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Polymer Compatibilization Through Hydrogen Bonding

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ABSTRACT

Partially modified polystyrene containing vinyl phenyl hexafluorodimethyl carbinol was mixed with a number of counterpolymers containing poly(vinylacetate), poly(methyl methacrylate), poly(ethyl methacrylate, poly(n-butyl methacrylate), poly(vinyl methyl ether), poly(2,6 dimethyl-1,4 phenylene oxide), bisphenol A polycarbonate poly(styrene-co-acrylonitrile), poly(dimethyl siloxane), a crystallizable polyester, an amorphous polyamide and two amorphous polyamides. Hydrogen bonding interactions to effect miscibility were related to the number of proton donating groups in the modified polystyrene, and these were studied in regard to lower critical solution temperatures and the glass transition temperatures of the hydrogen bonded blends.

I. INTRODUCTION

In two earlier publications,[1,2] the effect of hydrogen bonding on the miscibility of polymer was investigated. A partially modified polystyrene, poly(styrene-co-vinyl phenyl hexafluorodimethyl carbinol) was shown to be miscible with two amorphous polymers, bisphenol A polycarbonate and poly(n-butyl methacrylate), and partially miscible with a crystalline polymer, poly(ethylene oxide), with which polystyrene is incompatible. Apparanlty, the formation of hydrogen bonds between the modified

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polystyrene and its counterparts overcomes the otherwise unfavorable intermolecular forces.

In order to confirm that the concept of enhancement of polymer miscibility via hydrogen bonding has general applicability, we have extended the earlier studies to include a large variety of other counterpolymers which contain proton acceptor groups. The list of counterpolymers includes poly(vinyl acetate), poly(methyl methacrylate), poly(ethyl methacrylate) poly(n-butyl methacrylate), poly(vinyl methyl ether), poly(2,6 dimethyl-1,4 phenylene oxide), bisphenol A polycarbonate, poly(styrene-co-acrylonitrile), poly-dimethyl siloxane), a crystallizable polyester, an amorphous polyamide and two amorphous aliphatic polyesters.

In the present study, we focused our effort on the following aspects of polymer miscibility. First, we determined the minimum number of proton donating groups in the modified polystyrene required to achieve miscibility with different counterpolymers. To this end, the modifed polystyrenes were synthesized by copolymerization of styrene with p-(hexafluoro-2-hydroxyl isopropyl)styrene so that a wide range of copolymer compositions could be obtained. This procedure was found to be superior to the method used previously which was based on the reaction of polystyrene with hexafluoroacetone followed by hydrolysis. Secondly, the formation of hydrogen bonds in the solid state was studied by infrared spectroscopy. Thirdly, many miscible polymer blends have been found to undergo phase separation at elevated temperatures,[3,4,5] known as lower critical solution temperatures (LCST), and the temperature of phase separation has been predicted to be sensitive to the polymer-polymer interaction parameter.[6] Therefore we have examined the LCST phenomena in some detail in the hydrogen bonded blends with particular attention to the relationship between the cloud point temperature and the degree of PS modification. Lastly, we studied the glass transition temperatures of hydrogen bonded blends.

II. EXPERIMENTAL

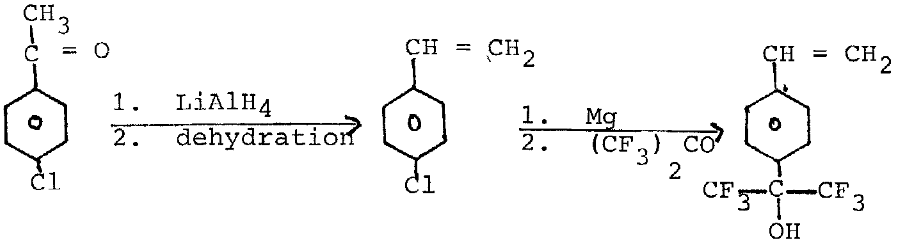
1. Materials

The basic starting materials for preparation of p-(hexafluro-2-hydroxyl isopropyl)styrene were p-chloroacetophenone (Aldrich Co. ,97%, m.p.=20°C) and hexafluoroacetone (obtained through the courtesy of E. I. DuPont de Nemours Co., b.p. =-28°C, a liquified gas stored in steel containers). Both compounds were used without further purification. Styrene monomer (Aldrich Co.) was washed with a 10% aqueous sodium hydroxide solution in an equal volume with styrene and dried by decanting it over activated molecular sieves. The purified styrene was obtained from a middle portion of distillate under vacuum distillation (15-25 mmHg).

The following counterpolymers were used in the miscibility study. Poly(vinyl methyl ether) (PVME) (Cellomer Associates intrinsic viscosity=0.378 measured in benzene at 30°C) was purified by filtration of a toluene solution prior to precipitation into large volume (10:1) of n-hexane and dried under vacuum at 100°C for 3 days. Poly(vinyl acetate) (PVAc) (Aldrich Co. intrinsic viscosity = 0.467), poly(methyl methacrylate) (PMMA) (Aldrich Co. intrinsic viscosity = 0.361), poly(ethyl methacrylate) (PEMA) (Aldrich Co. intrinsic viscosity = 0.901), poly(butyl methacrylate (PBMA) (Aldrich Co. intrinsic viscosity = 0.591) and poly(styrene-co-acrylonitrile) (PSAN) (Cellomer Associates 30 mol % of acrylonitrile) were dissolved in small amounts of methylene chloride and precipitated in large volumes of either methanol or n-hexane. After the polymers were dried under vacuum at 110°C, the intrinsic viscosities were measured in benzene at 30°C. Poly(vinyl methyl ketone) (PVMK) (Polyscience Co. intrinsic viscosity = 0.834 in chloroform at 30°C), poly(2,6-dimethyl phenylene oxide) (PPO) (Aldrich Co. M.W. = $3\text{-}4\times10^5$), bis-phenol A polycarbonate (PC) (Aldrich Co. M.W. = $5,6\times10^5$) and poly(phenylene sulfone) (PPSF) (Polyscience Co. M.W. = 3×10^4) were purified in the same way by using appropriate solvent-nonsolvent systems; chloroform-n-hexane for PVMK, chloroform-methanol for PPSF, toluene-methanol for PPO, and methylene chloride-methanol for PC. The purified polymers were dried under vacuum above their respective glass transition temperatures. Vitel PE-307 (VTL I), Vitel VPE-5545 (VTL II) were obtained from the Goodyear Tire and Rubber Co. in sheet form. The two amorphous polyesters are reported to be the products from the condensation of a mixture of several monomers. The resulting copolyesters have structural irregularities or bulky branched structures which prevent crystallization. The inherent viscosities of both polyesters when measured in benzene at 30°C and 0.5g/100ml were 0.334. Kodar Polyester (KOD), obtained from Tennessee Eastman Co. (KODAR PETG 6763) in pellet form, is a copolyester prepared from an equimolar mixture of terephthalic and isophthalic acid and a mixture of ethylene glycol and 1,4-dihydroxymethyl cyclohexane at a mole ratio of 7 to 3. The inherent viscosity of Kodar when measured in benzene at 30°C and 0.5g/100ml was 0.627. Poly(dimethyl siloxane) (PDMS) (Petrarch System, Inc., gum grade) qas obtained as an additive-free polymer and used without further purification. TROGAMID T (TRO) obtained as a courtesy from Dynamit Nobel Co. is a completely amorphous polyamide prepared from dimethyl terephthalate and trimethyl hexamethylene diamine.

2. Synthesis of Monomer

The new monomer, p-(hexafluoro-2-hydroxyl-propyl) styrene was prepared from p-chloroacetophenone and hexafluoroacetone through the following steps.



2.1 p-chlorophenyl methyl carbinol: 22g of lithium aluminum hydride ($LiAlH_4$) was dissolved in 100 ml of tetrahyrofuran (THF) (distilled from $LiAlH_4$) and placed in a three-necked flush equipped with a reflux condenser and mechanical stirrer. p-Chloroacetophenone (0.4 mole) diluted with 50 ml of THF was hydrogenated (60-70°C) by adding the solution slowly through a dropping funnel into a $LiAlH_4$ solution under reflux. After the hydrogenation reaction was completed (around 6 hr), free $LiAlH_4$ was destroyed by methanol until no exothermic reaction occurred and the dark gray complex product was dissolved with concentrated HCl aqueous solution until two layers of clear solution were obtained. The upper layer was decanted after extracting with ether and dried with magnesium sulfate overnight. p-Chlorophenol methyl carbinol was obtained simply by evaporating the ether solvent at elevated temperature under vacuum and was used for preparation of p-chlorostyrene without further purification.

2.2 <u>p-Chlorostyrene:</u> Liquid phase dehydration of p-chlorophenyl methyl carbinol in the presence of potassium acid sulfate was used to prepare p-chlorostyrene. A three-necked round-bottomed flask was attached to a dropping funnel and a short fractionating column (20 cm) equipped with a heating element. Heating of the fractionating column was applied to provide prompt distillation of p-chlorostyrene when formed. Nine grams of powdered potassium acid sulfate and 0.05g of p-tert-butylcatechol were placed in the reaction flask immersed in an oil bath maintained at 220-230^{o}C. Seventy grams (0.45 mol) of p-chlorophenyl methyl carbinol and 0.05g of p-tert-butylcatechol were placed in the dropping funnel and added dropwise at a rate (5-10 drops per minute) under vacuum (40-60mmHg). The p-chlorostyrene and water collected in a receiver were dried over active molecular seives and pure p-chlorostyrene was obtained by vacuum distillation (64-66^{o}C/4mmHg) in a yield of 50-55g (81-89%).

2.3 <u>p-(Hexafluoro-2-hydroxyl isopropyl) styrene</u>: Seven grams of magnesium were placed in a three-necked flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel. The system was maintained under nitrogen and at a reaction temperature of 35^{o}C. Thirty grams of p-chlorostyrene was dissolved in 100 ml of THF and 20 ml of this solution was added to the reaction flask with 2ml of ethyl bromide as an initiator. The test of the solution was added dropwise with stirring at a rate to maintain gentle reflux (1-2 hrs) and then the reaction was kept under continuous reflux for 1 hr after all the p-chlorostyrene solution had been added. After the reaction was completed, the mechanical stirrer and the dropping funnel were replaced with a gas inlet tube and a reflux condenser cooled with dry ice-acetone mixture, respectively. The outlet of the reflux condesner was sealed with chromic acid. Hexafluoroacetone gas was slowly blown into the stirred reaction solution at a rate to maintain gentle reflux. About 2-3 hr were required for the addition of 40g of hexafluoroacetone. The reaction mixture was then poured into an excess of ice-water, followed by hydrolysis with dilute HCl aqueous solution. A crude product, (hexafluoro-2-hydroxyl isopropyl)styrene was obtained from the organic layer. Since it contained a small amount of THF which was used as a solvent during the Grignard reaction and formed an isotropic mixture, the crude product was neutralized by 10% NaOH aqueous solution and the residual THF was removed. The resulting aqueous solution was acidified by dilute HCl and then (hexafluoro-2-hydroxyl isopropyl) styrene was separated. After drying it over a molecular sieve, the purified product was obtained from vacuum distillation (89-91°C/4mm).

3. Polymerization

Copolymers of styrene with p-(hexafluoro-2-hydroxyl isopropyl)styrene were prepared by the radical polymerization in solution. The monomer mixtures were disolved in benzene at a 1:3 volume ratio and then azobisisobutyronitrile (AIBN) which had been recrystalized from methanol solution was added as an initiator at the concentration of $1x10^{-2}$ mole/l. The benzene solution containing the monomers and the initiator was placed in a polymerization ampule, and underwent freezing and degassing procedures twice under liquid nitrogen. Then the sealed ampule was immersed in a water bath maintained at 60+0.1°C for polymerization. The reaction time, 4 to 9 hours, was adjusted so that the polymerization did not exceed 10% yield by weight. After polymerization, the content of the ampule was poured into a volume of n-hexane twenty times as large as that of the solution with vigorous stirring. The resulting polymers were redissolved in small aounts of methylene chloride and reprecipitated dropwise in stirred n-hexane. Compositions of the copolymers after drying at 110°C under vacuum were calculated from the elemental analysis of fluorine, obtained by Schwarzkopf Microanalytical Laboratory, New York, with a reported maximum error of +0.2%.

4. Preparation of Polymer Blends

Polymer blends were prepared by solution blending in the common solvents which had been freshly distilled and undergone proper treatments for removing trace amounts of moisture. The solutions were prepared by weighing appropriate amounts of the polymer components at ratios of 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, and 1/9 and then dissolving the mixtures in the common solvents at an initial concentration of 0.05g/ml (wt./solvent volume). Toluene was used as a common solvent for the blends of various styrene copolymers with PVME, PVAc, PMMA, PEMA, PBMA, PPO, PC, VTL(1) and VTL(II), methylene chloride for blends with PSAN and PDMS, chloroform for blends with PVMK and PPSE, and m-cresol for blends with KOD and TRO. Films were prepared by casting blend solutions onto a glass or Teflon plate at ambient temperature, except for m-cresol solutions which were cast onto a glass plate by placing it in a vacuum oven maintained at 110°C and applying low vacuum for rapid evaporation of m-cresol without thermal decomposition of the samples. Since some of the blend solutions composed of copolymers with high hydroxyl contents became opague upon standing, as a result of complex formation between the copolymer and the counterpolymer, freshly prepared solutions were vigorously stirred before pouring them onto a glass or Teflon plate to prevent premature hydrogen bonding complex precipitation. After the solvents were evaporated, the blends were dried under vacuum at 20-30°C above the Tg's of the polymer blends for 24-48 hours. The resulting films were used for thermal analysis and cloud point measurement. Solvent-free films having uniform thickness were prepared with special care for infrared spectroscopy studies.

5. Thermal Analysis

Differential Scanning Calorimeters, DuPont Model 990 or 1090, was used for glass transition temperature measurements. DSC samples were prepared by cutting solvent-cast films into proper sizes weighing about 10-11mg. An empty aluminum pan was used as a reference. Before DSC measurements were made, each sample was preheated in the cell at a heating rate of 10°C/min. to a suitably high temperature where the component polymer molecules were assumed to have enough mobility to reach phase equilibrium. The preheating temperatures were chosen so that they were above the Tg of the component polymer having the higher Tg. The preheating temperatures for various polymer blends are listed in the Table II. The preheated samples were rapidly quenched below their Tg's by liquid nitrogen so that the thermal history of each specimen could be reproduced. Thermograms were obtained at heating rate of 10°C/min. and a sensitivity of 0.5mcal/in under a nitrogen atmosphere.

The temperature at the half height of the heat capacity change was used as the Tg. The Tg measurement was repeated at least twice for each sample until the reproducibility of the Tg value was witin +1.0°C.

6. Cloud Point Measurement

A microscope equipped with a Mettler FP-52 hot stage was used for the cloud point measurement.[4] The film to be studied was cut into 5-10 mm squares and mounted on a glass microscope slide to ensure good heat transfer during measurement. Thin spacers, 0.01cm thick, were placed around the specimen and a cover glass was applied to protect the sample. The cover glass was carefully pressed down on the film which had been heated to above the glass transition temperature to obtain uniform thickness and to eliminate airspace between the glass and the film. After the film was slowly cooled to room temperature to relieve residual stress due to the above operation, the assembly was placed on the microscope hot stage. A thermometer and a thermocouple attached to the hot stage served as temperature indicators. Temperature was increased at a rate of 2°C/min. and the intensity of the transmitted light was monitored through a photocell mounted on the microscope eyepiece. The temperature at which the light intensity began to decrease abruptly was defined as the cloud point. Sometimes the change of the light intensity occurred very slowly as a result of the low mobility of both components at the temperature chosen. In such cases, the composition of the modified PS was varied so that phase separation took place at higher temperatures at which the polymer mobilities and the rates of separation were higher and the cloud points could be more easily identified.

The dependence of the cloud point of the film on heating rate was slight. The cloud point changed by less than 2°C when the heating rate increased from 1°C/min. to 10°C/min. On the other hand, the phase transition from opaque films to transparent ones upon lowering the temperature depended strongly on the cooling rate.

7. Infrared Spectroscopy

III. Results

1. Synthesis and Properties of Copolymers

1.1 Synthesis of p-(hexafluoro-2-hydroxyisopropyl) Styrene and its Copolymers with Styrene

The monomer, p-(hexafluoro-2-hydroxyisopropyl) styrene, was synthesized from p-chloroacetophenone in the two step reaction described above with a high yield. The yield of p-chlorostyrene from p-chloroacetophenone was 86% and the yield of the monomer from p-chlorostyrene was 85%. The monomer was stable and no appreciable polymeric residue was left after vacuum distillation (the actual internal reactor temperature was around 190°C with a distillation time of 2-3 hrs).

During the copolymerization reaction of the new monomer with styrene, conversion was limited to about 10% so that a relatively uniform composition of the copolymer could be obtained. In an experiment in which the conversion reached 22.7% after 15.6 hrs, the copolymer composition changed from 17.5% (mol) of the modified styrene to 15.9%; at 10% conversion the mole fraciton of modified styrene in the copolymer was 16.7%.

In the course of this study, twenty different copolymers were prepared, with compositions ranging from 0.1 to 87 mol % modified styrene. From the relationship between the monomer feed composition and the copolymer composition, as determined by fluorine element analysis, the reactivity ratios of the two monomers are calculated to be nealry identical, 0.59.

For the sake of convenience, the copolymers are represented in the text as modified polystyrene, MPS. The numeral which precedes the notation MPS indicates the mole percent of p-(hexafluoro-1-hydroxyisopropyl)styrene in the copolymer.

Copolymers containing less than 9.7 mole percent of the modified styrene have glass transition tmperatures nearly indistinguishable from that of

Table I. Compositions and physical properties of modified styrenes.

CODE	Compositions (mol % of OH group)	η (THF,30°C)	T_g,°C Onset	Midpoint
9.7MPS	9.7±0.3	0.180	105.5	109
17 MPS	17.7±0.5	0.177	110.5	113
40 MPS	40.9±1.0	0.238	114.3	117
71 MPS	71.4±1.5	0.201	120.2	124
87 MPS	86.8±1.5	0.354	122.0	126

polystyrene. Their intrinsic viscosities measured in tetrahydrofuran at 30°C are between 0.18 and 0.19. Copolymers containing higher percentage of the modified styrene have higher [η] and Tg values. as shown in Table 1.

1.2 Infrared Spectra of p-(hexafluoro-2-hydroxyisopropyl)styrene and Its Copolymers

The infrared spectra of p-(hexafluoro-2- hydroxyisopropyl)styrene and its copolymers show two strong absroption peaks at 3600 and 3520 cm^{-1} in the hydroxyl absorption region (Figs. 1,2). The former peak is ascribed to the stretching of the free hydroxyl groups and the latter, to the absorption of hydroxyl groups bonded with each other. The basis for the above assignment is the observation that the peak at 3600 cm^{-1} increases in intensity when the monomer is diluted with carbon tetrachloride while the peak at 3520 cm^{-1} decreases (Fig. 1). The same phenomenon occurs when phenol or cyclohexnol is diluted with CCl_4 (Fig.s 3,4) and the equilibrium between the free and bonded hydroxyl groups shifts in favor of the non-bonded species.

2. General Observations of Miscibility

2.1 Miscibility in the Solid State

The conventional criteria of film clarity and single Tg are used for determining the miscibility of

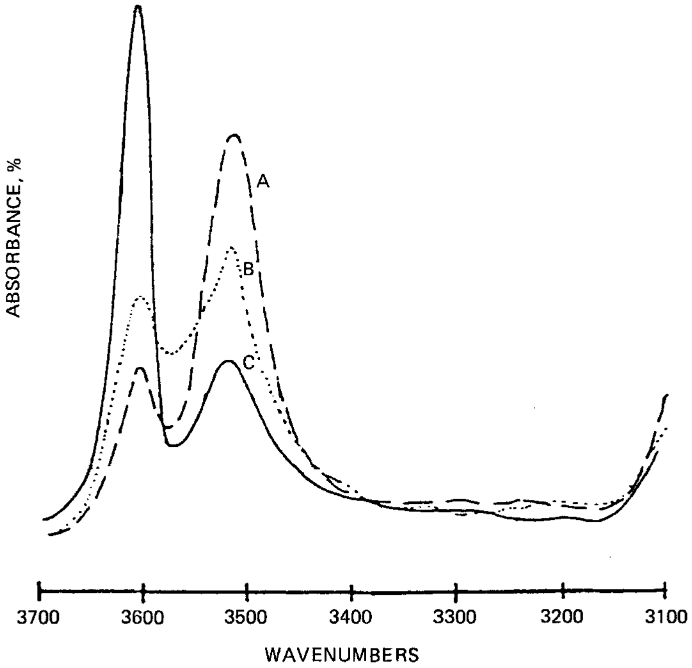


Fig.1 4-(2-hydroxyhexafluoroisopropyl) Styrene

(A) Liquid (B) 1.25M in CCl_4 (C) 0.5 in CCl_4

MPS with the counterpolymers, and the results of the miscibility studies are summarized in Table II. Except for poly(dimethyl siloxane) which is incompatible with MPS even at 87% modification and for poly(phenyl sulfone) which is miscible with 87 MPS only in a limited composition range (0.1, 0.8, 0.9 weight fraction MPS), all the other counterpolymers form miscible pairs with MPS. In the case of PMMA or PSAN as the counterpolymer, the proximity of the Tg of the counterpolymer to that of MPS renders the criterion of single Tg inapplicable. However, glass transition temperature and cloud point data to be described later support the contention that the blends can be classified as compatible systems.

2.2 Miscibility in Ternary Solutions Containing Two Polymers and A Common Solvent

In the course of preparing ternary solutions for the casting of films, several interesting phenomena have been noted and are reported here.

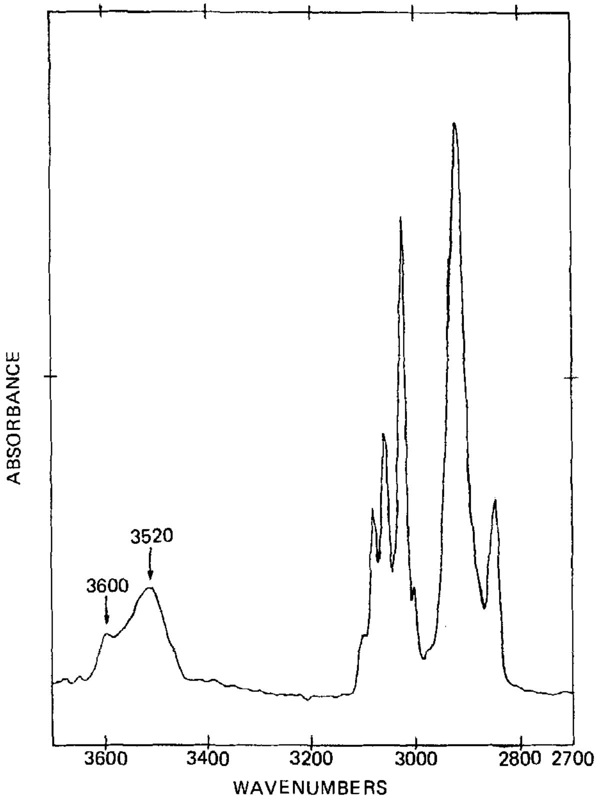


Fig.2 FTIR spectrum of 9.7MPS.

2.2.1 Poly(vinylmethylether)

The miscibility of polystyrene with poly(vinylmethylether) has been the subject of extensive investigation in the past.[3] It has been found that blend films cast from toluene solutions are transparent and exhibit a single Tg for each composition while films cast from chlorinated solvents as trichloroethylene or methylene chloride are heterogeneous. When MPS was used instead of PS, transparent films were obtained from both toluene and methylene chloride. However, when the degree of substitution in MPS reached 9.7%, the toluene solutions of the blends (5g/100ml) were optically transparent only for MPS weight fractions less than 0.4 or greater than 0.9 but showed turbidity in the

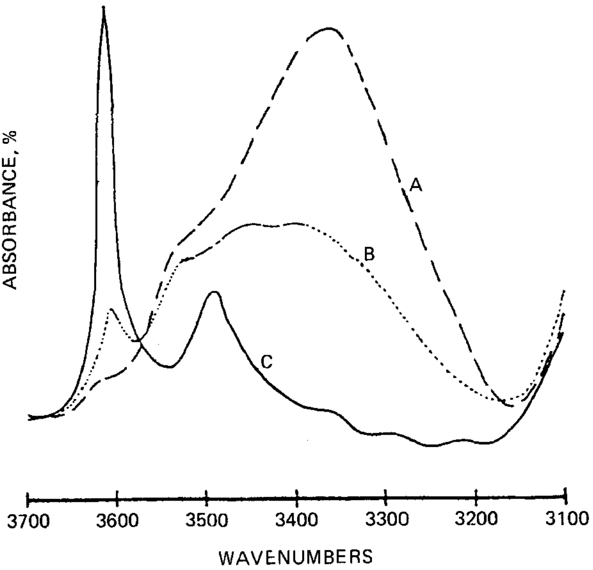


Fig.3 Phenol in CCl_4

(A) Saturated (B) 0.3M (C) 0.05M

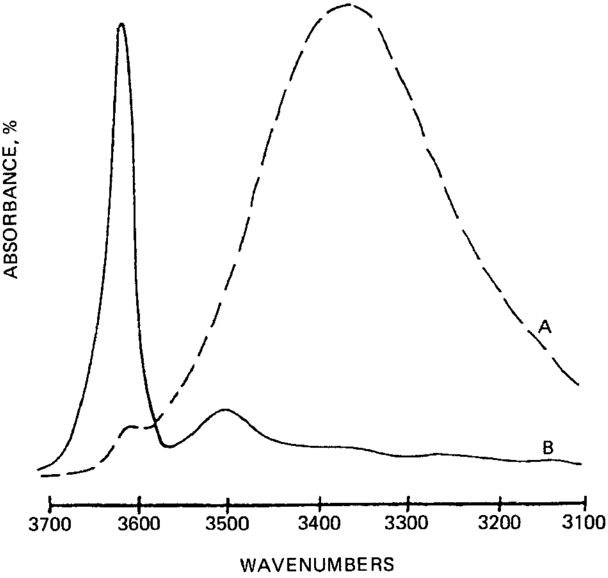


Fig.4 Cyclohexanol in CCl_4

(A) 9.4M (B) 9.4×10^{-2}M

Table II Compatibility of Various Polymers with Modified Polystyrenes

Counterpolymer		MPS	Casting	Preheating	Compatibility
Type	T_g,°C	mol % Modification	Solvent	Temperature,°C	
PVME	-31.7	0.1	toluene	150	C
		0.2	toluene	160	C
		0.4	toluene	180	C
		9.7	toluene	200	C
PVAc	37.0	9.7	toluene	200	C
PVMK	82.3	9.7	chloroform	170	C
PMMA	105.0	3.9	toluene	180	C
		4.4	toluene	180	C
		9.7	toluene	180	C
PEMA	63.7	1.1	toluene	150	C
		1.2	toluene	150	C
		1.3	toluene	150	C
		1.5	toluene	150	C
		9.7	toluene	150	C
PBMA	24.5	1.0	toluene	150	PC
		1.8	toluene	150	C
		2.4	toluene	150	C
		2.9	toluene	150	C
		9.7	toluene	150	C
PSAN (30%AN)	99.7	9.7	methylene chloride	150	C
PPO	217	9.7	toluene	220	C
PC	147	17	toluene	200	I
		40	toluene	120	C
		40	toluene	200	phase separation
		71	toluene	200	C
VTL(1)	8.5	9.7	toluene	150	C
		17	toluene	150	C
VTL(2)	-11.0	9.7	toluene	150	PC
		17	toluene	150	C
KOD	75.2	9.7	m-cresol	180	I
		17	m-cresol	180	I
		40	m-cresol	180	C
TRO	147.3	17	m-cresol	200	I
		40	m-cresol	200	C
PPSF	190	71	chloroform	220	I
		87	chloroform	220	PC
PDMS	-123	87	methylene chloride	150	I

C -- compatible over the entire composition range
PC-- compatible for some but not all compositions
I -- incompatible

middle composition range. For a constant blend composition the toluene solutions of PVME blends showed increased turbidity with higher degree of modificaiton of PS. Films cast from these solutions nevertheless retained high degrees of clarity and exhibited single Tg for each composition.

2.2.2 Poly(vinylacetate)

Toluene solutions containing both poly(vinylacetate) and polystyrene separated into two dilute phases and cast films were opaque and showed two glass transition temperatures. Solutions containing PVAc and 9.7 MPS also separated into two phases, a dilute phase and a compact, concentrated phase. The dilute phase contained predominantly the solvent and the two polymers seemed to reside together in the concentrated phase. But films cast from these solutions were transparent and showed single Tg for each composition.

The concentrated phase dissolved in the dilute phase to form a homogeneous solution when heated to near the boiling point of toluene.

2.2.3 Poly(ethylmethacrylate) and Poly (butylmethacrylate)

The miscibility of PEMA- MPS blends in ternary systems was examined in four different solvents, toluene, methylene chloride, chloroform and acetone. A blend composition of 50/50 by weight and a solution concentration of 0.5g/100ml were used throughout the experiments. The results are summarized in Table III.

Poly(butylmethacrylate) and 9.7 MPS dissolved together in toluene formed homogeneous solutions but PBMA-17MPS blends in the same solvent separated into two phases when the weight fraction of PBMA was between 0.3 and 0.6. The concentrated phase again dissolved in the dilute phase upon heating. The blend with 40MPS, however, showed the presence of a concentrated phase which was not completely soluble in the dilute solution at 70°C.

2.2.4 Poly(2,6 dimethyl-1,4 Phenylene Oxide)

Similar phenomenon was observed for blends of poly(2,6 dimethyl-1,4 phenylene oxide). Since PPO was

Table III The Miscibility of Poly(ethylmethacrylate) and Modified Polystyrene in Various Solvents and the Clarity of the Cast Films.

	toluene		methylene chloride		chloroform		acetone	
	solution	film	solution	film	solution	film	solution	film
9.7MPS	homogeneous	clear						
12MPS	two phases	clear	homogeneous	opaque	homogeneous	clear	homogeneous	opaque
30MPS	two phases	clear	two phases	clear	two phases	clear	homogeneous	clear

blend composition: 50/50 by weight
solution concentration: 0.5g/100ml

miscible with PS, the formation of hydrogen bonding between PPO did not change miscibility as determined by the single Tg criterion. But the solubilities of PPO blends with various MPS's in tolune showed changes from homogeneous solutions to two-phased solutions containing a concentrated phase as the density of interacting groups increased.

3. Spectroscopic Evidence of Specific Interaction

The interactions between the hydroxyl group of the MPS and the appropriate proton accepting groups of the counterpolymers can be detected readily by infrared spectroscopy. In Fig. 5, the FTIR spectra of blends (50/50 by weight) of 9.7MPS with PMMA, PEMA and PBMA are displayed. In each spectrum the two absorption peaks at 3600 and 3520 cm^{-1}, characteristic of the hydroxyl group of MPS, have disappeared completely and a new peak emerges at 3400 cm^{-1}. Furthermore, the intensity of the new peak is approximately proportional to the number of the hydroxyl groups in MPS (Fig. 6). In blends of 9.7MPS with PVAc or PVME, again no trace of the original hydroxyl group absorptions can be discerned and the new peaks appear at 3375 and 3215 cm^{-1}, respectively. Taken together, these results indicate that the hydroxyl groups of MPS in these blends are quantitively engaged in hydrogen bonding with the carbonyl groups or the ether groups of the

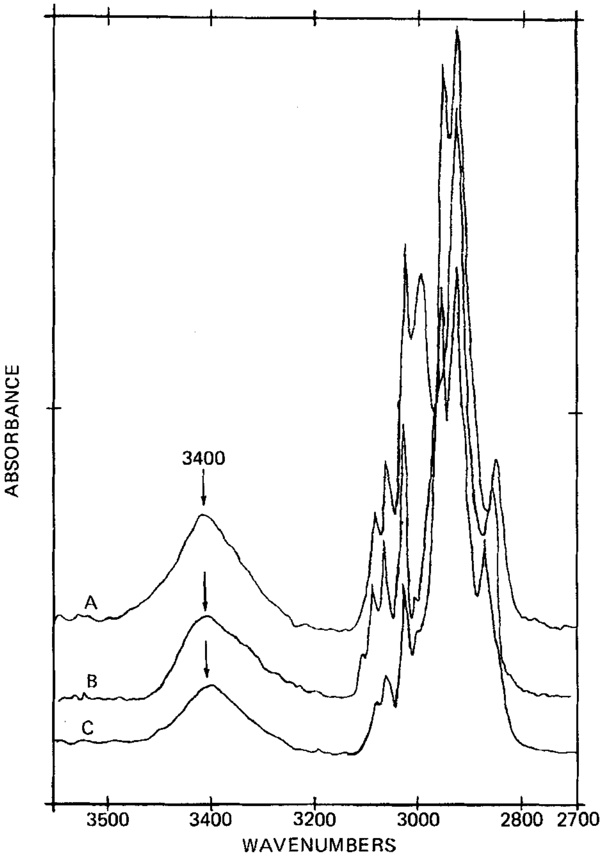


Fig.5 FTIR spectrum of 9.7MPS and poly(methacrylates) at the blend composition of 5/5 (wt/wt); A) PMMA, B) PEMA, C) PBMA.

counterpolymers. Large shifts in the wavelength of absorption are also observed with other counterpolymers and the results are listed in Table IV.

The specific interaction between MPS and the counterpolymers is also revealed in a change in the infrared spectra of the proton accepting groups. The carbonyl stretching band of PMMA is split to form a doublet with some of the absorption remaining at 1727 cm^{-1} and the new peak occurring at a lower frequency of 1715 cm^{-1} (Fig. 7). In the blend with polycarbonate, the carbonyl absorption peak is shifted

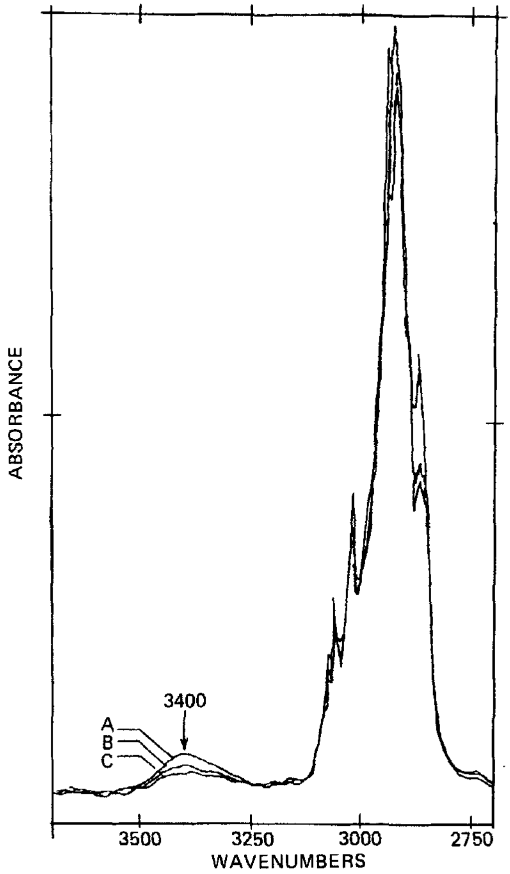


Fig.6 FTIR spectrum of various MPS's and PBMA systems at the blend composition of 5/5 (wt/wt); C) 1.8MPS, B) 2.4MPS, A) 2.9MPS.

to 1762 cm^{-1} with a shoulder remaining at the orginal frequency of 1779 cm^{-1} (Fig. 8). These observations are similar to the findings reported for blends of novolac resins with polymethacrylates and polycarbonate.[7] In the case of PSAN, the nitrile absorption peak shifts from 2233 to 2242 cm^{-1}. The shift toward a higher frequency has been reported in mixtures of phenol and nitrile containing compounds such as acrylonitrile, phenylcyanide and diphenylacetonitrile.[8,9]

Table IV Infrared Absorption of OH in polymer blends at the blend composition of 5/5 (wt/wt)

Counter Polymer	MPS	ν OH(cm^{-1})	$\Delta\nu$ ^{a}(cm^{-1})	$\Delta\nu^{b}$ (cm^{-1})
	9.7MPS	3600, 3520		
PVME	9.7MPS	3214	386	306
PSAN	9.7MPS	3335	265	185
PVK	9.7MPS	3340	260	180
PVAc	9.7MPS	3375	225	145
PMMA	9.7MPS	3400	200	120
PEMA	9.7MPS			
PBMA	9.7MPS			
VTL(I)	9.7MPS	3400	200	120
VTL(II)				
PPSF	40 MPS	3420	180	100
PCAB	40 MPS	3440	160	80
PPO	17 MPS	3450	150	70

a: Shift from the free hydroxyl group absorption peak, 3600 cm^{-1}.

b: Shift from the bonded hydroxyl group absorption peak of MPS, 3520 cm^{-1}.

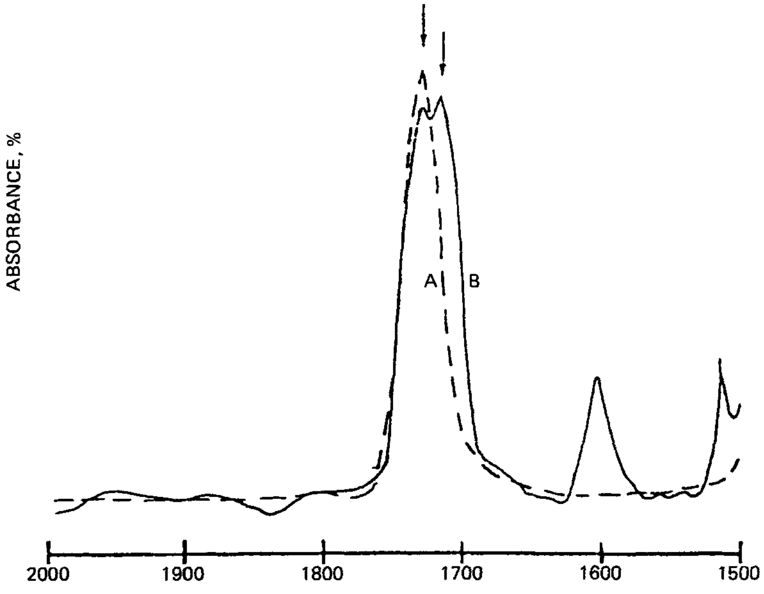


Fig.7 Absorption of the Carbonyl group in PMMA
(A) PMMA (B) PMMA/9.7 MPS(1/9,W/W)

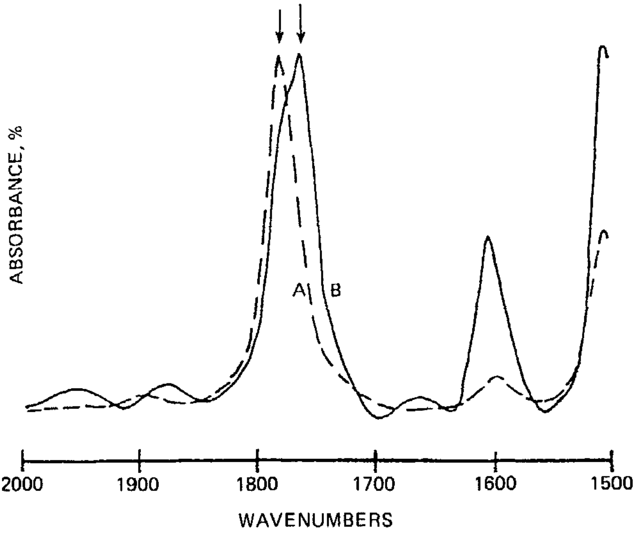


Fig.8 Absorption of $-\overset{\overset{\displaystyle O}{\|}}{C}-$ in Polycarbonate

(A) PCAB (B) PCAB/40MPS (1/4, W/W)

4. Phase Separation at High Temperatures

The cloud point temperature of blends of MPS with PVME, PMMA, PEMA and PBMA are displayed in Figures 9 to 12. As the degree of PS modification increases, the temperature of phase separation also increases. The increase in the cloud point temperature is very sensitive to small changes in the extent of hydrogen bonding. For example, the cloud point temperatures increase by about 50°C when 0.4MPS instead of PS is mixed with PVME. Similar increases in the cloud temperatures are found for blends of MPS with the three methacrylate polymers.

5. Glass Transition Temperatures

A large body of T_g data has been collected in this study but a few representative cases suffice to demonstrate the effect of hydrogen bonding on the glass transition temperatures of blends. In the first two examples, the T_g results of blends of MPS with PVME and PPO, both of which are miscible with PS

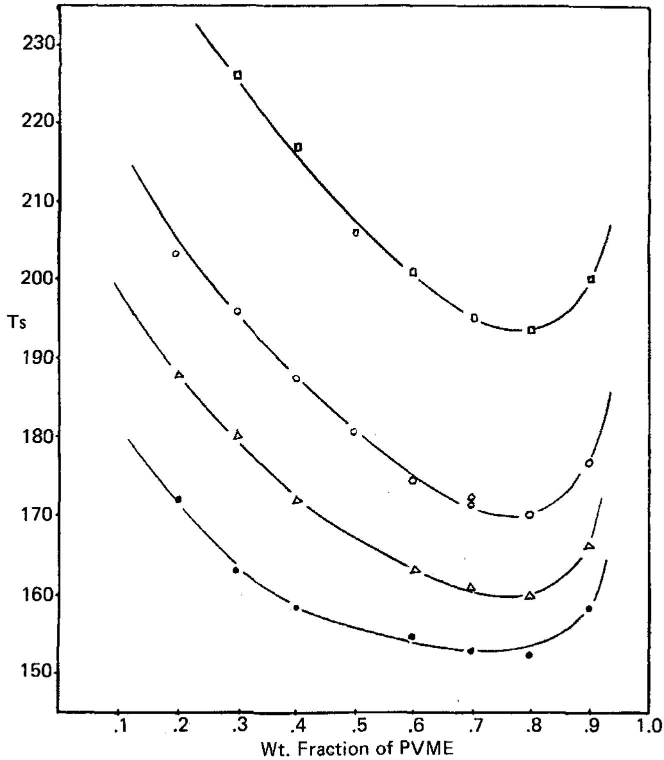


Fig.9 The LCST phenomena of the variously modified PS's and PVME systems at the heating rate of 2°C/min; a) □ ; 0.4MPS, b) ○ ; 0.2MPS, c) △ ; 0.1MPS, d) ● ; pure PS.

without modification, are presented. The MPS specimens chosen for this portion of the study have glass transition temperatures close to that of PS so that the T_g values of the MPS and PS blends would have been comparable from a consideration of the pure-component property, if the hydrogen bonding effect had been absent. Any disparity between the glass temperatures of the MPS blends versus the corresponding PS blends then provides a direct assessment of the contribution of the hydrogen bonding. In four additional examples, the counterpolymers PBMA, PMMA, PVMK and PSAN are immiscible with PS and the unusual T_g values of their blends with MPS, effected by hydrogen bonding, are discussed.

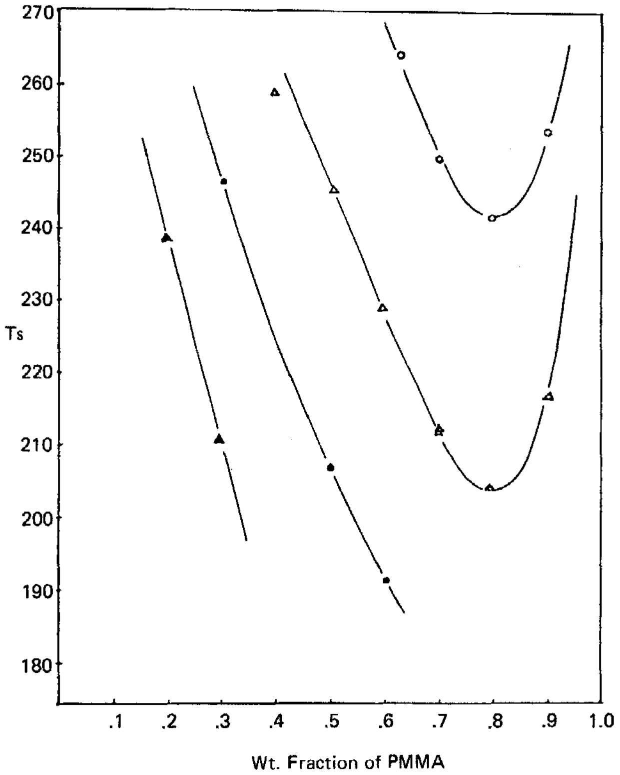


Fig.10 The LCST phenomena of the variously modified PS's and PMMA systems at the heating rate of 2 C/min; a) ; 4.4MPS, b) ; 3.9MPS, c) ; 3.4MPS, d) ; 2.9MPS.

5.1 Blends of MPS with PVME and PPO

The glass transition temperatures of PVME blends with PS, 1,8MPS, 3.9MPS and 9.7MPS are plotted as a function of blend composition in Fig. 13 and also as a function of the mole percent of hydroxyl groups in MPS at constant blend compositions (Fig. 14). When the weight fraction of MPS in the blend is less than 0.3, there are very little differences between the Tg's of MPS blend and a PS blend. The difference becomes noticeable after the weight fraction of MPS exceeds 0.4 and reaches a maximum value of 18°C at a weight fraction of about 0.85 for 9.7MPS (Fig. 15). Simarlarly, the maximum ΔTg values are 11.5°C for 3.9MPS and 6.3°C for 1.8MPS blends respectively, both

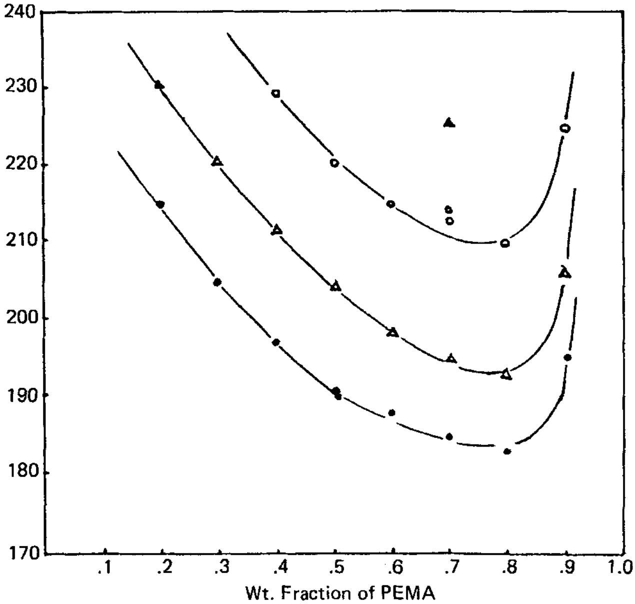


Fig.11 The LCST phenomena of the variously modified PS's and PEMA systems at the heating rate of 2°C/min; a) ▲; 1.5MPS, b) ○ ;1.3MPS, c) △; 1.2MPS, d) ● ; 1.1MPS. T_s means the temperature.

at MPS weight fraction of about 0.9. The magnitude at the ΔTg far exceeds what can be accounted for by the slightly higher Tg values of MPS compared to PS. For the PPO blends (Fig. 16), the maximum value of ΔTg is about 13°C for 16.7MPS blends at a weight fraction of about 0.7.

5.2 Blends of MPS with PBMA

The results for PBMA blends are shown in Fig. 17. Since PS is incompatible with PBMA, a direct comparison of the Tg data for MPS versus PS blends is not possible. Instead, the Tg data are replotted in Fig. 18 against the mole percent of hydroxyl groups in MPS at constant blend compositions. As in the case of PVME mixtures, there is little change in the magnitude of Tg when MPS is present in small amounts in the blends. The dependence of Tg on the degree of modification of PS becomes increasingly significant when the blends contain more MPS.

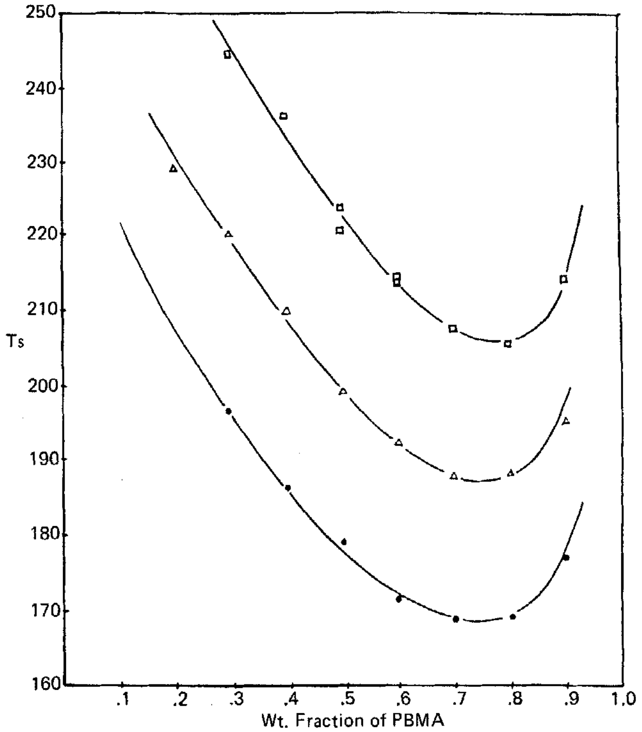


Fig.12 The LCST phenomena of the variously modified PS's and PBMA systems at the heating rate of 2°C/min; a) □ ; 2.9MPS, b) △ ; 2.4 MPS, c) ● ; 1.8MPS.

The above data are extrapolated to zero mole percent hydroxyl group to obtain a Tg value for a fictive PS-PBMA blend if the two polymers were miscible. The difference between the Tg of a MPS blend and a corresponding fictive PS blend is shown in Fig. 19. Again the maximum ΔTg occurs at MPS weight fraction of about 0.8.

In examining the data in Fig. 17, we have noted that the glass transition temperatures of PBMA-16.7MPS blends exceed the weight-average values of the component Tg's when the weight fractions of MPS in the blends exceed 0.5. The positive deviations from the weight-average values confirm the findings reported in reference (1).

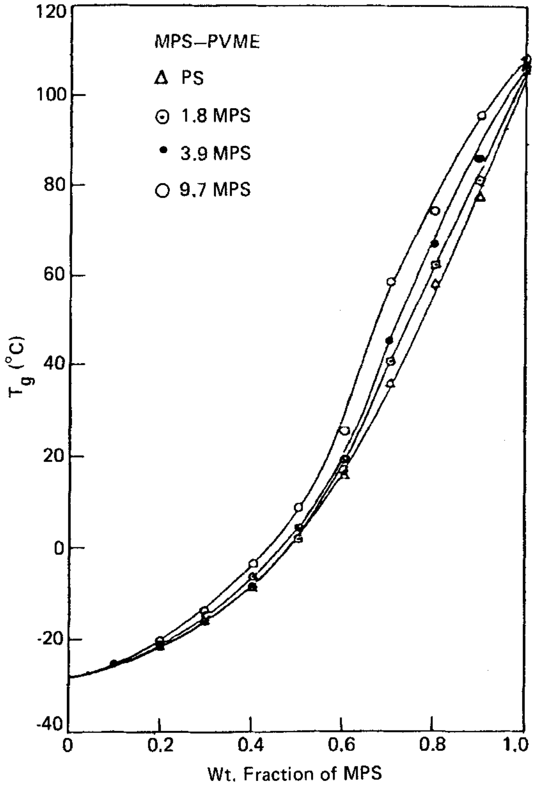


Fig. 13

5.3 Blends of MPS with PMMA, PVMK and PSAN

The blends of 9.7PPS with PMMA, PVMK or PSAN also show positive deviations of Tg from the weight-average value of the component Tg when PMS is present as the major ingredient in the blend (Fig. 20). Although the deviation is small, the magnitude is beyond the limit of experimental uncertainty. When the onset (extrapolated) of heat capacity increase is used as Tg instead of the midpoint of the C change, the same deviation is observed.

IV. DISCUSSION

1. Miscibility

1.1 Dual Phases in Ternary Solutions

It has been known for many years that films of PS-PVME blends cast from aromatic hydrocarbons such as

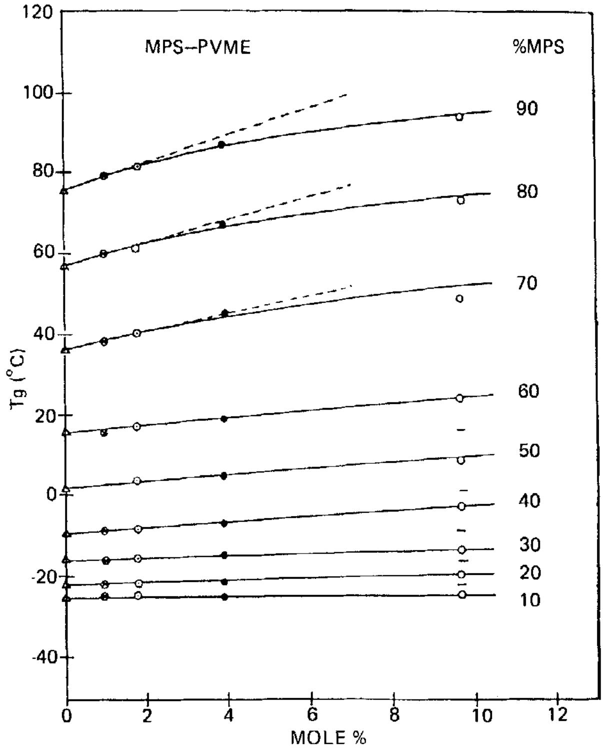


Fig. 14

toluene are transparent but those cast from chlorinated solvents such as trichloroethylene or methylene chloride are opaque and heterogeneous. The "solvent effect"(3,10) on the homogeneity of cast films has been explained by Robard, Patterson and Delmas(11) in terms of the difference in the two polymer-solvent interaction parameters $/\chi_{12} - \chi_{13}/$, or$/\Delta\chi/$, the difference being small in benzene but large in chloroform. According to the authors, a homogeneous system is attained only with a suitably small $/\Delta\chi/$ in addition to the necessary requirement of a very small polymer-polymer interaction parameter χ_{23}.

When 0.4 MPS was used in place of PS in our study, transparent films were obtained from both toluene and methylene chloride. It appears that the more negative polymer-polymer interaction parameter,

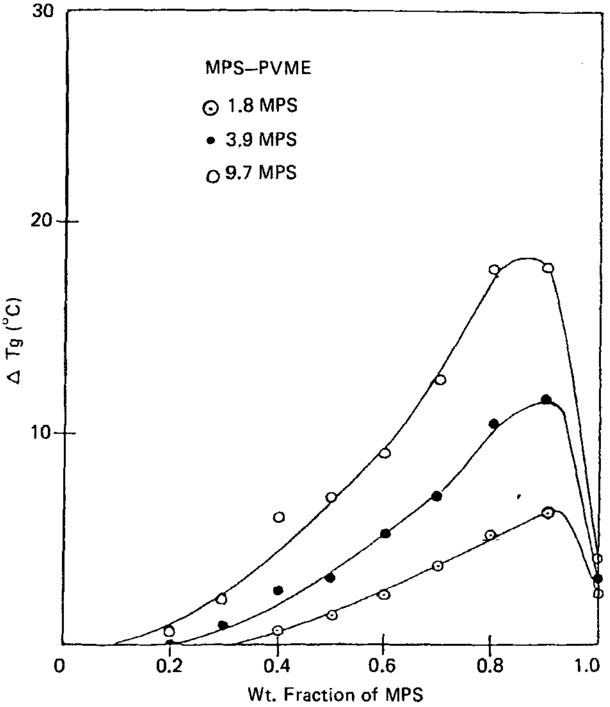


Fig. 15

χ_{23}, for MPS-PVME outweights the unfavorable /Δχ/ effect with methylene chloride as solvent, and the ternary solution remains as a single phase in the entire range of compositions.

However, the relationship between the multiple phases in a ternary solution and the homogeneity of the cast film is more complex than we have first realized. Toluene solutions of PVME blends with 3.9MPS were homogeneous throughout the entire range of compositions. But blend solutions containing 9.7MPS in which the weight fractions of MPS were between 0.4 and 0.9 showed turbidity. Yet films cast from these solutions were "compatible". Furthermore, the turbidity of the toluene solution increased with higher degrees of modification of PS. Therefore, we are inclined to think that the concentrated phase, most likely composed of an insoluble complex between MPS and PVME, is formed as a result the increased

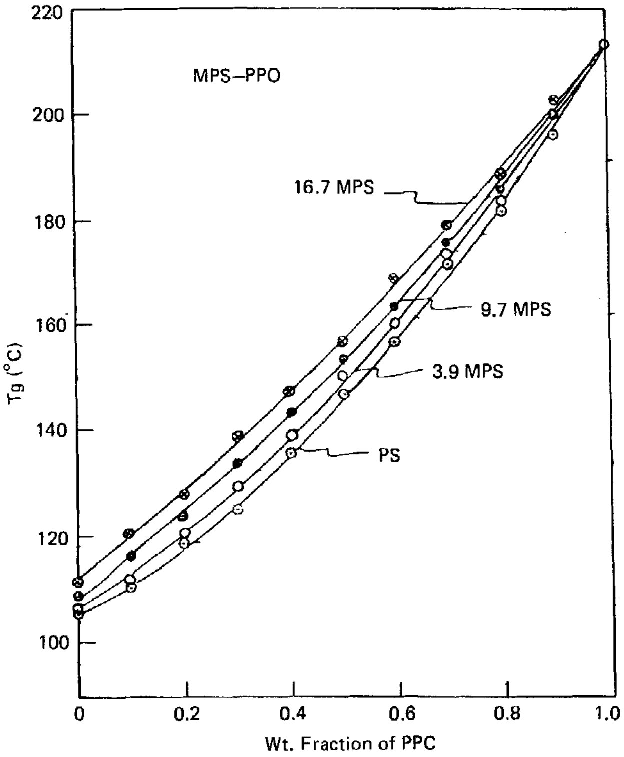


Fig. 16

specific reaction. Almost all the polymers reside in the concentrated phase and consequently the cast film shows only a single Tg. We believe that the same explanation applied to PPO and PVAc blends in toluene.

1.2 The Nature of the Solvent

The proton donor-acceptor interaction between polymers is affected by the polarity of the solvent in a ternary system. The influence of the solvent on the miscibility of PEMA with MPS is seen clearly from the results shown in Table III. In a non-polar solvent, toluene, the solution was single-phased when 9.7MPS was used but separated into two phases when the degree of modification of PS increased to 12 or 30%. With the use of polar solvents, methylene chloride, chloroform or acetone, homogeneous solutions were

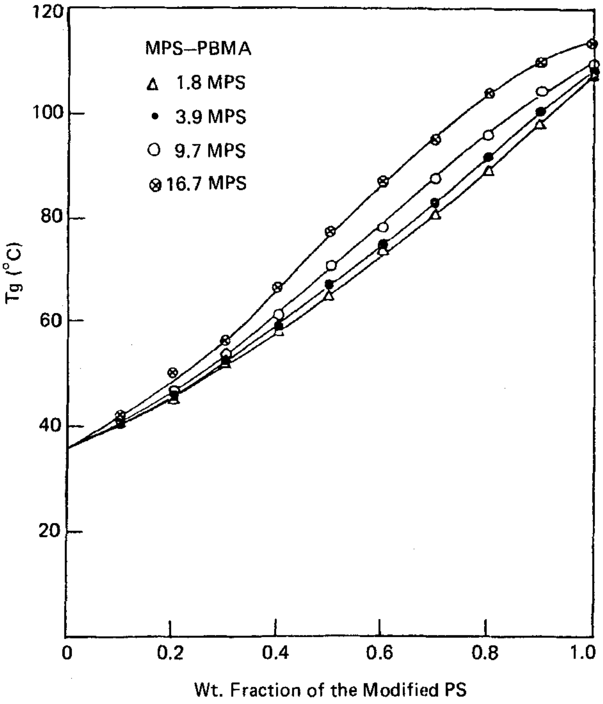


Fig. 17

obtained with 12MPS-PEMA. But as the density of the interacting groups increases further, only acetone forms a homogeneous solution with 30PMS-PEMA. We note that acetone is a competitor with PEMA as a proton acceptor for the hydroxyl group. Thus extensive hydrogen bonding between PMS and PEMA is an acetone solution is unlikely to occur and the solution remains homogeneous. In methylene chloride and chloroform which are weak proton donating as well as weak proton accepting solvents, hydrogen bonding between 30MPS and PEMA apparently takes place to an extent sufficient to cause phase separation.

Based on the discussion in the previous section, a one-to-one relationship between the homogeneity of a ternary solution and that of a binary film cast from the solution can not be assured. The results listed in Table III provide ample demonstration of this lack of correspondence. Films cast from homogeneous

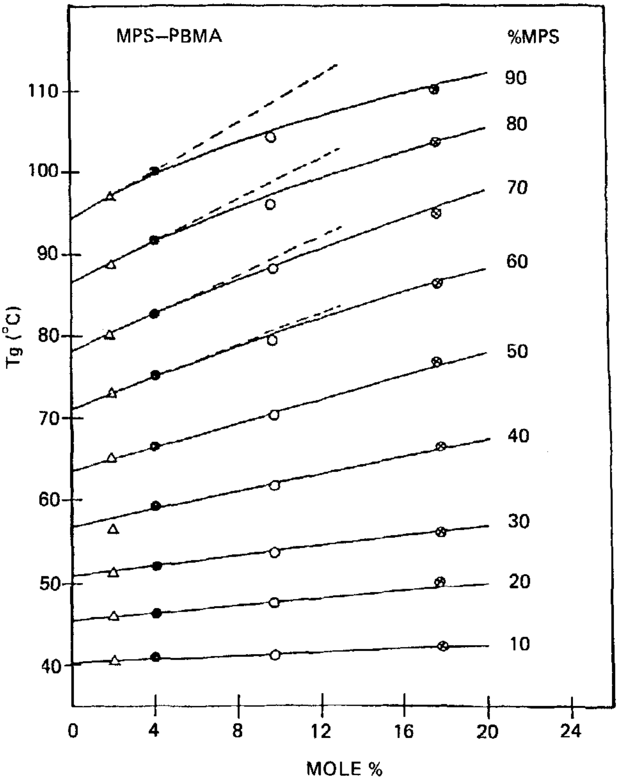


Fig. 18

solutions can be opaque, most likely due to the /Δχ/ effect, and films cast from a two-phase solution can be clear because the strong interaction between the two polymers results in a concentrated phase in which the polymers form a hydrogen bonded complex. A definitive explanation requires a careful measurement of the phase diagrams of ternary systems which will be undertaken in the future. But our experimental results are fully consistent with the findings of Djadoun et. al.(12) on ternary systems containing an acidic copolymer, a basic copolymer and a solvent. The authors concluded that (1) increasing the densities of strongly interacting groups tended to convert ternary solutions containing two dilute phases to those containing a dilute phase and a concentrated phase via a one-phase system, (2) the nature of the

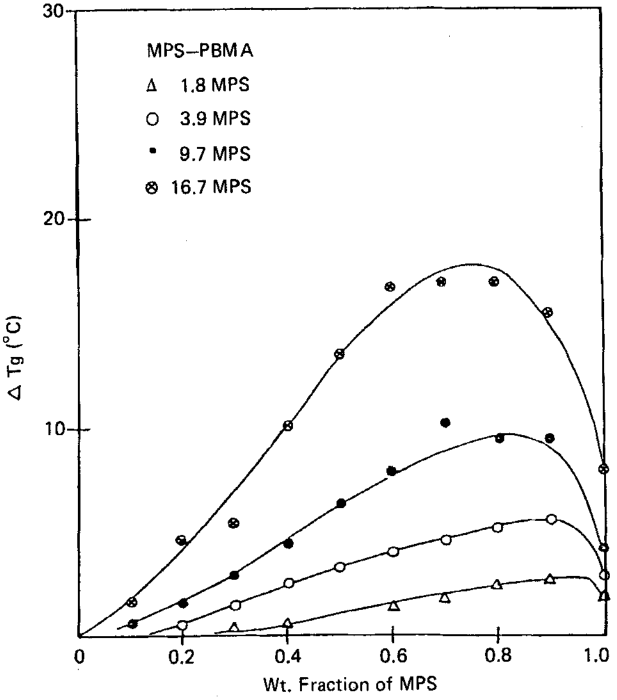


Fig. 19

solvent influenced the concentration of acid and base groups required to produce a one-phase system, and (3) the presence of a concentrated phase in a ternary solution may be taken as strongly presumptive evidence for polymer miscibility after removal of the solvent.

1.3 Other Polymers

Polycarbonate, Kodar polyester and the branched polyamide require high concentrations of hexafluoro-2-hydroxyisopropyl groups in MPS to achieve miscibility (Table II). Apparently, the strong intermolecular forces ε_{11} can be overcome only when there is a multitude of proton donating groups. Blends of poly(phenylsulfone) with 87MPS show single transitions only for MPS weight fractions of 0.1, 0.8 and 0.9 probably because the interaction with the sulfone group is relatively weak (see the frequency shift) and the miscibility gap extends to low temperatures (below room temperature) in the intermediate composition range.

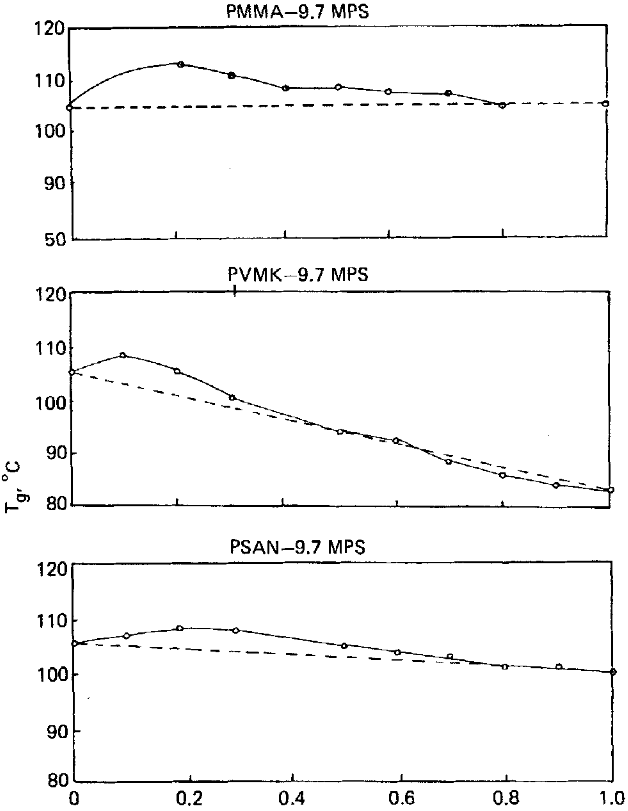


Fig. 20 Weight fraction of the second component

2. Infrared Spectroscopy

The shifts in the frequency of hydroxyl group absorption of MPS when mixed with counterpolymers (Table IV) are conclusive evidence of specific interaction between polymers. The accompanying changes in the carbonyl group absorption of PSAN lend further support to our conclusion. The magnitude of the shift in the frequency of the hydroxyl absorption peak, 70 to 386 cm^{-1}, is comparable to those found in mixtures of phenol with proton acceptors, e.g., 160 cm^{-1} with acetronitrile,(13) 160–180 cm^{-1} with carbonyl groups(14) and 271 cm^{-1} with diethyl ether.(14)

3. Cloud Point Temperatures

The increase in the cloud point temperature with increasing polymer-polymer interaction (Figs. 9-12) is in complete accord with the predictions of McMaster.[6] In a separate study, hydrogen bonds between poly(ethylene oxide) and a similar MPS, which was synthesized via a different route of direct reaction of PS with hexafluoroacetone, were found to dissociate at 175°C but re-associate upon cooling to 25°C. In the examples cited in this study, dissociation of hydrogen bonds is expected to have taken place at elevated temperatures at which phase separation occurs. The correspondence, if any, between the temperature of complete dissociation of hydrogen bonds and the cloud point temperature will be the subject of another study.

4. Glass Transition Temperatures

In PVME blends containing only minor amounts of MPS, the glass transition temperatures of the blends are nearly the same as those of the corresponding PS blends. From the data displayed in Figs. 13-15, a hydrogen-bond density of $1\text{x}10^{-4}$mole/g produces a ΔTg of $\sim$1.1°C. At hydrogen-bond concentration (ρ) less than $1\text{x}10^{-4}$mole/g polymer the Tg of MPS blend is experimentally indistinguishable from that of the PS blend because the uncertainty in the Tg measurement is ±1.0°C. When compared with other hydrogen bonded polymers, e.g., poly(ethylene-co-acrylic acid)(15) in which the dimerization of carboxyl groups raises the Tg of the amorphous region by about 3.5°C per $1\text{x}10^{-4}$ moles of acid dimer per gram, ΔTg is smaller for the blends. The slope of the ΔTg vs ρ(mole % MPS) curve increases with increasing $\Delta$for a given blend series. This is to be contrasted with the linear relationship commonly observed between ΔTg and ρ, for small ρ, for randomly distributed covalent or hydrogen-bonded crosslinks. The reason for the differences can be understood, on a qualitative basis, from a consideration of the spatial distribution of the hydrogen bonds in a mixture in which MPS is a minor constituent and the hydroxyl content of MPS is small. The situation is akin to a very dilute polymer solution in which there are high local concentration of segments, in this case MPS, separated by large regions of pure solvent, in this case PVME. The distribution of hydrogen bonds in the mixture is inhomogeneous. Some of the PVME molecules may have only a few hydrogen-bonds attached to parts of the molecules. The restriction imposed by these non-uniformly distributed hydrogen bonds on segmental motion giving rise to glass transition is less effective than the randomly distributed crosslinks and consequently ΔTg is small in comparison. As the weight fraction of MPS in a blend increases, the segment distribution in a concentration solution becomes less inhomogeneous. The cooperative influence of the more uniformly distributed hydrogen bonds on segmental motion is now more effective in raising the Tg of the mixture. Therefore the value of ΔTg increases at a faster rate that the increase in ρ.

When the experimental data are compared among the three blend series, we notice that the weight fraction of MPS in the blend needed to produce a given ΔTg decreases as the hydroxyl content of MPS increases but the corresponding hydrogen bond density actually increases. That is, more hydrogen bonds are needed to produce a given .Tg in a 9.7 MPS blend than in a 1.8 MPS blend. Again, the reason can be traced to the inhomogeneous spatial distribution of hydrogen bonds. At the same level of hydrogen bond density, a 1.8 MPS blend contains a larger number of MPS chains than a 9.7 MPS blend and has a more uniform spatial distribution of hydrogen bonds which, according to the argument presented above, is more effective in raising the Tg of the system.

The Tg data for PPO and PBMA blends follow the same general trend as the PVME blends and need no further elaboration.

Lastly, the positive deviations of the glass transition temperatures of PBMA-16.7MPS blend and of 9.7MPS blend with PMMA, PVMK and PSAN from the weight-average values of the component Tg's illustrate convincingly the effect of hydrogen bonding on restricting segmental motion. Similar positive deviations have been reported for other polymer mixtures in which storing interactions prevail.(1,7)

V. Conclusions

The body of experimental data described above substantiates the notion of miscibility enhancement through specific interaction. Hydrogen bond formation has the advantage of being readily detectable by conventional experimental methods. But other types of specific interaction should also be explored.

Aside from phase diagrams of ternary solutions and the temperature dependence of hydrogen bond formation which need further elucidation, there is an important question left unanswered in this study. While we are encouraged by the finding that a mere 1.8% of the hydroxyl moiety attached to PS suffices to "compatibilize" the hiterto immiscible pair of PS and PBMA, we are nevertheless faced with a conceptual difficulty. In the above mixtures, hydrogen bonds are sparsely distributed, and there are long sequences of PS segments, approximately 50 on the average between hydrogen bonds (Fig. 21). These long sequences of PS segments are inherently immiscible with PBMA segments and the question may very well be asked as to the scele of homogeneity of mixing on a segmental scale. In several earlier studies of polymer mixtures, the maximum sizes of the heterogeneities of the mixture have been estimated from nuclear spin diffusion lengths.(5,16) We intend to carry out nuclear magnetic resonance measurements in the hope of acquiring a better understanding of the scale of mixing homogeneity.

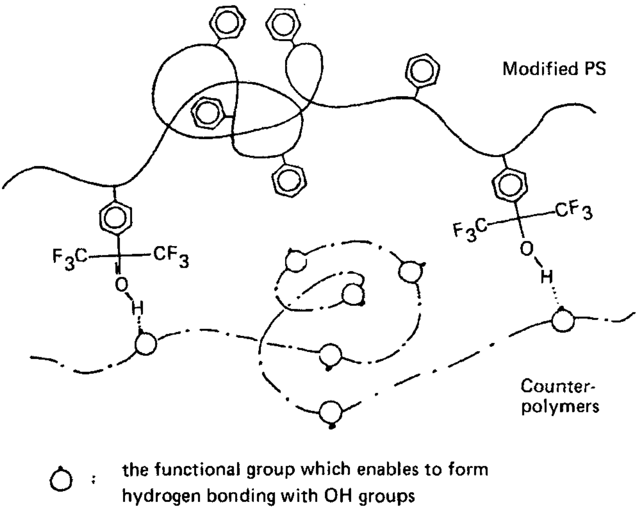


Fig. 21

ACKNOWLEDGEMENT - We acknowledge the partial support of the Department of Energy and the Plastics Inst. of America.

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