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Macromers

Macromers by Carbocationic Polymerization

7. Emulsion Copolymerization of α-(p-Vinylphenyl) Polyisobutylene with Styrene and the Impact Strength of Poly(Styrene-g-Isobutylene)

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Summary

Copolymerization of α-(p-vinylphenyl)polyisobutylene(p-polyisobutenylstyrene, PIB-St) with styrene (St) in emulsion has been investigated. Copolymerization occurs only when the reaction locus is the monomer droplet. Conventional emulsion copolymerizations, in which the polymerization occurs in the micelle/aqueous phase, yielded mainly polystyrene. The monomer droplet method yielded graft polymers in good yield. The impact strength of poly(styrene-g-isobutylene) has been studied. The graft with relatively long PIB branches ($\overline{M}_n = 5x10^4$) exhibited improved impact strength over that of polystyrene, while the graft with short PIB branches ($\overline{M}_n = 6x10^3$) gave lower impact values.

Introduction

In the preceding paper (1) we have examined the copolymerization of various molecular weight PIB-St's (M_1) with styrene (M_2) in solution. Low molecular weight PIB-St ($\overline{M}_n = 4.2x10^3$) copolymerized with St uniformly ($r_2 = 1.0$-1.2) while high molecular weight PIB-St ($\overline{M}_n = 5x10^4$) was sluggish in copolymerization ($r_2 = 6.6$) perhaps due to microphase separation (1). This paper concerns the copolymerization of PIB-St in emulsion systems. Such systems may overcome the problem of massive phase separation in solution systems.

We also report the impact property of the resultant graft polymer, poly(styrene-g-isobutylene). This property is of particular interest since the graft contains an UV-stable PIB moiety as impact modifier. Commercial high-impact polystyrene usually contains polybutadiene-based impact modifiers which have insufficient UV stability for outdoor use.

Experimental

Materials. The synthesis and purification of PIB-St has been described (2). St (Aldrich) was washed with 10% aqueous NaOH and water, dried over $MgSO_4$ and freshly distilled. Azobisisobutyronitrile, AIBN (Eastman), was recrystallized from methanol. Potassium persulfate (Fisher) and Alipal 434 (GAF) were used as received.

Polymerization

Conventional Emulsion System. To a 6-ounce bottle were charged 80g distilled water, 1.5g Alipal 434, 25g PIB-St dissolved in St (10:90 w/w), and 0.23g $K_2S_2O_4$. The system was purged with N_2 for 10 minutes, sealed, and clamped to a rotating shaft submerged in a water bath at 60°C for 12-14 hrs. The resultant latex was precipitated into excess methanol, washed several times with n-heptane and MEK to remove PIB-St and polystyrene, respectively, and dried in a vacuum oven at room temperature.

Monomer Droplet Emulsion System. A stock solution of distilled water, Alipal 434, and PIB-St in St (80:1.5:25 w/w) was homogenized to reduce the particle size by using a two stage Gaulin Laboratory Homogenizer (Model 15M) for three cycles (6000 psi). Then 0.23g AIBN was added and the polymerization was carried out at 60°C in the same manner as with the conventional system.

Measurements. The ^{1}H-NMR spectrum was recorded on a Varian T-60 spectrometer. Glass transition temperatures were determined with a Dupont 1090 Thermal Analyzer. A Nicomp Model 270 equipped with a He-Ne laser beam (6328A) was used to determine the size of monomer droplet. Impact tests were made on compression-molded test specimens by ASTM D-256. The molding cycle was: 10 minutes without pressure at 350°F, 10 minutes under 20 psi at 350°F, followed by cooling to ambient temperature under 20 psi. The impact strength was measured by an Izod Impact Tester, Model TM 52004 (Testing Machines Inc.)

Results and Discussions

Emulsion Copolymerization of PIB-St with St. Emulsion copolymerization of macromers has not yet been reported. This system differs from ordinary emulsion polymerizations in that most macromers are highly viscous liquids or solids, and it is extremely difficult to disperse them in an aqueous phase by agitation in the presence of a surfactant. In this study, the PIB-St macromer was first dissolved in styrene to form a cement (PIB-St/St = 1/9, w/w). Then a crude emulsion was prepared by mixing the cement with distilled water and Alipal 434 (anionic emulsifier, sodium salt of nonylphenoxypolyethoxyethanol). The use of Alipal 434 for the preparation of a stable PIB emulsion has been described (3).

Two types of emulsion systems, a conventional and a monomer droplet method (4), have been evaluated for the copolymerization of PIB-St with styrene. In the conventional emulsion copolymerization method, the crude emulsion was used directly and the copolymerization was initiated by a water-soluble initiator (i.e., $K_2S_2O_4$) at 60°C. After the completion of the reaction, a viscous PIB layer separated on top of the latex. The product isolated from the latex was essentially polystyrene as identified by ^{1}H-NMR spectroscopy. Apparently copolymerization did not occur as anticipated. This negative result can be readily interpreted in terms of the mechanism of emulsion polymerization. In conventional emulsion systems the locus of polymerization is in the emulsion particles formed by either micellar or homogeneous nucleation in the aqueous phase during the early stages of the polymerization, and not in the monomer droplets. The function of monomer droplets is to provide monomer during the polymerization. In this experiment, among the monomers initially present in the monomer droplet, styrene is slightly soluble whereas the PIB-St macromer is completely insoluble in the aqueous phase. Thus during the copolymerization, only the styrene may diffuse across the aqueous phase to the growing polymer particles. This transport process gradually depletes most of the styrene in the monomer droplet and leaves the PIB-St macromer unsolubilized. In the absence of the solubilizing agent, the PIB-St macromer precipitates from the aqueous phase.

In the monomer droplet copolymerization, the crude emulsion described above was further homogenized using a Gaulin Homogenizer and a process by Vanderhoff, El-Aasser and Ugelstad that produces aqueous emulsions with droplet sizes less than 0.5μ (5,6). In our case the diameter of the monomer droplet, determined by quasielastic light scattering, was 0.24μ (mean value). In polymerizations with such small and stable monomer droplet emulsions, as developed by Hansen and Ugelstad (7), particle nucleation is believed to take place mainly in the monomer droplets. According to these authors (7) very small monomer droplets approach micelles in terms of surface area and number; and more importantly, most of the emulsifier is absorbed on the monomer droplets leaving little emulsifier in the aqueous phase for particle nucleation. To further reduce the opportunity for free radical initiation in the aqueous phase, an oil-soluble initiator (i.e., AIBN) was used. As shown by the data in Table I, the results obtained in the conventional and monomer droplet emulsions are dramatically different. In the conventional system polystyrene and unreacted PIB-St macromer were recovered while in the monomer droplet system a high yield (i.e., 70% after solvent extraction) of poly(styrene-*g*-isobutylene) was obtained.

Figures 1 and 2 show, respectively, the ^{1}H-NMR spectrum and DSC scans of poly(styrene-*g*-isobutylene). These characterization methods indicate graft polymer formation. According to the ^{1}H-NMR spectrum the sample (after selective extractions with n-pentane and MEK) contained both components: PSt and PIB. As indicated by the DSC scan the graft sample exhibited two discrete transitions i.e., at -52 and 30°C. This result seems to indicate a segregated two phase system, one phase of which is rich in PSt and the other rich in PIB. The apparent decrease in the Tg of the PSt-rich phase is most likely due to some degree of mixing of PIB in PSt. Similarly a certain extent of mixing of PSt in the PIB phase cause an increase in the Tg of PIB.

Impact Strength of Poly(styrene-g-isobutylene). The Izod impact strengths of polystyrene and various poly(styrene-*g*-isobutylene) copolymers have been studied. The materials used and results are summarized in Table II. The impact strength of polystyrene was found to be 0.2 ft-lb/in. for both samples, $\bar{M}_n = 5x10^4$ and $8x10^5$, examined. Evidently the impact strength of polystyrene is largely independent of molecular weight in this range. The poly(styrene-*g*-isobutylene) containing short PIB branches ($\bar{M}_n = 6x10^3$) exhibited lower impact strength. It is not surprising that low molecular weight PIB macromers are unsuitable to impart impact improvement, perhaps due to higher compatibility with polystyrene or increased free volume. Typical impact modifiers (i.e., high mol. wt. rubbers, have been shown to be semicompatible with the rigid phase (8), i.e., they

TABLE I

Copolymerization of PIB-St with St in Emulsion Systems [a]

Method	Monomer Droplet Size (μ)	Initiator	Loci of Initiation	Result
Conventional	2-5	$K_2S_2O_4$	Micelle and aqueous phase	PSt and unreacted PIB-St
Monomer droplet [b]	0.24[c]	AIBN	Monomer droplet	Poly(St-*g*-IB)

a. PIB-St in St/surfactant/H_2O

b. The crude emulsion was homogenized by a Gaulin Colloid Mill at 6000 psi

c. Determined with Nicomp Model 270

Figure 1

^{1}H-NMR Spectrum of Poly(St-g-IB)
(PIB content: 37 mole%)

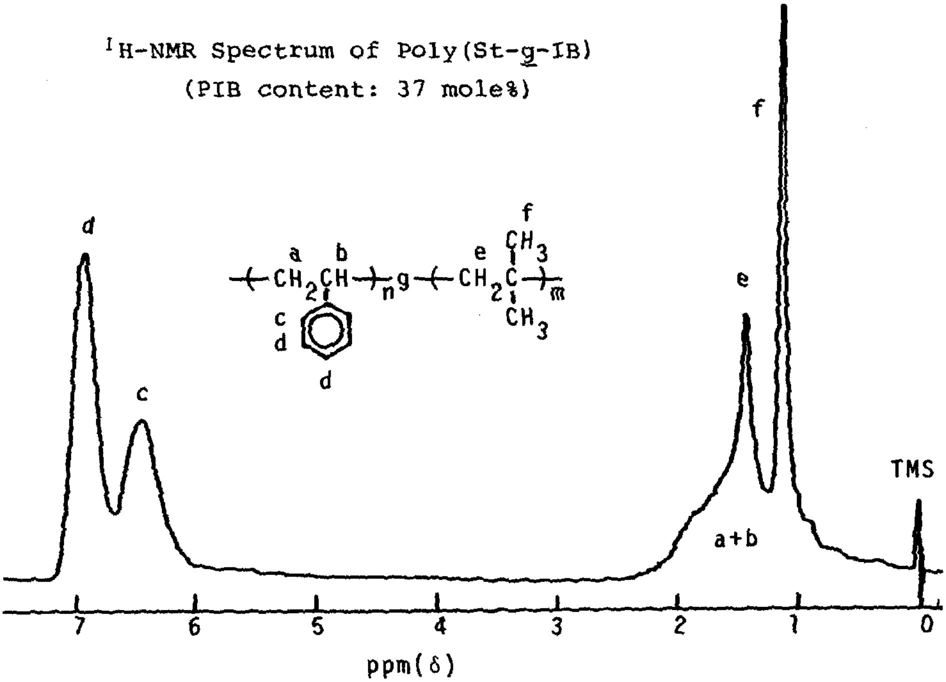

Figure 2
DSC Scans for Poly(styrene-g-isobutylene)
Polystyrene, and Polyisobutylene

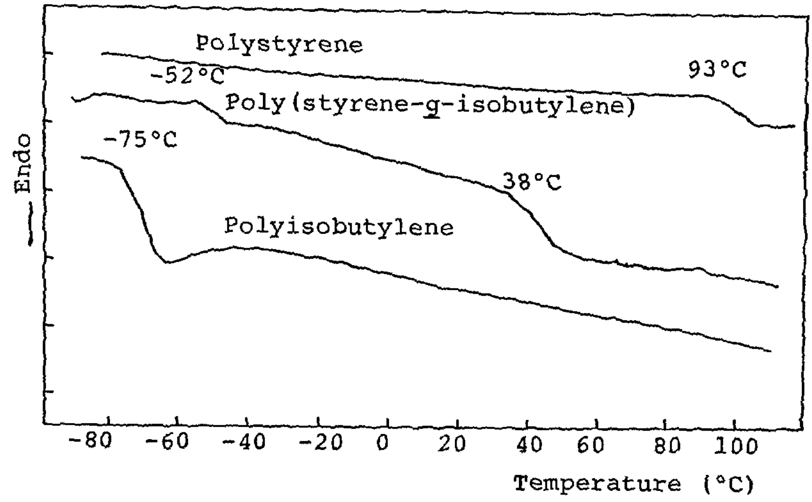

TABLE II

Characteristics of Polystyrene (PSt) and Poly(styrene-g-isobutylene) (PSt-g-PIB) Samples and Their Impact Properties

Samples	$\bar{M}_n$ [a] x10^{-4}	PIB Content[b] %	M_n of PIB x10^{-3}	Izod Impact[c] (ft-lb/in)
PSt[d]	5	0		0.2
PSt[e]	80	0		0.2
PSt-g-PIB[d]	5	10	6,000	0.15
PSt-g-PIB[e]	80	10	50,000	0.50

a. determined by membrane osmometry
b. determined by ^{1}H NMR
c. determined on compression molded bars according to ASTM D256 (notched), average of four measurements
d. by solution polymerization
e. by emulsion polymerization

are sufficiently compatible to have good dispersion and adhesion between the two phases but are not too compatible to yield a homogeneous system. The graft copolymer containing relatively long PIB branches ($\bar{M}_n$ = 5x10^4) more than doubled the impact strength (0.5 ft-lb/in.). Although this impact strength is still lower than expected, further improvements could arise by the use of higher molecular weight macromers, by improving the polymerization and fabrication processes, and by optimizing the morphology of the system.

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