

Compatibility Studies on Polyacrylate and Polymethacrylate Systems

L. J. HUGHES and G. E. BRITT

Rohm and Haas Company, Philadelphia, Pennsylvania

A study of polymer I/polymer II compatibility was initiated for two purposes. The first was to accumulate multicomponent phase equilibrium data on polyacrylates and polymethacrylates of use in the systematic characterization of graft copolymers. A second objective was to test the prediction that polymers which interact favorably with one another, through suitable polar substituents, for example, should be compatible.^{1,2} The systems examined included polymers and copolymers of acrylic and methacrylic acids, their esters and sodium salts. The polymers were investigated in pairs (with few exceptions) in a solvent with which each was completely miscible at 25°C. In order to see if favorable chain-chain contact points could be promoted sufficiently to result in high miscibility, pairs of the following types were mixed: (a) highly similar polymers, (b) copolymers having a common monomer component, and (c) polymers and copolymers having carboxylic acid substituents which present the possibility of strong hydrogen bonding interactions. Table I lists the polymers used and appropriate abbreviations for them. Polystyrene was included as a typical nonester polymer highly immiscible with poly(methyl methacrylate) and poly(methyl acrylate).

THEORY OF PHASE SEPARATION

For a large number of ternary systems composed of two different polymers and a mutual solvent, it has been found that the polymers are incompatible, and two-phase separation occurs.¹⁻⁶ The two phases are usually sharply delineated by a horizontal boundary. When the mixture is first prepared, either by mixing separate solutions of each polymer or by dissolving the two polymers together, it frequently has a grainy or textured appearance which is indicative of heterogeneity. Upon standing, usually overnight to several days, the two layers form. In sufficiently dilute solutions no phase separation is evident, even for highly incompatible polymers. For mixtures which are slow

to separate, either because of similar densities of the (solvated) polymers or because of high solution viscosities, centrifugation speeds separation. Such immiscibility is generally observed even for pairs of polymers having chemically similar monomers, e.g., polystyrene/poly(*p*-methylstyrene), poly(*o*-methylstyrene)/poly(*p*-methylstyrene). In fact the following pairs are the only ones reported to be highly compatible: poly(methyl acrylate)/poly(vinyl acetate) polystyrene/poly(*o*-methylstyrene), poly(methyl methacrylate)/nitrocellulose, and poly(vinyl acetate)/nitrocellulose.

The literature also points out the following about such ternary systems.^{1,2} (a) When two-phase separation occurs, each phase contains most of one polymer and a few per cent of the other. (b) Molecular weight is important; a polymer is more easily precipitated the higher its molecular weight. (c) Two polymers (nonelectrolytes) immiscible in one solvent are immiscible in other common solvents. Some ambiguity exists concerning the effect of temperature on phase separation. Dobry and Boyer-Kawenoki³ found temperature had little effect on their results, but Kern's work⁷ indicates some thermal dependence.

The experimentally observed polymer/polymer immiscibility has been explained theoretically in terms of the statistical thermodynamics of polymer solutions.^{1,2} The mixing process is governed by the well established relation: $\Delta F = \Delta H - T\Delta S$, where T is the absolute temperature, ΔH is the heat term resulting from intermolecular interactions, ΔS is the entropy change, and ΔF is the free energy change for the mixing. Spontaneous mixing, of course, requires that the free energy decreases, i.e., ΔF is negative. The entropy which is associated with the degree of disorder or randomness increases in processes which lead to increasing disorder. For mixing of relatively nonpolar polymers, the ΔS values have been found to be, in general, small and positive. The physical basis of this is that the number of molecules involved in the mixing

TABLE I

Polymer or compositions (in mole-%)	Abbreviation	[η]		δ , (cal./cc.) ^{1/2}
		(Benzene, 30°C.), dl./g.	$\bar{M}_v \times 10^6$	
Poly(ethyl acrylate) ^a	PEA	2.32	1.2	9.2
Poly(methyl methacrylate) ^a	PMMA	1.68	0.848	9.3
Poly(butyl acrylate) ^a	PBA	3.51	1.5	8.7
Polystyrene ^a	PS	1.59	0.50	9.1
Poly(acrylic acid)	PAA	0.576 ^b	0.16	—
Poly(methacrylic acid)	PMAA	0.145 ^b	0.033	—
50/50 EA-MMA	—	3.16	(2) ^d	—
50/50 Ba-MMA	—	4.32	(3)	—
50/50 EA-S	—	3.94	(1)	—
47/53 EA-MAA ^a	—	1.90 ^b	(0.9)	—
72.28, EA-MAA ^a	—	2.10 ^b	(1)	—
50/50, EA-AA ^c	—	1.99 ^b	(0.8)	—
47/53, MMA-MAA ^a	—	1.33 ^b	(0.5)	—
72/28, MMA-MAA ^a	—	1.11 ^b	(0.5)	—
Poly(methyl acrylate)	PMA	1.45	0.60	9.7
Poly(<i>tert</i> -butyl acrylate)	PtBA	—	—	—
Poly(isopropyl acrylate)	PiPA	2.10	1.3	—
Poly(isobornyl methacrylate)	PiBoMa	—	—	8.1
Poly(benzyl methacrylate)	PBzMA	0.629	—	—
Poly(<i>tert</i> -butyl vinyl ether)	PtBVE	0.551	—	—
Poly(isobutyl vinyl ether)	PiBVE	0.569	—	—
Poly(vinyl acetate)	PVAc	—	—	9.4
90/10 MMA-AA	—	—	—	—
Poly(vinyl alcohol)	PVOH	—	—	—
Poly(isobutyl methacrylate)	PiBMA	—	—	—
Poly(ethyl methacrylate)	PEMA	2.83	(0.56)	—

^a Emulsion polymer.

^b [η] of the methyl esters.

^c Suspension polymer.

^d Values in parentheses are estimated values.

is relatively small, i.e., small compared to the number involved if each monomer unit in the chain was a separate molecule. Connecting the monomer units by chemical bonds imposes restrictions on the degree of randomness attainable.

Whether ΔF is positive or negative is seen to be determined by a balance between the heat term (ΔH) and the $T\Delta S$ term. The small ΔS makes it possible for only a small positive heat value to prevent mixing. Experimentally, it is well known that polymers as well as small molecules mix most frequently with positive heats of mixing (heat absorbed), so incompatibility of macromolecules tends to be the usual observation. It has been anticipated^{1,2} that the few exceptions to this generalization would be for: (1) extremely similar polymers having ΔH essentially zero or positive and small; and (2) highly polar polymers with interactions which result in negative ΔH 's.

The interaction parameter^{1,2} χ_{ij} which arises in the statistical thermodynamic derivation of the free energy of mixing is highly useful in discussions of the phase relationships of polymer solutions. This quantity which arises in theory developed for nonpolar molecules demonstrates that polymer immiscibility arises when the χ_{ij} value for the polymer pair is positive and not extremely small; these are the usual conditions encountered.

For highly polar molecules, quantitative solution theories are still being formulated. It is expected that the pronounced interactions between neighboring molecules in solution will produce orientation effects which greatly affect the values of the interchange energies and entropies of mixing.^{2,8} The values of ΔH and ΔS have been found to be affected much more than ΔF by such orientations.

SOLUBILITY PARAMETERS AND SOLVENCY

Solubility parameters (δ) and solubility spectra of various polymers were established (1) to ascertain suitable mutual solvents, (2) to aid in the selection of appropriate polymer pairs, and (3) to provide a qualitative measure of the "polarity" of the polymers. The δ value of a polymer is de-

TABLE II
Additional Solubility Parameters

Polymer	δ (cal./cc.) ^{1/2}
Poly(stearyl methacrylate)	7.8
Poly(isobornyl acrylate)	8.2
Poly(lauryl methacrylate)	8.2
Poly(<i>tert</i> -butyl methacrylate)	8.3
Poly(<i>n</i> -octyl methacrylate)	8.4
Poly(<i>n</i> -hexyl methacrylate)	8.6
Poly(<i>n</i> -butyl methacrylate)	8.7
Poly(<i>n</i> -propyl methacrylate)	8.8
Poly(methyl α -chloroacrylate)	10.1
Poly(methyl α -cyanoacrylate)	14.0

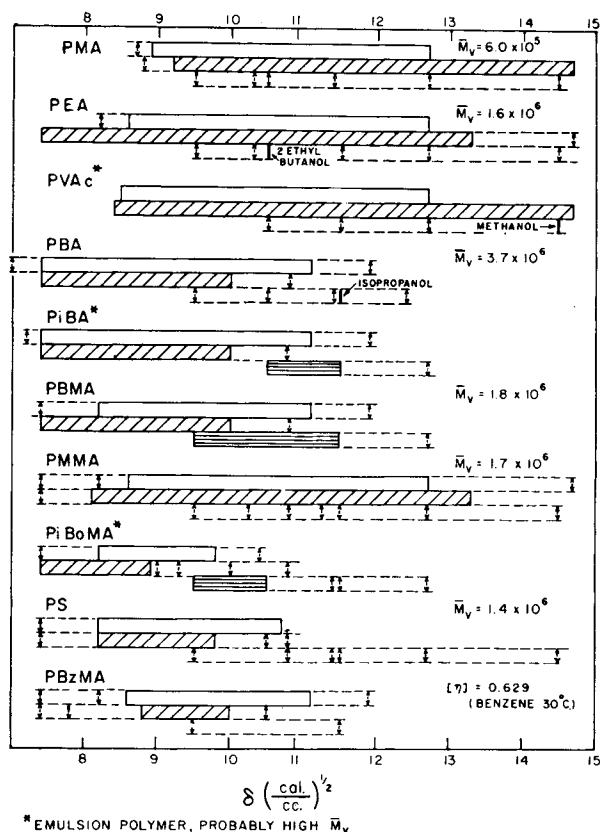


Fig. 1. Solubility spectra of various polymers. Solvents are classified as poorly, moderately, and strongly hydrogen bonded, as shown in upper, middle, and lower bars. Values of the solubility parameter of liquids tried which are nonsolvents are indicated by arrows.

defined as the square root of the cohesive energy (CED) of the material and indicates the magnitude of the intermolecular forces within it. Hildebrand and others⁷⁻¹⁰ consider the heat of mixing to arise from the differences in energy between different kinds of intermolecular contacts. Thus, ΔH is related² to the solubility parameters by $\Delta H_{cc} = V_p V_s (\delta_s - \delta_p)$, where V_p and V_s correspond to volume fraction of polymer and solvent, respectively.

Methods of determining δ values are discussed in the reference cited. Tables I and II show the values for common polymers, and are those we consider to be the best currently available. High δ 's are associated with polar functional groups. Longster and Walker¹¹ have published an interesting paper on the effect of permanent dipoles on the cohesive energy and solvent action of highly polar substances. Figure 1 shows solubility spectra of various polymers determined by us except for PVAc and PS which were merely extended accord-

ing to Burrell's technique.¹² The shaded portions of the spectra indicate the range of solubility of each polymer in solvents covering a range of δ 's. The solvents are grouped into poorly, moderately, and strongly hydrogen-bonding liquids; the figure shows that the distinction is significant. Typical solvents used in determining the spectra are given in Table III; the classification of these is also indicated. A polymer was considered soluble at 25°C.

TABLE III
Typical Solvents Used in Determination of Solubility Spectra

Nature of hydrogen bonding	Solvent	δ , (cal./cc.) ^{1/2}	
Poor Aliphatic and aromatic hydrocarbons, chlorinated and nitroparaffins	<i>n</i> -Hexane	7.4	
	Cyclohexane	8.2	
	Carbon tetrachloride	8.6	
	Toluene	8.9	
	Chloroform	9.3	
	Ethylene dichloride	9.8	
	Nitropropane	10.4	
	Nitroethane	11.1	
	Acetonitrile	11.9	
	Moderate Esters, ketones, and ethers	Diethyl ether	7.4
		Diisobutyl ketone	7.8
Heptanone-4		8.9	
Methyl hexyl ketone		8.9	
Methyl ethyl ketone		9.3	
Acetone		10.0	
Methyl cellosolve		10.8	
Propylene carbonate		13.3	
Ethylene carbonate		14.7	
Strong Alcohols and water		2-Ethyl hexanol	9.5
	2-Ethyl butanol	10.5	
	<i>n</i> -butanol	11.4	
	Isopropanol	11.5	
	Ethanol	12.7	
Methanol	14.5		
Water	23.4		

if a small amount of it (0.1 to 0.2 g.) dissolved completely in 10 cc. solvent. Naturally the polymer molecular weight is significant, with higher homologs being always less soluble, so the boundaries are not as well defined as perhaps is implied by Figure 1. High molecular weight polymers were used to partially overcome this deficiency. The borderline or Θ solvents can be expected to have δ 's near the boundaries of the ranges; thus decreasing the molecular weight slightly or raising the temperature a few degrees could make a polymer soluble in a solvent indicated to be outside the solubility range of Figure 1. The symbol (\downarrow) indicates δ values of nonsolvents which were tried, and thus help to delineate the spectra. The δ for a polymer coincides with that of solvents with which it mixes

TABLE IV
Midpoints of Solubility Spectra (Δ values) of Polymers^a

Polymer	Δ_N	$j \Delta_M$	Δ_A
PiBoMA	9.0 \pm 0.8	8.2 \pm 0.8	10.0 \pm 0.5
PiBA	9.2 \pm 1.8	8.7 \pm 1.3	11.0 \pm 0.5
PBA	9.2 \pm 1.8	8.7 \pm 1.3	11.5
PBMA	9.6 \pm 1.4	8.7 \pm 1.3	10.5 \pm 1.0
PS	9.4 \pm 1.2	9.0 \pm 0.6	—
PBzMA	9.8 \pm 1.2	10.0 \pm 1.2	—
PEA	10.6 \pm 2.0	10.4 \pm 3.0	10.5
PMMA	10.7 \pm 2.1	10.7 \pm 2.6	—
PVAc	10.6 \pm 2.1	11.6 \pm 3.2	14.5
PMA	10.8 \pm 1.9	12.0 \pm 2.8	—

^a Δ_N , Δ_M , and Δ_A , denote Δ values for nonbonding or poorly hydrogen-bonding liquids, moderately hydrogen-bonding, and strongly hydrogen-bonding solvents, respectively.

ideally, i.e., with no heat effect and no volume change. The midpoints of the solubility ranges, which will be called Δ values for each polymer in the three classes of solvents are given in Table IV together with $\pm 1/2$ the total solubility range. The Δ values generally do not coincide with the true δ ; this is especially true for polymers and solvents having the more polar functional groups; this however, does not invalidate the decided usefulness of the solubility spectra.

It is of interest to consider some of the generalizations which are shown by Figure 1 and Tables I and IV. Note that a moderately or nonhydrogen-bonding solvent with $\delta = 9.5$ would dissolve any of the noncarboxylic and nonhydroxyl-containing polymers listed. It can be seen that the relative order of the polymers when arranged according to increasing Δ values remains the same, within experimental error, for nonpolar and moderately polar liquids. When Δ and δ differ, Δ is higher. PMA, PEA, PVAc, and PMMA are soluble in a wide range of liquids, and with few exceptions (PVAc in methanol and PEA in 2-ethylbutanol) are insoluble at 25°C. in the polar, hydroxyl-containing solvents. Note that PiBA and PBMA show a range of solubility in alcohols, and PBA dissolves in isopropanol. For both polyacrylates and polymethacrylates, as the number of carbons in the alcohol alkyl group increases, Δ shifts to lower values, i.e., the polymers are soluble in more hydrocarbonlike liquids. The solubility where there are greater than four carbons in the alcohol alkyl in moderately hydrogen-bonded solvents does not extend as high as acetone, $\delta = 10$.

The polymers with aromatic rings all show rather restricted solubility ranges. No common alcohols

were found to attack high molecular weight PS or PBzMA, although alcohols with $\delta = 9.5$ –10.5 do dissolve PiBoMA.

EXPERIMENTAL

Most of the polymers used were high molecular weight emulsion samples especially prepared for this study. Several, however, were solution or suspension polymerized, as Table I indicates. The less well characterized samples listed were small quantities made available by co-workers. The emulsion polymers as well as PAA and PMMA were purified to remove ionic impurities with the ion exchange resin Monobed-1. About 30 g. of each polymer was obtained in bulk form by freeze-drying, precipitation from a solvent, or coagulation of an emulsion; all polymers were ultimately dried to constant weight under high vacuum.

Molecular Weight Determinations

The intrinsic viscosities, $[\eta]$, of benzene-soluble polymers were determined in that solvent at 30.00 \pm 0.05°C. with No. 1 Ubbelohde viscometers. The usual kinetic energy correction was applied. Where available, the appropriate \bar{M}_v - $[\eta]$ relations were used to calculate molecular weights, and in the absence of such equations estimates of \bar{M}_v were made. For the polyacids and their copolymers, which are all insoluble in benzene, the carboxyl substituents were esterified with diazomethane¹³ and the $[\eta]$'s of the resulting polyesters were obtained.

Conversion of the Polyacids to Their Sodium Salts

Determinations of the actual acid content of each acid copolymer and the preparation of polysodium salts were done potentiometrically by dissolving the polymers in methanol (about 100 ml.), diluting twofold with deionized water, and titrating with standard sodium hydroxide. Endpoints were taken as pH of 10; blank titrations were done on the solvent. Enough polymer was used to require about 25 ml. of 0.1*N* sodium hydroxide for neutralization.

Samples of the salts large enough to carry out phase studies with were most conveniently obtained by dissolving the weighed acid polymer in an organic solvent, methanol or acetone, and adding to this the equivalent amount of 0.5*N* base. Successive evaporations and additions of water followed by freeze-drying the salts from water permitted isolation of the bulk salts which were further dried under vacuum. The 72/28 and 47/53 molar ratios

correspond to 75/25 and 50/50 weight ratios of the acid form. The mole per cent compositions listed in Table I have an error of about ± 1 to 2 associated with them.

Technique Involved in the Phase Tests

The polymeric mixtures are prepared by adding the appropriate weights of pure dry polymers to a large weighing bottle with a ground-glass stopper. One of the polymers is weighed directly in the bottle; the second is weighed separately and added quantitatively to the first. Solvent is added directly to the bottle by burets or pipets, and mixing is accomplished either by means of a magnetic stirrer (the stirring bar is left in the solution throughout the series of measurements) or by agitation on a wrist-action shaker. After both polymers are completely dissolved, the character of the mixture is observed and then the sample is allowed to stand undisturbed to permit incipient phase separation to occur. Usual initial polymer concentrations c are about 20.0 g./dl. If this seems too viscous to permit separation, dilution to an appropriate concentration is made. After a day or two, the number of phases in the vessel, their physical appearance, and volume fractions are noted. Then, depending upon the particular case, the mixture is diluted further, centrifuged to hasten or enhance phase separation, or allowed to stand undisturbed for an additional period. The major consideration at this stage is whether or not combinations of high polymers are compatible and the approximate concentration range of mutual compatibility. The polymers used were unfractionated and the limitations involved here are recognized. More quantitative phase studies, at varying conditions of temperature, molecular weight, solvents, and with fractionated samples are an obvious next step. At concentrations below which phase separation no longer occurs (usually in the range of 1–5 g./dl.) or has not occurred with relatively nonviscous, moderately concentrated solutions even after centrifugation, films were made by casting from mercury surfaces. Qualitative observations of the physical properties of these films were made.

RESULTS AND INTERPRETATION

On the basis of principles already discussed two polymers are considered incompatible at 25°C. if they show two-phase separation in a common solvent at a total concentration greater than about 5 g./dl. solvent, for then at higher concentrations or

in the bulk mixture immiscibility would also occur. Previous work showed that the presence of solvent can enhance somewhat the mutual tolerance of one polymer for another, but does not affect miscibility, as here the interaction parameter μ_{ij} between the polymers is the critical factor. Once this point is established, the major reason for continuing to do the tests in solution is to minimize the time scale. The solvent permits equilibrium conditions to be established relatively rapidly by decreasing the viscosity of the polymeric mixture. The results obtained are discussed under three major headings as follows:

A. Compatibility Results on Mixture of Homopolymers (Nonelectrolytes)

The compatibility of various pairs of polymers shown in Table V was checked as described in the experimental section. Chloroform was the usual common solvent because of its excellent solvent properties for so many of the samples and its availability at reagent grade quality. Since for all cases shown, two-phase separation occurred at moderate to high concentrations ($c = 5.0$ – 20.0) it was concluded that all the polymer pairs in the table are incompatible. Table VI describes typical results for PEA/PMMA and PEMA/PMMA combinations; details for the other combinations are omitted to conserve space. The PEMA/PEA pair gave indications of being the most nearly compatible pair tried. The solution was textured and hazy indicating heterogeneity, but two phases were not obtained even after centrifuging.

Samples of the two isomeric polyethers PiBVE and PtBVE became available in the course of this

TABLE V
Incompatible Polymers (Nonelectrolytes)*

PMA/PEA	PBA/PiBMA
PMA/PMMA	PsBA/PtBA
PMA/PBA	PiBMA/PMMA
PEA/PMMA	PMMA/PBzMA
PEA/PMMA (DMF)	PMMA/PiBoMA
PEA/PEMA	PBzMA/PiBoMA
PEA/PBMA	PMA/PtBVE
PEA/PiPA	PtBVE/PiBVE
PEA/PBA	PMA/PS
PEA/PiBoMA	PEA/PS
PEMA/PMMA	PBA/PS
PiPA/PBA	PBMA/PS
PiPA/PtBA	PMMA/PS
PBA/PMMA	PiBoMA/PS
PBA/PsBA	PBzMA/PS
PBA/PtBA	

* Solvent is chloroform except where DMF is indicated.

work, and a compatibility experiment was run in chloroform to see if these very similar molecules would mix in all proportions. Two-phase separation was found to occur, however, just as in the other cases tried.

system, so a few additional experiments were tried to see how general the above result was.

PMMA/PMA/PEA/PS. A mixture of equal weights of these four polymers was prepared in chloroform at $c = 20.0$. Only three distinct phases

TABLE VI
Phase Separation Data for Typical Systems¹

Polymer I	Polymer II	Polymer concn., g./dl.	Solvent	Duration of standing, days	Results for 1/1 weight ratio of polymers*
PEA	PMMA	7.5	CHCl ₃	2	Transparent and textured; separated into two distinct clear layers when centrifuged
PEA	PMMA	5.0	"	2	Two very clear layers
		20.0	DMF	1	Two phases of equal volume: top phase transparent; bottom phase opaque
		10.0	"	1	Two phases: top ($V_t = 3/5$) translucent; bottom translucent
PMMA	PEMA	5.0	"	1	Single clear phase
		10.0	CHCl ₃	2	Two phases: top ($V_t = 1/2$) very clear; bottom translucent
50/50 EA-MMA	PEA	5.0	"	7	One clear phase
		20.0	"	3	Two phases of equal volume: bottom clear; top cloudy
		8.0	"	14	Two phases: top ($V_t = 2/5$) cloudy; bottom clear
		6.7	"	7	Two clear phases ($V_t = 1/5$)
		4.0	"	9	No separation; single, clear phase even after centrifugation
50/50 EA-MMA	50/50 BA-MMA	20.0	"	11	Very viscous, clear
		10.0	"	14	Two clear phases of equal volume
		8.0	"	7	Two clear phases ($V_t = 2/3$)
PAA	PMAA	5.0	"	8	Single clear phase
		20.0	H ₂ O	3	Two phases: top ($V_t = 2/3$) quite clear; bottom opaque
PAA	PMAA	13.3	"	15	No separation
		20.0	DMS	15	One clear phase
PNaA	PNaMA	20.0	H ₂ O	10	One clear phase
PAA	PNaMA	20.0	"	4	Two phases: top ($V_t = 4/5$) translucent; bottom cloudy.
		10.0	"	6	One clear phase

* V_t denotes volume fraction of top phase.

Four Polymers in a Common Solvent. Kern and Slocombe⁵ found that four polymers, PS, PVAc, poly(methyl vinyl ketone), and poly(2-methyl-5-vinylpyridine) in dioxane at 20% concentration formed a four-phase system. No theory is available to predict the number of phases which should be formed from such a multicomponent

formed. At dilutions to $c = 15.4$, 10.0 , and 6.7 again only three phases were noted.

PMMA/PMA/PEA/PBA. A second mixture of four polymers was prepared as above and analogous results were obtained. Over a concentration range of $c = 20.0$ to 5.0 , only three phases formed.

PMMA/PVAc/PS/PiBoMA. A final system

with four chemically more different polymers than those used in the previous two series was tried; in this case four phases were observed at $c = 20, 15.4,$ and 10.0 . At $c = 5.0$, however, only three layers could be discerned.

Two mixtures of three polymers each were prepared, PS/PMMA/PMA and PMMA/PMA/PEA. In the region of $c = 20.0$ to $c = 5.0$ only two-phase separation was observed. It was concluded that the number of phases formed in solutions of mixtures of different polymers does not necessarily equal the number of polymers in the mixture.

B. Compatibility Results on Mixtures of Polymers and Random Copolymers with a Common Monomer Component

Having noted the immiscibility of combinations of polyacrylates and polymethacrylates, it seemed a logical next step to establish whether or not two homopolymers could be compatibilized by copolymerization techniques. It is well known that in random copolymers made from two monomers, A and B, that the chemical bonding imposes mutual solubility on the two chemically different constituents. This is subject to the restriction that in the copolymer —ABAABBABBB— the segments of like units must be short; block copolymers with long sequences of like segments can be expected to have unusual properties and may not be self-compatible in the usual sense.

The following combinations were examined (note the inclusion of a common monomer constituent to increase the possibility of similar molecular environments and enhanced favorable chain-chain interactions): PEA with 50/50 EA-MMA; PMMA with 50/50 EA-MMA; PEA with 50/50 EA-S; PBA with 50/50 BA-MMA; PMMA with 50/50 BA-MMA; PS with 50/50 EA-S; 50/50 EA-MMA with 50/50 BA-MMA.

Weight ratios of copolymer/homopolymer of 1/1 and 3/1 were used; total polymer concentrations were in the range of c of 3.0–20.0. Table VI again shows only representative data. The major conclusions are summarized below.

With mixtures of PEA or PMMA with their 50/50 EA-MMA copolymer, two-phase separation was observed at both weight ratios. Thus, random copolymerization of EA with MMA does not result in a polymer which is miscible in all proportions with either PEA or PMMA. There are indications, however, that more quantitative studies would show that these mixtures are more compatible than

mixtures of the homopolymers. Thus, higher concentrations were required in the former cases before phase separation occurred, and in addition all the films formed from the copolymer-containing mixtures were nonlayered and either transparent or translucent. Films from the PEA/PMMA mixtures showed pronounced heterogeneity.

For the mixtures of either PEA or PS with their random copolymer, two-phase separation was also observed. Only at very low concentrations ($c = 3$) where mutual compatibility can be expected for most polymer pairs, was a clear, single phase obtained. All the films, in sharp contrast to those of PEA/PS mixtures, were unlayered and somewhat translucent.

For PBA with the BA-MMA copolymer, two layers were obtained at the 1/1 weight ratio but not at the 3/1 ratio, although the latter solution was cloudy. The results with PMMA and the copolymer were analogous. These mixtures showed the most definite indications that copolymerization increased compatibility.

The mixture of two copolymers containing a common monomer, BA-MMA plus EA-MMA, was first prepared at $c = 20.0$. At this concentration a very clear but very viscous solution formed which did not resolve into two phases. At lower concentrations, $c = 8-10$, two-phase separation occurred. At $c = 5.0$, a single, clear phase was obtained. The film formed from this solution had excellent optical clarity and did not whiten significantly when stressed; layering could not be detected.

A paper by Slocombe¹⁴ gives some interesting insights into copolymer compatibility. He found that for many three-monomer combinations which formed two azeotropic copolymers, for example, acrylonitrile with both styrene and α -methylstyrene the compositions of monomer mixtures required to produce clear, compatible copolymers could be ascertained. The two azeotropic copolymers were highly miscible, as were the terpolymers whose initial compositions fell on or near the azeotropic line which is formed by connecting the compositions of the two azeotropic copolymers on the ternary phase diagram. An azeotropic copolymerization results with certain critical mixtures of monomers having reactivity ratios less than one. In such polymerizations, it will be recalled, the composition of polymer being formed coincides with that of the monomer mixture, and polymerization proceeds without change in composition. This work thus suggests that the distribution of monomers in the

TABLE VII
 Solubilities of Polyacids at 25°C.^a

Solvent	δ (cal./ cc.) ^{1/2}	Polyacid								
		PAA	PMMA	47/53 EA- MAA	72/28 EA- MAA	50/50 EA-AA	47/53 MMA- MAA	72/28 MMA- MAA	PEA	PMMA
Diethyl ether	7.4	I	I	I	I	I	I	I	S	I
Cyclohexane	8.2	I	I	I	I	I	I	I	I	I
Benzene	9.2	I	I	I	I	I	I	I	S	S
Chloroform	9.3	I	I	I	I	I	I	I	S	S
Dioxane	9.9	S	S	S	S	S	S	S	S	S
Acetone	10.0	I	I	I	S	S	I	S	S	S
Isopropanol	11.5	S	I	I	I	I	I	I	I	I
Acetonitrile	11.9	I	I	I	I	I	I	I	S	S
Dimethylformamide	12.7	S	S	S	S	S	S	S	S	S
Ethanol	12.7	S	S	S	S	S	S	I	I	I
Propylene carbonate	13.3	I	I	—	—	—	—	—	—	—
Methanol	14.5	S	S	S	S	S	S	I	I	I
Ethylene carbonate	14.7	I	I	I	—	—	I	—	—	—
Water	23.4	S	S	I	I	I	I	I	I	I

^a S denotes soluble; I denotes insoluble.

 TABLE VIII
 Solubility of Polymeric Sodium Salts at 25°C.^a

Solvent	δ , (cal./cc.) ^{1/2}	Polymer					
		PNaA	PaNMA	50/50 EA-NaMa	75/25 EA-NaMA	50/50 EA-NaA	50/50 MMA-NAMA
Dimethylformamide	12.7	I	I	—	I	I	I
Methanol	14.5	I	I	—	S	I	S
Water	23.4	S	S	S	S	S	S

^a S denotes soluble system; I denotes insoluble.

chain significantly affects solubility, and miscibility is enhanced by a uniform distribution.

C. Results for Polyacids and Their Sodium Salts

The effects of very polar and ionic substituents were investigated with the acidic polymers listed in Table VII and their sodium salts. Table VII summarizes qualitative solubility tests on the polyacids; data for PEA and PMMA are included for comparison. The introduction of acrylic or methacrylic acid units (above mole fraction of 1/4) into either PEA or PMMA causes them to be insoluble in some of their usual solvents, e.g., benzene and chloroform, but to dissolve in more polar, strongly hydrogen-bonding solvents. On the other hand, water solubility of pure PAA and PMMA is not exhibited by acid copolymers of the composition studied. In short, the solubility parameters of the acid copolymers are intermediate to those of the constituent homopolymers. Two of the solvents, dimethylformamide (DMF) and dioxane,

dissolve polymers having δ 's which differ appreciably.

A few solubility checks were done on the salt forms of the polyacids (see Table VIII). All these salts were water-soluble but insoluble in DMF. Methanol dissolved several of them, but apparently is not generally a solvent for polymers and copolymers containing large amounts of ionic substituents.

Results with Acid Copolymers

Early in this investigation it was found that PAA and PMAA showed two-phase separation at $c = 20$ in water and only one phase at $c = 13$. It was concluded that hydrogen bonding was more favorable internally, i.e., between carboxyl units of the same chain or like chains, or between acid units and water than between chains of different types. Miscibility could be attained at somewhat higher concentrations than with nonpoelectrolyte polymers, but this could be due to the comparatively low molecular weight of the PMAA, 2.82×10^4 .

High molecular weight PMMA is water-insoluble. A 9/1 MAA-AA sample of unknown molecular weight was obtained at this time. It was found that at $c = 20$, PMAA could be mixed with it without the formation of two phases, but that PAA gave two phases. It would thus seem that the introduction of 10 mole-% of AA into a PMAA polymer does not give a copolymer compatible with PAA nor incompatible with PMAA. The effect of temperature should be investigated for these acid pairs.

It was subsequently found that no two-phase separation developed for 1/1 PAA/PMAA in concentrated solutions, $c = 20$ or 40, of dimethylformamide. Even if these were centrifuged for 7 hr., only a single, clear phase was observable. DMF has extraordinarily good solvent capacity; it dissolves a wide variety of polymers including all of those in Table I. Thus, it served as a convenient common solvent. Since the high dielectric constant of DMF was believed to be a factor in the lack of separation of PAA and PMAA, the experiment was repeated in dimethyl sulfoxide (DMS). At $c = 20$ one clear phase was again observed.

Since bridging between adjacent carboxyls seemed especially likely, various copolymers were prepared of AA and MAA with EA and MMA; the nonacid components were to "dilute" or space the acid units in a given chain to decrease the possibility for interaction of substituents on adjacent monomer units. The results on the polyelectrolyte copolymers are summarized below; Table V shows typical data.

50/50 EA-AA and 47/53 EA-MAA. Phase studies were done on 1/1 mixtures of the above copolymers which have a common nonacid component and different acid constituents. Two phases were found at $c = 20$ and 10 in methanol. Thus, PAA and PMAA are not compatibilized by the introduction into each of about 50 mole-% of an acrylate monomer. In DMF solutions at $c = 20$, the copolymer mixture, just as the mixture of pure acids, showed only a single, clear phase, even after prolonged standing or centrifugation. In DMS at $c = 20$, one transparent phase was found. The fact that phase separation can occur in DMF was shown by 1/1 mixtures of PEA and PMMA, and by PEA with 50/50 EA-AA.

47/53 EA-MAA and 47/53 MMA-MAA. The copolymers in this case consist of a common acid constituent and noncommon, nonacid constituents which, however, are isomeric. In methanol or ethanol two phases formed readily at $c = 20$ and

10. At high dilutions, e.g., $c = 3$, traces of insoluble polymer were noticed even though the individual polymers are soluble in this solvent. This result was confirmed in both methanol and ethanol. The explanation is unknown; possibly some heterogeneity in the polymerization is responsible.

For both DMF and DMS only one phase was observed at $c = 20$. The common acid constituent, at the compositions used, could not compatibilize two different polymer components, even though the latter are isomeric and have similar solubilities, unless a solvent of high dielectric constant was used.

47/53 MMA-MAA and 72/28 MMA-MAA. Dimethylformamide and DMS were the only convenient, common solvents for these polymers. In DMF at $c = 15$ and 10, two phases formed. In DMS, only one phase was present at $c = 20$, and this was transparent and clear. Note that different compositions of the same two monomers can differ greatly in solubility and can be incompatible.

72/28 MMA-MAA and 72/28 EA-MAA. These polymers were separately soluble in acetone at $c = 20$. In the 1/1 mixture of copolymers, two liquid phases were readily observable at high concentrations, e.g., $c = 20$ or 15; in dilute solutions, $c = 3-5$, there was a clear liquid layer plus a small amount of precipitated polymer.

In DMF two clear phases formed at $c = 20$, but only one at $c = 10$. In DMS two phases formed at $c = 20$.

47/53 EA-MAA and 72/28 EA-MAA. These two polymers showed two-phase separation in methanol, $c = 10-20$, and are hence incompatible.

PAA and PVOH and PMAA and PVOH. A few scouting experiments were done with these two systems. With PAA/PVOH, two-phase separation was observed at moderate concentration; with PMAA/PVOH, precipitation occurred as soon as the two solutions were mixed. PAA would be expected to be a stronger acid than PMAA.

Results with Sodium Salts of Polyacids

Results on 1/1 physical mixtures of sodium salts of various acid copolymers are summarized below. Water was the solvent in all cases.

PNaA and PNaMA. At $c = 20$ a single, clear phase formed. The salts are highly compatible; this was the expected result.

PAA and PNaA. As one would expect, only one phase was found at high concentration ($c = 20$), even after centrifuging for 4 hr. The sample was opaque, however. This result was confirmed on

another pair of samples at $c = 12$. Because of the dynamic equilibria involved, this experiment actually concerns two AA-NaA copolymers.

PMAA and PNaMA. Polymethacrylic acid and its sodium salts are also completely compatible at high concentration, e.g., $c = 20$. Only a single clear phase is observable for 1/1 mixtures.

PAA and PNaMA. These two polymers were incompatible at $c = 20$, but formed only a single clear phase at $c = 10$. Because of the equilibria, it is again probably more proper to say that the AA-NaA copolymer is incompatible with the MAA-NaMA copolymer.

PMAA and PNaA. The result was incompatibility at $c = 20$, but compatibility at $c = 10$. Note the relationship of this system to the previous one. Films formed from both of these solutions looked heterogeneous.

50/50 EA-NaA and 47/53 EA-NaMA. The results here were not clear-cut. At $c = 20$, the solution was transparent; although two layers were not discernible, the flow was not perfectly smooth, which is indicative of heterogeneity. At $c = 15$, after centrifugation, a small, viscous layer could be noted if the tube was inverted. Earlier work with a 1/1 ratio of 50/50 EA-NH₄MA and 50/50 EA-NH₄A showed pronounced two-phase separation at $c = 25$ and $c = 10$ after prolonged standing.

47/53 MMA-NaMA and 47/53 EA-NaMA. At $c = 15$, two distinct layers formed. Thus, the NaMA content does not effectively compatibilize PEA and PMMA.

72/28 MMA-NaMA and 47/53 MMA-NaMA. After the mixture of polymers was freeze-dried to remove the acetone (required in the conversion of the acids to the salts), it was found at $c = 12$ in water that two phases formed; at $c = 5$, however, only one phase was observed.

47/53 EA-NaMA and 72/28 EA-NaMA. The mixture was opaque at $c = 20$, but no two layers formed. Flow was smooth.

The results with the copolymer salts were not as definitive as would be desirable. Apparently, the polyelectrolyte content of these polymers does not completely dominate their compatibility characteristics.

GENERAL DISCUSSION

It is well established that a polyelectrolyte consists of long chain molecules with sites of charge distributed along their lengths, and that because of electrostatic repulsions between the like charges the

size of the polymer domains and the conformations of the chains in dilute solution are dependent upon the total polymer concentration and the particular solvent. The expansion of the molecular coils is smaller in solvents of high dielectric strength which effectively shield the charges. Ionizable polymers of necessity have regions of high charge density regardless of the degree of dilution because the charges are constrained in relatively close proximity. Both PAA and PMAA are weak electrolytes, whereas PNaA and PNaMA are strong ones. With these points in mind, two aspects of the miscibility results merit further discussion. One is the complete miscibility of the sodium salts of PAA and PMAA in contrast to the incompatibility of the mixture of the polyacids or of mixtures of acid and salt polymers; the second is the pronounced solvent effect on the acid systems.

Within a given polyacid solution hydrogen bonding can occur between backbone carboxyls which are: (a) adjacent on the same chain which would seem particularly favorable; (b) nonadjacent on the same chain but brought into close proximity because of a flexible chain backbone; (c) on different chains of the same type, and also between the solvent and polymer. The fact that PAA, PMAA, and copolymers containing them are not completely miscible in water at 25°C. suggests that the entropy change for hydrogen bonding between carboxyls of two different types of chains is not very favorable. Dobry and Boyer-Kawenoki³ found nitrocellulose and cellulose acetate were incompatible in acetone but compatible in acetic acid. They found also that poly(vinyl alcohol) and methyl cellulose are incompatible in aqueous solutions. It is very likely that in water the carboxyls are bonded predominantly with solvent rather than with other carboxylic groups just as dimers of formic and acetic acids are broken up in water. Morawetz has shown for styrene-methacrylic acid copolymers in nonpolar solvents that hydrogen bonding is mostly intramolecular, but that a small fraction of carboxyls participate in intermolecular bridging.¹⁵

It is significant that in the present work only the polymers with high acid contents showed compatibilities dependent upon solvent. It is conceivable that highly solvated chains of different types appear to be highly similar to one another and hence mix in all proportions. In contrast with the behavior in nonpolar systems, strong specific interactions with solvent molecules apparently can lead to heat and entropy effects which dominate the miscibility of mixtures of polyacids and their copolymers. It is

not surprising, of course, that for the highly polar polymers solvent/polymer interactions are of more significance than for slightly or nonpolar polymer pairs.

PNaA and PNaMA were completely miscible even at high concentrations. It can be assumed that no aggregation occurs with the polysalts, since the hydrogen-bridging possibility is gone. It might be expected that repulsions of negative charges on the two types of chains would cause phase separation. Possibly, the chains which are considerably extended are less able to distinguish "foreign" (solvated) molecules and interact about as favorably as with their own molecules. This result of the incompatibility of chains with highly similar monomers suggests that chain conformation and/or the orientations of substituents are significant factors in mixing (see also references 2, 6, and 8). The conformations, describing the size and shape of the polymer coils in solution, and the configurations which characterize the orientations in space of the substituents, dictate in conjunction with solvation effects the overall surface which a chain presents to a second chain molecule. Thus, these factors influence the nature, number, and kind of polymer/polymer and polymer/solvent contacts; these, in turn, affect the free energy of mixing. The fact that such apparently similar molecules as PEMA and PMMA are not compatible suggests an unfavorable heat of mixing which arises because the ester substituents, which might be expected to provide favorable contact points, are either not oriented in an appropriate way or are buried in the polymer coil.

Theoretical interpretation of phase separation in polyelectrolytes is obviously complicated. Development of theories for concentrated solutions of simple electrolytes and for dilute solutions of polyelectrolytes are still in their formative stages. It is clear, of course, that to the ΔF change for mixing an electrostatic contribution must be added. I. Michaeli¹⁶ suggests that, in general, the electrostatic contribution will favor phase separation; no experimental data were given, however.

Fuoss¹⁷ has given data for the mutual interaction of two polyelectrolytes wherein one polymer is a polycation and the other a polyanion. In both systems tried, poly(sodium acrylate) plus poly[4-vinyl-*N*-(*n*-butyl)pyridinium bromide], and this latter polymer with poly(sodium styrenesulfonate), the result, which can be expected to be general, was mutual precipitation. The strong electrostatic interactions between the fields of the polyions result

in the formation of an insoluble aggregate cross-linked by electrostatic forces.

It is concluded that molecular interactions must be carefully balanced if compatibility is to be achieved. Inclusion of substituents into chains which might be expected to lead to favorable chain-chain interactions may favor more strongly intrachain and polymer-solvent interactions. The polycation/polyanion mixture represents a limiting case wherein the interactions between chains of different type are so favorable that a three-dimensional network results which is immiscible with a small molecule solvent.

The authors wish to acknowledge the synthesis of the polymers by Dr. B. Larsson, Dr. F. Glavis, Mr. W. Toy, and Mr. J. Gormley; the technical assistance of Mr. A. Tracton and Mr. J. Cavanaugh, and the helpful discussions with Dr. G. L. Brown, Dr. L. P. Hammet, and Dr. D. Curtin.

References

1. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, Chapter 13.
2. Tompa, H., *Polymer Solutions*, Academic Press, New York, 1956.
3. Dobry, A., and F. Boyer-Kawenoki, *J. Polymer Sci.*, **2**, 90 (1947).
4. Scott, R. L., *J. Chem. Phys.*, **17**, 249 (1949).
5. Kern, R. J., and R. J. Slocombe, *J. Polymer Sci.*, **15**, 183 (1955).
6. Kern, R. J., *J. Polymer Sci.*, **21**, 19 (1956).
7. Hildebrand, J., and R. Scott, *The Solubility of Non-Electrolytes*, 3rd Ed. Reinhold, New York, 1949.
8. Tompa, H., *J. Chem. Phys.*, **21**, 250 (1953).
9. Small, P. A., *J. Appl. Chem. (London)*, **3**, 71 (1953).
10. Walker, E. E., *J. Appl. Chem. (London)*, **2**, 470 (1952).
11. Longster, G. F., and E. E. Walker, *Trans. Faraday Soc.* **49**, 228 (1953).
12. Burrell, H., *Interchem. Rev.*, **14**, No. 1 (1955); *ibid.*, No. 2 (1955).
13. Katchalsky, A., and H. Eisenberg, *J. Polymer Sci.*, **6**, 145 (1951).
14. Slocombe, R. J., *J. Polymer Sci.*, **26**, 9 (1957).
15. Chang, S., and H. Morawetz, *J. Phys. Chem.*, **60**, 782 (1956).
16. Michaeli, I., *J. Polymer Sci.*, **23**, 443 (1957).
17. Fuoss, R. M., and H. Sadek, *Science*, **110**, 552 (1949).

Synopsis

The predicted general incompatibility of mixtures of polymers has been further confirmed. Thirty-one mixtures of homopolymer pairs showed phase separation in a common solvent. These included closely related polymers such as polyacrylates with both polymethacrylates and other polyacrylates and pairs of different polymethacrylates. Typical immiscible combinations are PMA/PEA and PEMA and PEMA/PMMA. It was also found that the presence of a common monomer constituent did not result in complete compatibility of either a homopolymer with a copolymer or a

mixture of two copolymers. Apparently, none of the combinations tried were sufficiently similar to result in heats of interaction small enough to be counteracted by the small entropy change involved. Since another possibility for attaining miscibility is through polar interactions, the effects of ionic and hydrogen-bonding substituents upon polymer-polymer compatibility were considered, and selected experiments were done on a series of carboxyl-containing polymers and their sodium salts. It was concluded that hydrogen bridging occurs preferentially either intramolecularly or between polymer and solvent rather than between two different types of chains each having hydrogen-bonding ability. Thus, poly(acrylic acid) and poly(methacrylic acid) show two-phase separation in water. Although poly(sodium acrylate) and poly(sodium methacrylate) are completely miscible, mixtures of the partially neutralized acids, e.g., PAA and PNaMA mixtures, show separation. In contrast to predictions for less polar polymers, compatibility of mixtures of polymers containing high mole fractions of carboxylic acid monomers showed a pronounced dependence upon solvent. Thus, the two copolymers 45/53 EA-MAA and 47/53 MMA-MAA are incompatible in methanol or ethanol but form homogeneous solutions in DMF or DMS.

Résumé

On a, à nouveau, confirmé l'incompatibilité générale et prévue des mélanges de polymère. Trente-et-un mélanges de paires de homopolymères ont montré une séparation de phase dans un solvant commun. Ceux-ci comprenaient des polymères étroitement reliés, comme par exemple des polyacrylates avec des polyméthacrylates et d'autres polyacrylates et des paires de polyméthacrylates différents. Des combinaisons immiscibles typiques sont: PMA/PEA et PE/MA et PEMA/PMMA. On a également trouvé que la présence d'un constituant monomère commun n'entraînait pas une compatibilité complète de chaque homopolymère avec un copolymère ou un mélange de deux copolymères. Apparemment, aucune des combinaisons étudiées étaient suffisamment semblables pour donner des chaleurs d'interaction suffisamment faibles que pour être contrebalancées par le faible changement d'entropie impliqué. Puisqu'il existe une autre possibilité de réaliser une miscibilité par des interactions polaires, on a étudié les effets des substituants des liaisons ioniques et des liaisons hydrogène sur la compatibilité polymère-polymère, et on a réalisé des expériences sélectives sur une série de polymères carboxylés et leurs sels sodiques. On est arrivé à la conclusion que le pont hydrogène a lieu de préférence par action intermoléculaire ou entre le polymère et le solvant plutôt qu'entre deux types de chaînes ayant chacune des possibilités de former des ponts hydrogène. Ainsi, l'acide polyacrylique et l'acide polyméthacrylique donne une séparation en deux phases dans l'eau. Quoique le polyacrylate de sodium et le polyméthacrylate de sodium soient parfaitement miscibles, des mé-

anges de ces acides partiellement neutralisés se séparent, par exemple des mélanges de PAA et PNaMA. Contrairement à ce qui était prévu pour des polymères moins polaires, la comptabilité des mélanges de polymère contenant des fractions molaires élevées de monomères acides carboxyliques manifeste une dépendance marquée en fonctions du solvant. Ainsi, les deux copolymères 47/53, EA - MAA et 47/53 MMA-MAA sont incompatibles dans le méthanol ou l'éthanol, mais ils forment des solutions homogènes dans le DMF ou le DMS.

Zusammenfassung

Die Annahme einer allgemeinen Unverträglichkeit von Polymermischungen wurde weiterhin bestätigt. Einunddreissig Mischungspaare von Homopolymeren zeigten in einem gemeinsamen Lösungsmittel Phasentrennung. Darunter befanden sich eng verwandte Polymere, wie Polyacrylate mit sowohl Polymethacrylaten als auch anderen Polyacrylaten und Paare von verschiedenen Polymethacrylaten. Typisch nicht-mischbare Kombinationen sind: PMA/PEA und PEMA/PMMA. Es wurde auch gefunden, dass die Anwesenheit einer gemeinsamen Monomereinheit weder für die vollständige Verträglichkeit eines Homopolymeren mit einem Copolymeren, noch für die zweier Copolymerer ausreichte. Offenbar war keine der untersuchten Kombinationen ähnlich genug, um so kleine Wechselwirkungswärmen zu liefern, dass sie durch die kleine auftretende Entropieänderung kompensiert werden können. Da eine andere Möglichkeit zur Erreichung einer Mischbarkeit durch polare Wechselwirkungen gegeben ist, wurde der Einfluss ionischer Substituenten und solcher mit Wasserstoffbindungen auf die Verträglichkeit von Polymeren untersucht und einige Versuche an einer Reihe von carboxylhaltigen Polymeren und ihren Natriumsalzen durchgeführt. Man kam zu dem Schluss, dass Wasserstoffbindungen bevorzugt intramolekular oder zwischen Polymerem und Lösungsmittel und nicht zwischen zwei verschiedenen Kettentypen, von denen jede die Fähigkeit zur Bildung von Wasserstoffbindungen besitzt, auftreten. So zeigen Poly(acrylsäure) und Poly(methacrylsäure) in Wasser Trennung in zwei Phasen. Obwohl Poly(natriumacrylate) und Poly(natriummethacrylat) vollständig mischbar sind, zeigen Mischungen der partiell neutralisierten Säuren, z.B. PAA- und PNaMA-Mischungen Phasentrennung. Im Gegensatz zu den weniger polaren Polymeren, zeigte die Verträglichkeit von Mischungen von Polymeren mit einem hohen Molenbruch an Carbonsäure-Monomeren eine ausgeprägte Abhängigkeit vom Lösungsmittel. So sind die beiden Copolymeren 45/53 EA-MAA und 47/53 MMA-MAA in Methanol oder Athanol nicht verträglich, bilden aber in DMF oder DMS homogene Lösungen.

Received July 21, 1960