Heterogeneous Polymer Systems.
II. Characterization of Graft Copolymers of Styrene on Polyethyl Acrylate

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Introduction

Our initial investigation of heterogeneous polymers[1] involved solution compatibility and modulus-temperature studies on bicomponent polymer mixtures prepared by a variety of techniques. The present investigation extends these studies to the examination of true graft copolymers.

Polyethyl acrylate/polystyrene combinations were selected for study because: (a) the relative positions of the dilatometric glass temperature −24 and 100°C. provide a system composed of (at room temperature) one glassy and one rubbery polymer; (b) the separation of this polymer pair by solvent extraction procedure is feasible.

Experimental

Preparation of Polymer

The graft copolymer (GCP) was prepared by emulsion grafting.[2,3] Backbone polymer was prepared with Rohm & Haas Co. monomer at 65°C. with 0.088% ammonium persulfate and 1% sodium lauryl sulfate. The $\overline{M}_v$ of ungrafted polyethyl acrylate (PEA) later extracted from the sample was 3.1 × 10⁶. Freshly distilled styrene was mixed for 2 hr. under N₂ with the PEA emulsion; after 0.066% more catalyst was added, the mixture was heated to 80°C. for the polymerization. This sample will be designated as mixture B. A second polymerization was done using the same backbone polymer. The styrene monomer was stirred with the PEA emulsion overnight at 25°C. under nitrogen; during this mixing period about 30% of the monomer polymerized. The reaction was completed the following day by heating at 80°C. with no additional catalyst. This product will be called mixture A.

Ionic emulsifiers and other ionic impurities were removed by stirring the emulsion, at about 15% solids, with mixed bed ion-exchange resin (Amberlite MB-1) for 1 hr. Coagulation of the filtered emulsion was effected by freezing, repeatedly if necessary. The coagulum was dried, dissolved in

benzene, freeze-dried, and dried to constant weight under vacuum at 30–40°C.

Separation of Graft Copolymers

Each mixture was resolved into graft copolymer and the two homopolymers by extraction using two selective solvents, each a solvent for one of the homopolymers but not for the graft copolymer or the other homopolymer. Cyclohexane was used for extracting polystyrene (theta temperature = 35°C.) and diethyl ether or acetonitrile for polyethyl acrylate.

Ungrafted polystyrene was first extracted from the mixture with cyclohexane at 45–47°C., by placing sample and extractant in a flask. After an extensive period of agitation, polymer was allowed to settle and supernatant solution was decanted. This solution was freeze-dried and then vacuum-dried to constant weight. Extraction was continued as long as more than 1% polymer was removed by each step. At this point, polymer residue was taken up in benzene, freeze-dried, and a similar extraction series conducted with diethyl ether. Centrifugation was here employed prior to decantation of polymer solution. The polymer remaining after all extraction steps was dried, dissolved in benzene, and finally freeze-dried. Compositions of the fractions were readily ascertained by microanalytical carbon-hydrogen analyses. Results of the separation of mixture A are summarized in Table I. Each extraction number represents two identical extraction steps, from which solutions were combined for later solute isolation.

It is convenient to define three grafting efficiencies: E_1 and E_2, the weight fractions of each of the monomers incorporated into the graft polymer, and E_t, the efficiency of incorporation of the total monomer charge. These efficiencies and the compositions are presented for the two systems examined in Table II.

The backbone efficiencies were not significantly different, but the branch efficiencies varied appreciably. Polymerization conditions for mixture A involved lower initial grafting temperature, lower catalyst concentration, and a longer mixing period of monomer and polymer than for mixture B. No catalyst beyond that used for the preparation of backbone PEA was used for mixture A. This suggests the presence of long-lived radicals.

The separation technique was tested by application to a 1/1 mixture of polyethyl acrylate ($\bar{M}_v = 1.6 \times 10^6$) and polystyrene ($\bar{M}_v = 1.4 \times 10^6$) prepared by freeze drying a benzene solution of mixed polymers. Removal of either homopolymer by the appropriate solvent was essentially quantitative in two extractions.

One attempt was made to graft ethyl acrylate to polystyrene. The ethyl acrylate was polymerized at 30°C.; in the presence of an equal weight of a polystyrene (PS) as emulsion polymer. From the determined efficiencies $E_1 = 0.073 \pm 0.004$, $E_2 = 0.28 \pm 0.02$, and $E_t = 0.16 \pm 0.01$ it was concluded that PS is not very effective as a backbone for growing branches of ethyl acrylate by chain transfer grafting.

TABLE I

Resolution of Mixture A into Homopolymers and Graft Copolymer

Extraction No.	Extraction conditions	Total sample, wt.-%	Composition of fraction, weight-%		
			Carbon	Styrene	Ethyl acrylate
Original sample	—	100	75.3 ± 0.2	47.3 ± 0.2	52.7 ± 0.2
1	152 hr. 45°C. with cyclohexane	10.3	91.7	98.2	1.8
2	48 hr. 45°C. with cyclohexane	2.3	91.2	96.6	3.4
3	69 hr. 45°C. with cyclohexane	3.3	91.4	97.3	2.7
4	31 hr. 45°C. with cyclohexane	0.6	—	—	—
5	168 hr. 25°C. with diethyl ether	39.3	60.3	0.0	100.0
6	125 hr. 25°C. with diethyl ether	2.4	61.4	4.5	95.5
7	165 hr. 25°C. with diethyl ether	0.6	—	—	—
Residue—graft co-polymer A		38.9	85.2	77.9 ± 0.4	22.1 ± 0.4

TABLE II. Summary of Grafting Efficiencies and Compositions of Graft Copolymers

Mixture	E_1	E_2	E_t	Weight fraction of ethyl acrylate	
				In mixture	In graft copolymer
A	0.20 ± 0.01	0.66 ± 0.02	0.42 ± 0.01	0.53	0.22
B	0.23 ± 0.02	0.21 ± 0.01	0.22 ± 0.01	0.53	0.54

TABLE III. Solubility of GCP B and Constituent Homopolymers in Various Solvents at 25°C.

Solvent	δ (cal./cc.)$^{1/2}$	PS, $\delta = 9.3$[a]	PEA, $\delta = 9.2$[a]	GCP B[a]
Poor hydrogen bonding:				
Cyclohexane	8.3	$S(\theta = 34°C.)$	I	I
Carbon tetrachloride	8.6	S	S	S
Toluene	8.9	S	S	S
Benzene	9.1	S	S	S
Chloroform	9.4	S	S	S
Nitroethane	11.1	I	S	I (S at 88°C.)
Acetonitrile	11.9	I	S	I
Moderate hydrogen bonding:				
Diethyl ether	7.4	I	S	I
Diisopropyl ketone	7.8	I	S	I (S above 60°C.)
3-Pentanone	8.8	S	S	S
Methyl ethyl ketone	9.3	S	S	S
Acetone	10.0	I	S	I
Strong hydrogen bonding:				
2-Ethyl butanol	10.5	I	S	I (S at 90–147°C.)
Isopropanol	11.5	I	$S(\theta = 32°)$	I

[a] Here S means soluble, I means insoluble, θ is the theta temperature, and δ is the solubility parameter.

Solution Properties of Polyethyl Acrylate-Styrene Graft Copolymer

Table III gives a qualitative comparison at 25°C. of the solubilities of GCP B and the constituent homopolymers in various solvents covering a range of solubility parameters δ. It is seen that the GCP is soluble in liquids which are solvents (at 25°C.) for both constituents of the graft but does not dissolve completely in any liquid tried which is a nonsolvent for one of the component homopolymers. This result was confirmed on GCP
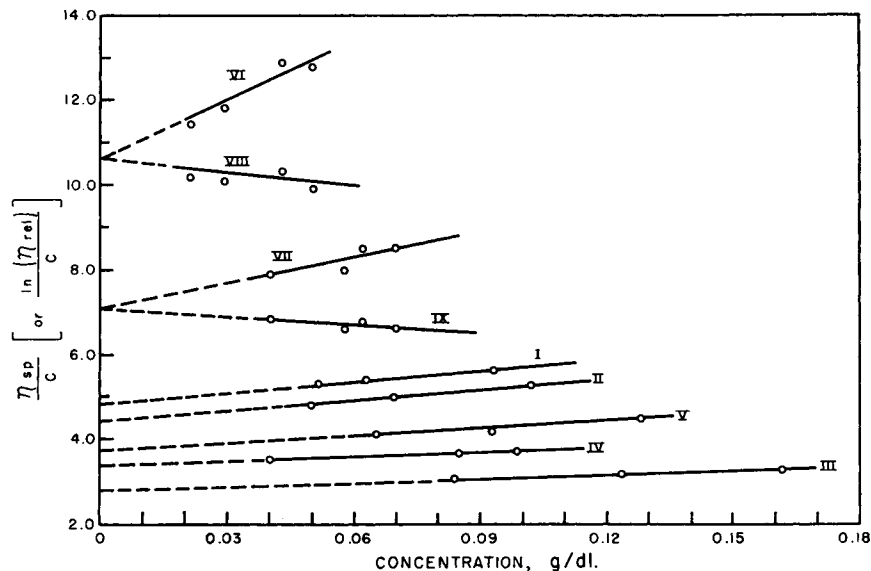

Fig. 1. Viscosity data for a graft copolymer of PEA-S and related physical mixtures: (I) PEA; (II) PEA (backbone of GCP); (III) PS; (IV) PEA/PS, 22/78 mixture; (V) PEA/PS, 53/47 mixture; (VI) GCP A; (VII) mixture A; (VIII) and (IX) [ln (η_{rel})]/(c) vs. c for VI and VII.

TABLE IV
Summary of Dilute Solution Data in Benzene, 30°C.

Sample	$[\eta]$	k'
PEA	4.85	0.37
PEA (backbone for GCP's)	4.48	0.38
PS	2.80	0.37
22/78, PEA/PS Physical mixture	3.33	0.41
	(3.25)[a]	
53/47, PEA/PS Physical mixture	3.77	0.38
	(3.89)[a]	
GCP A	10.6	0.39
Mixture A	7.11	0.38

[a] Calculated values.

A. Quantitative data were not obtained to show to what extent the solubility of the insoluble constituent may have been increased by grafting.

Little quantitative data exist on the solution properties of graft and block copolymers[4,5] or on mixtures of homopolymers. Data on the PEA/PS combination have not been previously reported. To gain some insight into the solution properties of grafts, η_{sp}/c vs. c plots were determined using benzene at 30°C. for GCP A and several relevant physical mixtures (see Fig. 1). The specific viscosity is η_{sp} and c is concentration in grams per deciliter. As seen from the figure, linear plots were obtained for all. Anomalies which might possibly occur at high concentrations where phase separation of the heterogeneous systems would be emphasized were not investigated. The Roman numerals used to identify the plots correspond to: (I) pure PEA used to prepare the physical mixtures; (II) pure PEA isolated from mixture A; (III) pure PS used in the mixtures; (IV) 22/78,

TABLE V Compatibility of PEA/PS Compositions

Sample	Solvent	Total polymer concn. g./dl. solvent	Results
1/1, PEA/PS Physical mixture	CHCl₃	10.0	Two phases.
		8.1	Two layers, top: hazy, bottom: textured and hazy.
		5.0	Two layers, top: slightly hazy; bottom: transparent but textured.
		2.5	1 phase.
	Toluene	10.0	Two layers.
		5.0	Two layers, top: transparent, slightly hazy; bottom: clear.
		2.0	One clear transparent phase.
Mixture B	Benzene	5.0	One hazy, viscous phase after extensive standing and centrifugation.
	CHCl₃	7.2	Viscous, whitish but translucent.
		4.0	Hazy, translucent, smooth flowing.
		2.0	Transparent, faint haze.
	Toluene	10.0	Very viscous, gelatinous, whitish.

PEA/PS physical mixture corresponding to GCP A; (V) 53/47, PEA/PS physical mixture corresponding to mixture A; (VI) GCP A; (VII) mixture A. Curves VIII and IX are the respective $[\ln (\eta_{rel})]/(c)$ vs. c plots for VI and VII, where η_{rel} is the relative viscosity.

The Huggins k' values[6] were evaluated from the relation, $\eta_{sp}/c = [\eta] + k' [\eta]^2 c$, where $[\eta]$ is the intrinsic viscosity. For a homologous series of a linear polymer k' is a constant to a very good approximation with a theoretical value of 0.38. For homopolymers k' is believed to increase somewhat with the degree of branching and the sample heterogeneity. However, all the k' values obtained in the present study (see Table IV) fell in the usual range of 0.35 to 0.40 usually observed for nonelectrolyte homopolymers.

The very high $[\eta]$ of 10.7 obtained from GCP A would seem to be strong evidence of grafting. For such a high $[\eta]$ shear correction should probably be made (extrapolation to zero shear), but in this preliminary work no

TABLE V (continued)

Sample	Solvent	Total polymer concn. g./dl. solvent	Results
		5.0	Translucent, whitish, smooth flowing, no separation into layers.
Mixture A	CHCl₃	7.3	Very viscous and gel-like, hazy and translucent.
		4.0	Hazy and translucent, no layering after several days.
		2.0	Transparent, faint haze, flows smoothly, no layering.
GCP B	CHCl₃	10.0	A gooey, viscous mass.
		5.8	Viscous, hazy, translucent, no layering.
		2.0	Hazy, translucent, smooth flowing, nonlayered.
GCP A	CHCl₃	5.0	Very viscous, no separation into layers.
		2.0	One hazy, viscous phase.

such corrections were made. For PEA homopolymer, an $[\eta]$ of 10.7 would correspond to a $\bar{M}_v$ of the order of nine million.

For the mixtures the k's, which are related to the polymer-solvent interactions, indicate that no unusual effects are occurring because of the heterogeneous nature of the sample; presumably, the dilutions are sufficiently great so that the domains of the individual molecules are well separated. It is of interest to note that the intrinsic viscosities of the PEA/PS mixtures can be calculated from $[\eta]$ mixture $= [\eta]_{PEA}W_{PEA} +$ $[\eta]_{PS}W_{PS}$, where W is the weight fraction of polymer. Both calculated and experimental values are shown in Table IV. In the case of the graft, where such total isolation of the different polymers is restricted by bonding, the high $[\eta]$ may reflect the fact that coiling is not as tight as would occur for a branched homopolymer because of the attempt of the PEA and PS to resist overlapping of their domains.

Phase Studies

A particularly interesting property of the graft is its ability to "compatibilize" PEA and PS in a common solvent. It is now well established[6,7] that two different polymers are usually incompatible in solution at moderate concentrations. Table V shows this for 1/1 physical mixtures of PEA/PS in chloroform and toluene. The immiscibility is shown by the separation of the mixture into two distinct layers. A film formed from this product consists of two layers (Table VI). In chloroform, two layers resulted over the polymer concentration range of 5–10 g./dl., and only below concentrations of 2 g./dl. was a single phase observed. The table also describes the "solutions" for mixtures A and B and for pure GCP's A and B. Note that for the grafts and the mixtures containing them, the two-phase separation could not be attained. Even centrifugation failed to produce two layers. It was thus found that phase separation can be used as a qualitative test for the presence of grafting. It has not yet been established to what extent grafting must be present to result in mutual tolerance by the two polymers.

Films

Table VI describes qualitatively the properties of the films prepared at room temperature from the above-mentioned solutions by casting on mercury. In addition three films cast directly from emulsion on glass are described.

Torsional Modulus-Temperature Curves

Figure 2 shows log G-T plots for GCP B and homopolymers of PEA and PS. The curves for the graft show two glassy transitions, one at $-30°C$. and the other between 80–90°C. As in previous work on bicomponent polymer mixtures, the lower transition corresponds to the glass temperature T_g of the polymer having the lower T_g.[1] Mixture B showed an analogous plot. The general characteristics of the curve of the graft are completely similar to those observed for the physical mixtures of homopoly-

mers including those for polybutyl methacrylate/PS. The PEA/PS physical mixture is expected to follow this pattern. It is concluded that static torsional modulus studies for polyacrylate/PS compositions are not capable of distinguishing the presence or absence of grafting.

TABLE VI
Description of PEA/PS Films

| Sample	Film casting procedure, 15°C.	Properties
Mixture A	Cast from CHCl₃ on Hg	Whitish and opaque, flexible, tears easily, nonelastic, apparently nonlayered.
Mixture B	Cast from CHCl₃ on Hg	Opaque, high gloss, nonbrittle but not very elastic, tears readily; gloss vanishes under stress.
GCP A	Cast from CHCl₃ on Hg	White with a pearl-like luster and high gloss, tough, whitens irreversibly when stressed. Thin and transparent near the edges.
GCP B	Cast from CHCl₃ on Hg	White with a pearl-like luster, almost translucent, whitens irreversibly when stressed.
1/1, PEA/PS Physical mixture	Cast from CHCl₃ on Hg	Layered. Top layer is translucent, smooth and hard: the bottom layer is tacky. Droplets are visible in the film. The top layer is brittle and tears easily.
Mixture A and B	Cast on glass from emulsion	Translucent, flexible, tears easily, nonlayered. Under stress it shows a high % elongation and whitens; the latter, however, dissipates upon relaxation.
1/1, PEA/PS Physical mixture	Cast on glass from emulsion	Transparent but hazy, elastic, high % elongation, whitens under stress but clears again upon relaxation, nonlayered.
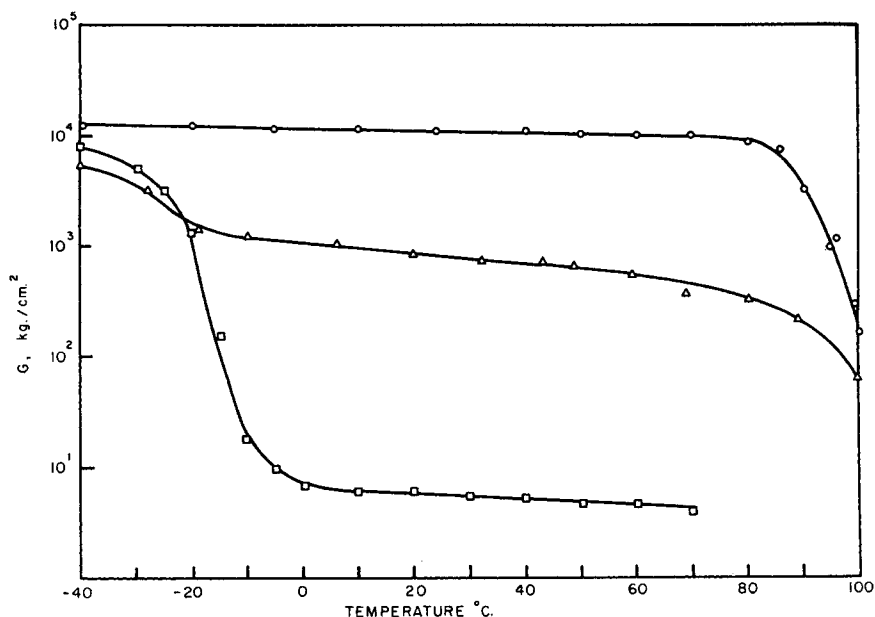
Fig. 2. Torsional modulus-temperature curves for PEA, PS, and graft copolymer B: (□) PEA, (△) GCP B, and (O) PS.

Discussion

Preparation of graft copolymers in emulsion involves adding a monomer M_2 to an emulsion of homopolymer of monomer M_1, under conditions such that M_2 is absorbed by the polymer particles and polymerizes therein. Chain transfer to poly(M_1) forms macroradical sites which subsequently initiate the polymerization of branches of poly(M_2). The active sites probably result from the abstraction of the tertiary α-hydrogen on the PEA backbone by a growing PS chain. Both excess emulsifier and high water solubility of M_2 promote the formation of new particles and thus affect grafting unfavorably.

The monomer-polymer pair must be selected carefully if grafting is to occur. Among the many variables expected to affect the success of grafting are temperature, catalyst type and concentration, emulsifier concentration, monomer/polymer ratio, concentration of emulsion particles, polymer/monomer compatibility, and the intrinsic polymerization constants of the monomers and polymers involved.

The probability that radicals of growing M_2 chains will attack poly(M_1) should be appreciably greater than the probability of attacking its own monomer. The macroradicals must form readily and once existing must be reactive enough to initiate polymerization of M_2 before other fates, e.g., termination, befall them. It seems likely that the high stability of the styrene macroradical plays a significant part in the failure of ethyl acrylate and other monomers to graft to polystyrene, and it is possible that the fact

that PS is a glassy polymer at the temperature grafting was attempted may also be a factor.

Investigation of the solution properties of graft copolymers as a function of the molecular weights of both backbone and branch polymers and the degree of grafting would be highly informative, particularly if light scattering and osmotic techniques are included. Quantitative knowledge of the phase relationships involved should suggest other means of isolating the grafts and ways to utilize them.

References

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Synopsis

The isolation of two graft copolymers of styrene on polyethyl acrylate from the ungrafted homopolymers by solvent extraction procedures is discussed. For the grafts and their corresponding mixtures η_{sp}/c versus c plots were determined, and no anomalies were observed. Qualitative data on the solubilities and phase properties of the grafts are given. Torsional modulus-temperature curves are shown for graft copolymer and the individual homopolymers.

Résumé

On discute des méthodes d'isolement par extraction aux solvants de deux copolymères greffés de styrène sur le polyacrylate d'éthyle à partir de homopolymères nongreffés. Les diagrammes de η_{sp}/c en fonction de c ont été effectués pour les greffés et les mélanges correspondants et on n'a observé aucune anomalie. On donne les résultats qualitatifs des solubilités et des propriétés de phase pour les produits greffés. On présente les courbes du module de torsion en fonction de la température pour le copolymère greffé et les homopolymères individuels.

Zusammenfassung

Die Abtrennung zweier Pfropfcopolymerer von Styrol und Polyäthylacrylat von den nichtaufgepfropften Homopolymeren durch Lösungsmittelextraktion wird diskutiert. η_{sp}/c gegen c Diagramme wurden für die Pfropfpolymeren und entsprechende Mischungen bestimmt und keine Anomalien beobachtet. Qualitative Daten für die Löslichkeit und die Phaseneigenschaften der Pfropfpolymeren werden angegeben. Torsionsmodul/Temperatur-Kurven für das Pfropfcopolymere und die einzelnen Homopolymeren werden angegeben.