase could not be separated satisfactorily for a determination of its composition.

in digital form and the peak area associated with the enthalpy of mixing was calculated by numerical integration of the time–voltage data. All measurements were carried out at a temperature of 25.00 °C.

Results

Phase Equilibria. Table II lists the qualitative nature of phase relations in the various systems investigated. The polymers are denoted by S or M depending on the major constituent (styrene or methyl methacrylate), followed by a number specifying the mol % of 4-vinylpyridine or methacrylic acid, respectively. The symbol C stands for compatible copolymer pairs forming a single phase over the concentration range studied; 2 DP signifies the presence of two dilute phases and DP + CP signifies the presence of a dilute phase and a concentrated phase containing both copolymers.

As expected, increasing densities of strongly interacting groups tended to favor compatibility of styrene copolymers with methyl methacrylate copolymers. However, the nature of the solvent medium was found to influence the concentration of acid and basic groups required to produce a one-phase system. As seen in Table II, the S-1.62/M-2.24 system formed two dilute phases in dioxane and butanone but a single phase in chloroform. Similarly, there were striking differences in the concentration of the interacting groups required for the separation of a concentrated phase containing both copolymers. In butanone and chloroform, this phenomenon occurred with the S-8.85/M-8.52 system, while in dioxane solution even S-16.1/M-15.7 exhibited a single phase and a concentrated phase was formed only at higher contents of either the acidic or the basic comonomer. In chloroform, methyl methacrylate copolymers with high methacrylic acid contents were unfortunately insoluble, so that phase equilibrium data are limited to copolymers containing up to 8.52 mol % methacrylic acid.

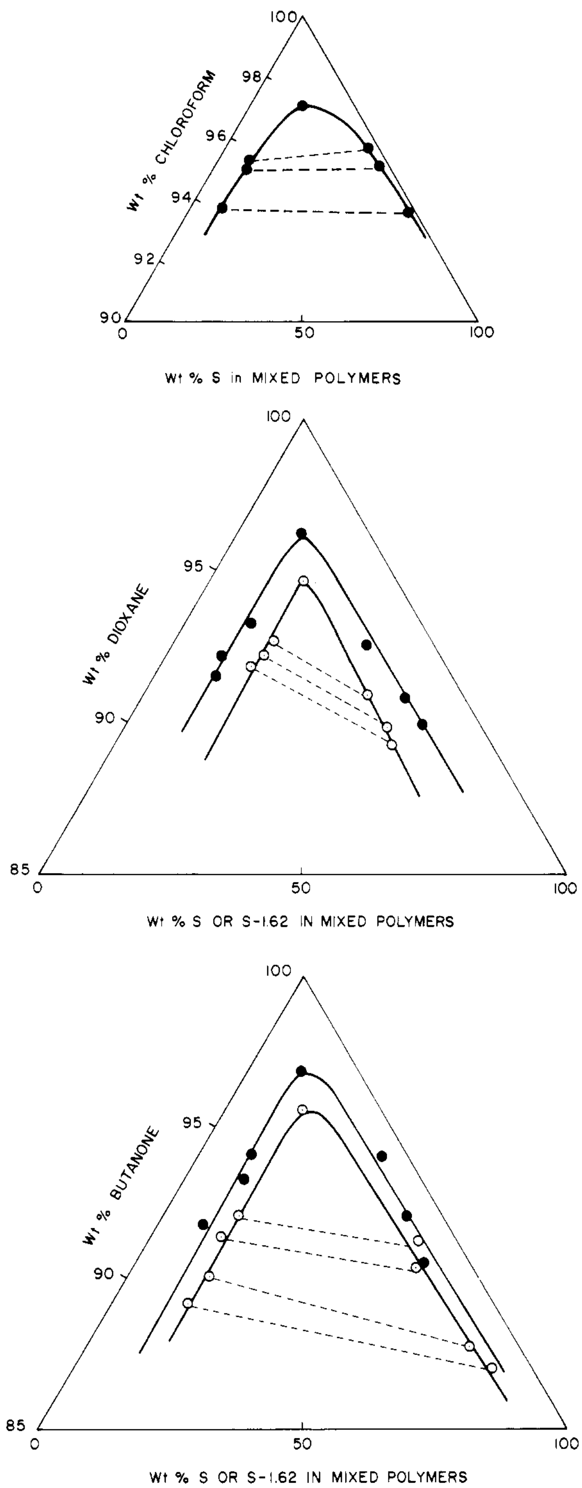

Figure 1. Phase diagrams of ternary systems forming two dilute phases: (●) systems containing S and M; (○) systems containing S-1.62 and M-2.24.

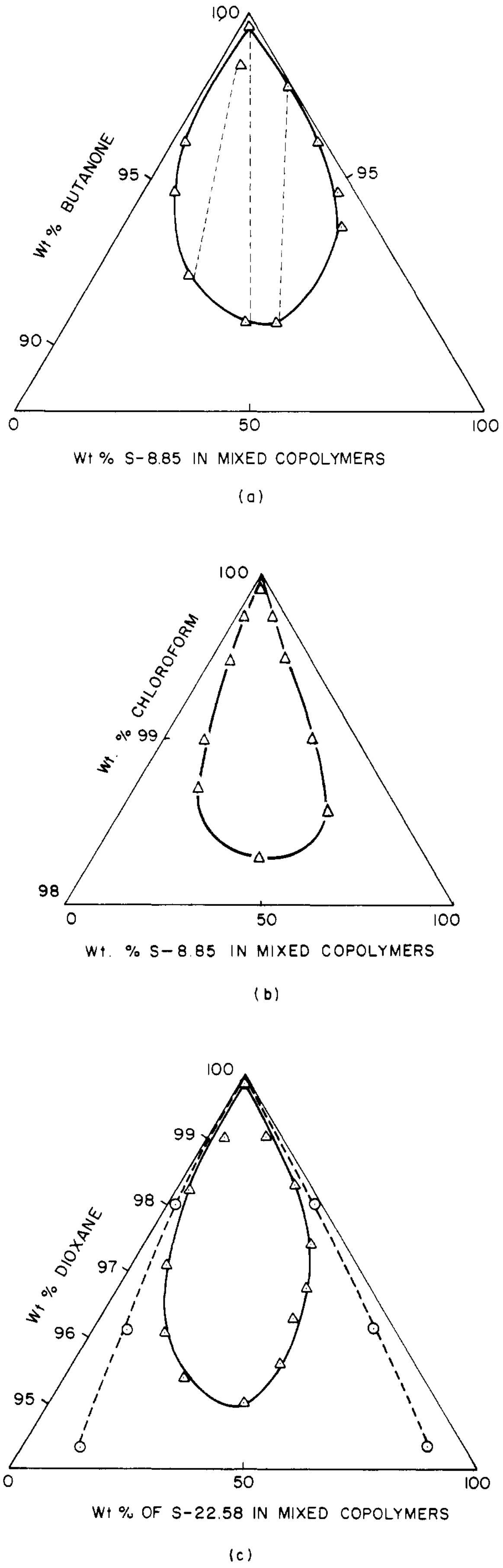

Figure 2. Phase diagrams of ternary systems in which a concentrated phase contains both copolymers: (a) and (b) S-8.85 and M-8.52 solutions; (c) dioxane solutions of (△) S-22.58 and M-15.72; (○) S-22.58 and M-22.27.

Figure 1 shows the phase diagrams of the systems in which two dilute phases were observed. Tie lines indicate the coexisting phases in some of the systems. Figure 2 shows the phase diagrams for the systems in which both copolymers were present in a concentrated phase.

Viscometry. Intrinsic viscosities of the two homopolymers and of the copolymers S-8.85 and M-8.52 were determined in dioxane, butanone, and chloroform to obtain a measure of the solvent power of the three media. The results are listed in Table III. For both polystyrene and poly(methyl methacrylate), the $[\eta]$ values are in the order chloroform > dioxane > butanone and this order also holds for styrene copolymers. For methyl methacrylate copolymers the solvent power of chloroform decreases sharply with an increasing methacrylic acid content since the solvent does not compete effectively with the tendency of the carboxyl groups to form hydrogen bonds with each other.

The slope of a reduced viscosity plot for a mixture of an acidic and a basic copolymer was found to be intermediate between the slopes of similar plots for either component of the mixture as shown in Figure 3. This is in contrast to the steep slope of the reduced viscosity plot of a mixture of an acidic and a basic copolymer of methyl methacrylate investigated previously in this laboratory.[16]

Calorimetry. To aid us in the interpretation of the observed phase equilibria, we carried out calorimetric measurements of the enthalpy of mixing of low molecular weight analogues of the monomer residues in the various copolymers used in this study. Ethylbenzene and 4-ethylpyridine were used to simulate the behavior of styrene and 4-vinylpyridine residues and isobutyric acid and its methyl ester that of methacrylic acid and methyl methacrylate residues.

In deriving the enthalpy of mixing of ethylbenzene and methyl isobutyrate a complication arises due to the vapor space above the two liquids in the calorimetric cell. Thus, a correction has to be applied to the measured enthalpy of mixing to account for the condensation of the vapor or evaporation of the liquid. The following argument was used to estimate this correction:

Before mixing, the space directly in contact with methyl isobutyrate will be saturated with its vapor. On the other hand, the equilibrium vapor pressure of methyl isobutyrate in contact with ethylbenzene will be zero. Assuming a constant gradient of the partial vapor pressure of methyl isobutyrate, its average vapor pressure will be half of the saturated vapor pressure value. An analogous argument holds for the ethylbenzene. After mixing, if we assume ideal solution behavior and a negligible volume change on mixing, the vapor pressure of each component will be the product of the saturated vapor pressure and the mole fraction of that component. Thus, the enthalpy due to vapor condensation and evaporation will be

$$\Delta H' = -v(X_{\mathrm{EB}} - \tfrac{1}{2})(C_{\mathrm{MI}}{}^{0}\Delta H^{\mathrm{v}}{}_{\mathrm{MI}} - C_{\mathrm{EB}}{}^{0}\Delta H^{\mathrm{v}}{}_{\mathrm{EB}}) \quad (1)$$

where v is the vapor space in mL, X is a mole fraction, and C^0 and ΔH^{v} are the number of moles per mL of saturated vapor and the molar enthalpy of vaporization, the subscripts EB and MI referring to ethylbenzene and methyl isobutyrate, respectively. To compute $\Delta H'$, we used vapor pressures of 9.5 and 50 Torr (obtained by interpolation of published data[17]) and ΔH^{v} values of 42.0 and 35.5 kJ/mol[19] for EB and MI, respectively. It may be seen from eq 1 that $\Delta H'$ vanishes for $X_{\mathrm{EB}} = \tfrac{1}{2}$; the corrections were generally in an acceptable range except for the two extreme compositions where they amounted to about 30% of the measured value. Values of $\Delta H_{\mathrm{corr}}/V$ (where $\Delta H_{\mathrm{corr}} = \Delta H_{\mathrm{obsd}} - \Delta H'$ and V is the volume of the solution) are plotted as a function of the volume fraction of ethyl benzene ϕ_{EB} on Figure 4. The plot does not exhibit the

Table III
Intrinsic Viscosities, Expansion Factors, and Polymer–Solvent Interaction Parameters

	Dioxane			Butanone			Chloroform		
	[η]	α	χ	[η]	α	χ	[η]	α	χ
S	1.22	1.318	0.471	0.695	1.097	0.495	1.35	1.363	0.464
S-8.85	1.19			0.72			1.78		
M	2.22	1.684	0.424	1.39	1.441	0.469	2.87	1.83	0.374
M-8.52	2.09			1.40			1.50		

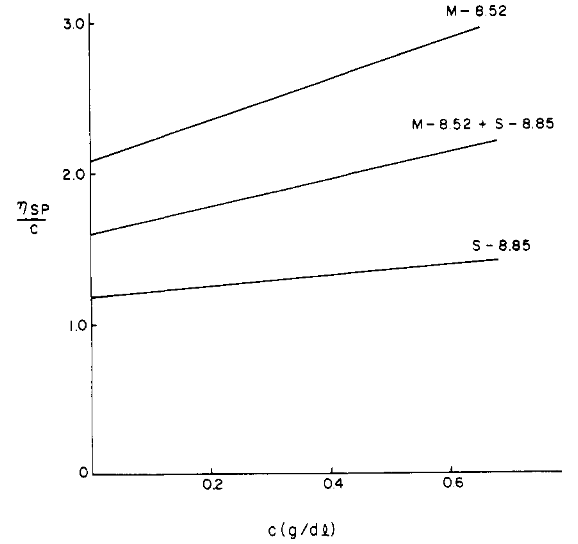

Figure 3. Reduced viscosity plot of dioxane solutions of S-8.85 and M-8.52 and of their 1:1 mixture.

parabolic dependence of $\Delta H/V$ on ϕ frequently observed in the mixing of nonpolar liquids.[18] The maximum in the $\Delta H/V$ corresponds to a difference of 0.6 in the "Hildebrand solubility parameters δ" [18] of the components of the mixture. This is in close agreement with the values of $\delta = 8.3$ for methyl isobutyrate and $\delta = 8.8$ for ethylbenzene.[19]

In view of the pronounced dependence of the phase relations which we have observed on the nature of the solvent medium, it was of interest to find whether the enthalpy of mixing of the polymer analogues is solvent dependent. We measured, therefore, the enthalpy of mixing of ethylbenzene and methyl isobutyrate, each diluted with four volumes of dioxane, butanone or chloroform. (In the case of chloroform solutions a complication arose since tumbling of the calorimetric cell containing chloroform alone led to an enthalpy change of −0.029 J. The cause of this phenomenon is unknown but an appropriate correction was applied to the enthalpies of mixing in chloroform solutions to take account of it.) The ΔH values obtained were +0.037, +0.025, and +0.004 J/mL in dioxane, butanone, and chloroform, respectively.

Enthalpies of mixing of isobutyric acid and 4-ethylpyridine solutions at concentrations of 0.4, 0.2, and 0.1 M were measured in the three solvent media, the results being expressed as an apparent enthalpy of mixing in Joules per mole of the limiting reactant. The results are listed in Table IV. All the values of $\Delta H/n$ are much lower than expected for the formation of hydrogen bonds (>20 000 J/mol). In the butanone solutions, $\Delta H/n$ is proportional to the reagent concentration, so that the acid–base complex must have a dissociation constant K_d large compared to the solution concentrations c and only a small fraction of the interacting species is associated. A similar conclusion may be reached from the data of the dioxane solutions. The mixing of chloroform solutions yields $\Delta H/n$ data which are substantially higher than in the other two media and they decrease much less rapidly with dilution.

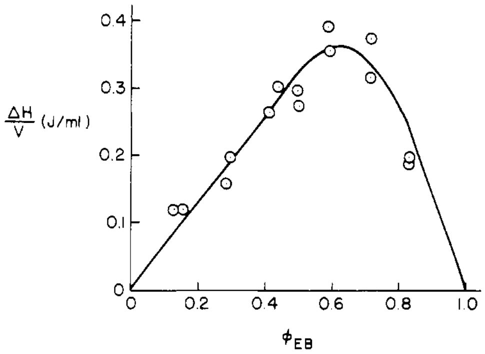

Figure 4. Heat of mixing of ethylbenzene with methyl isobutyrate at 25 °C.

Since the apparent molar enthalpy of the reaction ΔH is related to $\Delta H°$, the molar enthalpy of formation of the acid–base complex from its constituents, by

$$\Delta H = \Delta H°(2 + X - (X^2 - 4X)^{1/2})/2$$

$$X = K_d/c \qquad (2)$$

we may estimate from the data in Table IV $K_d \approx 0.16$ in chloroform with the acid–base complex 58% dissociated in the solution formed on mixing 0.4 M ethylpyridine with 0.4 M isobutyric acid.

Discussion

A theory of ternary systems containing two polymers and a solvent was first formulated by Scott.[20] Since he does not seem to have considered the possibility that polymer mixing might be exothermic, he concluded that polymer compatibility should be exceptional, depending on a near-zero heat of mixing. He also concluded that the solvent acts merely as a diluent, so that the phase diagram depends on the polymer–polymer interaction parameter χ_{12}, being independent of the polymer–solvent interaction parameters χ_{10} and χ_{20}. This concept was accepted by Berek et al.[21] who derived χ_{12} from the phase diagram of the atactic polypropylene–atactic polystyrene–toluene system. However, Kern[6] suggested, on the basis of his data, that the solution concentration at which phase separation occurred in systems containing equal volumes of polystyrene and poly(methyl methacrylate) varies widely with the solvent employed, from 0.13 vol % polymer with dimethylaniline to 0.025 vol % for p-xylene. He observed that phase separation at low concentrations seems to be favored by large differences in the affinity of the solvent for the two polymeric species and the same conclusion was later reached by Hugelin and Dondos.[23] A detailed computer calculation of ternary phase diagrams by Hsu and Prausnitz[24] gave results consistent with these experimental data.

Information concerning the relative values of χ_{10} and χ_{20} for the two homopolymers in the three solvent media used in the present study can be obtained from the intrinsic viscosities, the molecular weights, and literature data of intrinsic viscosities in theta solvents. Using for polystyrene $[\eta]_\theta = 8.2$

Table IV
Heats of Mixing of Solutions of 4-Ethylpyridine and Isobutyric Acid at 25 °C

Solvent	Molarity	$-\Delta H/n$,[a] J/mol
Dioxane	0.4	2320 ± 30
	0.2	1330 ± 10
	0.1	750 ± 5
Butanone	0.4	2240 ± 110
	0.2	1020[b]
	0.1	550[c]
Chloroform	0.4	7350 ± 220[d]
	0.2	5960 ± 50[d]
	0.1	3470 ± 130[d]

[a] Mean and duplicate values. [b] A duplicate value of 760 was obviously in error and was disregarded. [c] One determination only. [d] Corrected for chloroform interaction with the calorimetric cell.

$\times 10^{-4}$ $M^{0.5}$ dL g^{-1} and for poly(methyl methacrylate) $[\eta]_\theta = 4.8 \times 10^{-4}$ $M^{0.5}$ dL g^{-1},[25] we obtain for the expansion coefficients $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$ the values listed in Table III. According to Flory,[26]

$$\alpha^5 - \alpha^3 = 2C_M(\tfrac{1}{2} - \chi)M^{1/2} \quad (3)$$

where C_M may be expressed in terms of the partial specific volume $\bar{v}$ of the polymers, the molar volume V_1 of the solvent, the molecular weight of the monomer residue M_0, and the characteristic ratio C_∞[25] of the polymer by

$$C_M = 0.137(\bar{v}^2/V_1)(M_0/C_\infty)^{3/2} \quad (4)$$

Using $C_\infty = 10.2$ for polystyrene and $C_\infty = 6.9$ for poly(methyl methacrylate) leads to the polymer–solvent interaction parameters listed in Table III. The following points may be made: (1) For both polystyrene and poly(methyl methacrylate) the solvent power is in the order butanone < dioxane < chloroform. (2) All three solvents have higher affinities for poly(methyl methacrylate) than for polystyrene. This is also evident from the tie lines of the phase diagrams in Figure 1, which show that the phase containing poly(methyl methacrylate) (or a methyl methacrylate copolymer) is more dilute than the other solution phase. (3) The generalization of Kern,[6] of Hugelin and Dondos,[23] and Hsu and Prausnitz[24] according to which compatibility is favored by a similarity in the affinity of the solvent for the two polymers is not supported by our data. According to this conclusion, polystyrene and poly(methyl methacrylate) should be most incompatible in chloroform, which is characterized by the most dissimilar χ values for these two polymers. Yet, the smallest concentration of acidic and basic groups attached to these polymers is sufficient to lead to one-phase systems in chloroform.

Calorimetry offers another approach to the analysis of the solvent dependence of the phase diagrams. Let us assume that a mixture of two species, A and B, leads to a random distribution of the two components of the system and that a random distribution results also if solutions of A and B are mixed. In that case, the heat of mixing of A and B per unit volume will be reduced by a factor f^2 if each of the components was diluted by a factor f before the mixing. Deviation from this simple relationship will, therefore, indicate a deviation from random mixing. Our data (Figure 4) show that the mixing of equal volumes of ethylbenzene and methyl isobutyrate leads to $\Delta H \approx 0.3$ J/mL. Thus, if each of these substances is diluted by four volumes of solvent, the random mixing model would predict for the mixing of the two solutions $\Delta H/V = 0.012$ J/mL. This value should be compared with 0.037, 0.025, and 0.004 J/mL, observed for the mixing of dioxane, butanone, and chloroform solutions, respectively. We see then that contact between the two solutes is more frequent than that corresponding to random mixing in dioxane and butanone but less frequent in chloroform.

Similarly, we have found that the enthalpy of interactions between the analogues of pyridine and carboxyl residues of the copolymer is strongly solvent dependent. This is easily understood, since dioxane and butanone form hydrogen bonds with carboxylic acids and chloroform forms weak hydrogen bonds with pyridine groups.[22] These hydrogen bonds must be broken before a hydrogen bond can link the carboxylic group with the pyridine nitrogen.

It is then easy to understand why smaller concentrations of the vinylpyridine comonomer of styrene and the methacrylic acid comonomer of methyl methacrylate are sufficient to form one-phase solutions containing both copolymers in chloroform rather than in dioxane or butanone: The mixing of styrene and methyl methacrylate residues is less endothermic and the interactions between the acid and the basic groups are more exothermic in chloroform than in the other media. In dioxane and in butanone the two dilute solutions become mutually miscible at a similar concentration of the strongly interacting comonomers and the enthalpy of mixing of the acid and base is, in fact, rather similar in these two solvents. The more unfavorable enthalpy of mixing of ethyl benzene and methyl isobutyrate in dioxane, as compared to butanone solutions, may explain why a larger concentration of strongly interacting groups is required before a phase in which both copolymers are concentrated forms in this solvent. Unfortunately, we are at present not in a position to use our calorimetric data for a prediction of the copolymer compositions corresponding to their athermal mixing, since we do not know to what extent the acid–base interactions in the copolymers are cooperative. We hope to tackle this problem in the future by a spectroscopic method.

While many workers have studied ternary systems in which each of two dilute phases contains predominantly one of the polymeric species, ternary phase diagrams with a concentrated and a dilute phase, each containing both polymeric components, have been described only rarely. Bungenberg de Jong et al.[11] studied extensively the gelatin-gum arabic–water system and they found that concentrated and dilute solutions were in equilibrium with each other in the pH range in which the polymeric components carry charges of opposite sign. In this case, the density of strongly interacting groups is pH dependent and it is found that the concentrated phase is generally closer to an equivalence of anionic and cationic groups.[33] A similar type of phase equilibrium in a case which does not involve ionic interactions seems to have been first observed by Koningsveld, Chermin, and Gordon[27] in the polyethylene–polypropylene–diphenyl ether system. The phase diagram was studied over a range of temperatures above the melting point of polyethylene and it was found that, with atactic polypropylene, complete miscibility was attained above a critical temperature, indicating that phase separation was here (as in our systems exhibiting closed loops in the phase diagram) also an exothermic process, although both polymers were nonpolar. A computer calculation by Zeman and Patterson[28] shows that phase diagrams with closed loops should be expected also for zero or small negative values of χ_{12}, provided the χ_{10} and χ_{20} values are sufficiently different from each other. However, their case is different from ours in that the area of the phase diagram enclosed by the loop corresponds to systems in which each of the coexisting phases contains predominantly one of the polymeric species. Such behavior has been observed in the system polystyrene–poly(vinyl methyl ether)–chloroform.[37]

Just as a strong interaction between two polymers competes successfully with the affinity of the polymers for the solvent in the systems we have studied, so a strong association between two good solvents for a given polymer may render the polymer insoluble when the solvents are mixed with each other. Such a phenomenon was first described by Gee[34] who found that cellulose acetate is soluble in aniline and in acetic acid but not in their mixture. A similar behavior was observed in the polybromostyrene–chloroform–dioxane[35] and in the poly(1-butene sulfone)–chloroform–ethyl acetate systems.[36]

It has been pointed out by a number of authors[8,29–31] that compatibility of two polymers in solution does not necessarily imply compatibility in the absence of the solvent. On the other hand, if the ternary system exhibits a separation of a concentrated phase containing both polymers, this may be taken as strong presumptive evidence for polymer compatibility after removal of the solvent. An apparent exception is the system polyethylene–isotactic polypropylene–diphenyl ether,[27,31] but this system was studied below the melting point of the isotactic polypropylene. It is doubtful that two amorphous polymers could be incompatible if they form coexisting concentrated and dilute phases in a ternary system.[33] It should, however, be noted that a mixed polymer system which behaves as a single phase when studied by DSC or electrical relaxation methods may be in a metastable state. Thus, Bank et al.[32] found no evidence of phase separation when films of mixtures of polystyrene and poly(vinyl methyl ether) were cast from benzene or toluene, although two phases were clearly present when trichloroethylene or chloroform were the casting solvents.

Finally, we should like to add a remark on the general problem of polymer compatibility. We have implicitly assumed that any polymer pair mixing with an evolution of heat has to form thermodynamically stable mixtures. Slonimskii[38] has found an apparent exception in the polystyrene–polybutadiene system in which the polymers are incompatible although mixing at room temperature is exothermic. He has argued that the exothermicity is here the result of the volume contraction of the glassy polystyrene, which dominates the unfavorable polymer interaction energy.

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Note Added in Proof. The use of acidic and basic comonomers to obtain a compatible pair of polymers has been described previously by H. Keskkula (U.S. Patent 3 072 598, Jan. 8, 1963) who studied mixtures of acidic styrene copolymers with buffers containing vinylpyridine residues.

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