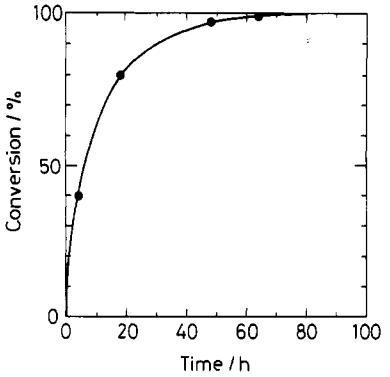

Figure 4. Time–conversion curve for the radical homopolymerization of α-VB-PVP (expt M-2). $[\alpha\text{-VB-PVP}]_0$ = 89.2 mmol/L; $[AIBN]_0$ = 16.1 mmol/L; in benzene at 60 °C.

was 1.91:3. This value is in good agreement with that obtained by the copolymerization methods, as shown in Table I.

For the alternative confirmation of the high functionality of α-VB-PVP, we carried out the radical homopolymerization of α-VB-PVP (expt M-2) under conditions of relatively high concentrations of initiator (AIBN) and macromer. Figure 4 shows the conversion of the macromer to poly(macromer) as a function of time. It is unequivocally found that α-VB-PVP is quantitatively homopolymerized to poly(α-VB-PVP), indicating the approximately 100% purity and the high polymerizability of the macromer.

Registry No. (VB)(VP)(MMA) (copolymer), 37569-87-2; poly(α-VB-PVP) (copolymer), 24980-54-9.

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Block and Graft Copolymers of Pivalolactone. 5. Graft Copolymers from Pivalolactone and Isobutylene[1]

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ABSTRACT: Isobutylene polymers have been converted to thermoplastic elastomers by the growing of pivalolactone segments at initiating sites positioned along the polyisobutylene backbone. These initiating sites were formed at benzylic carbons in poly(isobutylene-*co*-methylstyrene) by replacement of hydrogen with lithium followed by carboxylation and conversion of the carboxyls to tetrabutylammonium salts. Polymerization of pivalolactone at these sites completed the synthesis. The products could be melt-pressed to elastic films that, after orientation by drawing, had strengths up to 50 MPa. They could also be melt-spun to elastic fibers that were characterized by unusually low stress decay. This outstanding property is attributed to resistance of the polyisobutylene backbone to autoxidation.

Introduction

Block–graft copolymers of pivalolactone and isoprene studied previously possess crystalline domains formed by the polypivalolactone blocks that act as strong cross-links.[2-4] These poly(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone copolymers display stress-decay behavior similar to that observed for sulfur-cured gum rubber. Although these copolymers were protected with an antioxidant to retard autoxidation, it was suspected that the observed stress decay was due to breakdown of the polymer backbone by air autoxidation. In order to remove this vulnerability, a thermoplastic elastomeric pivalolactone copolymer system was sought that had no autoxidizable aliphatic unsaturation.

This goal was accomplished by the preparation of a graft copolymer with a polyisobutylene backbone as the rubbery phase cross-linked by means of grafted crystallizable polypivalolactone segments. The synthesis of such materials began with the copolymerization of isobutylene with a styrene, preferably a ring-methylated styrene. Lithiation of the benzylic sites in the copolymer, followed by carboxylation with carbon dioxide and conversion of the carboxyl groups to tetramethylammonium salts, afforded sites that were efficient initiators for the polymerization of pivalolactone. Poly[(isobutylene-*co*-methylstyrene)-*g*-pivalolactone] copolymers of varied composition and molecular weight have been prepared by this sequence of reactions, which is illustrated in Scheme I. This paper presents the results of a study of the preparation and characterization of these copolymers.

Experimental Section

Monomers. Isobutylene (Matheson Research Grade) was passed through two towers packed with KOH pellets and condensed into a dry ice cooled calibrated trap prior to transfer to the reaction vessel.

"Vinyltoluene" is a commercial mixture of isomers obtained from Polysciences and consists primarily of 3- and 4-methylstyrenes in a ratio of about 1:1. Styrene, α-methylstyrene, 4-methylstyrene, and α,4-dimethylstyrene were also obtained from Polysciences. All were distilled before use.

Pivalolactone was prepared as described by Blume.[5] It was passed through neutral alumina before use.

Initiators and Solvents. Alkylaluminum chlorides (Texas Alkyls) were used as received. Methyl chloride (Matheson CP Grade) was passed through two towers packed with KOH pellets prior to condensation in the reactor. Heptane (Fisher Certified Spectroanalyzed) was bubbled with dry nitrogen over 4A molecular

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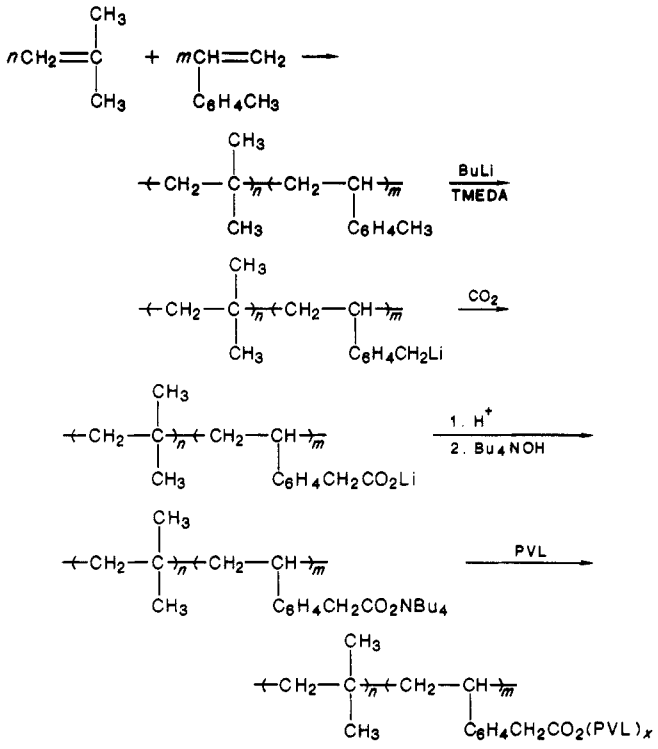
Scheme I
Preparation of
Poly[(isobutylene-*co*-methylstyrene)-*g*-pivalolactone]



sieves and passed through a column packed with Woelm acid alumina.

Cyclohexane and tetrahydrofuran were purified by continuous refluxing from sodium tape under nitrogen in a modified Soxhlet extractor. Solvent was withdrawn from the receiver by means of nitrogen back-pressure through a $^1/_8$-in. stainless steel U-tube inserted into the receiver and the reactor via syringe adapters.

Carbon Dioxide. "Coleman Grade" carbon dioxide was passed through drying tubes containing "Girdler's catalyst" and 4A molecular sieves before use.

Isobutylene Copolymer Preparation. All operations were carried out under dry nitrogen. All equipment was dried at 125 °C before assembly and flushed with dry nitrogen after assembly. The general procedure comprised cooling the reactor (a round-bottomed flask, equipped with a magnetic stirrer, a reflux condenser capped with a nitrogen bubbler, and a syringe adapter) to −78 °C, adding the solvent either by syringe (heptane) or by condensation from the vapor phase (methyl chloride), adding the comonomer via syringe, and then transferring the isobutylene (IB) via the vapor phase from a calibrated trap into which it had been condensed at −78 °C. The catalyst was added via syringe, whereupon a vigorous polymerization usually began at once. The reactor was kept at −78 °C for 0.5 h after the polymerization began, and then a 10% solution of ethanol in hexane was added to destroy the catalyst. After the mixture had warmed to room temperature, the polymer was precipitated by the addition of excess methanol (or ethanol when heptane was used as solvent). The polymer was then washed three times with methanol and dried in a vacuum oven at 75 °C. Inherent viscosities were determined in toluene (0.10%, 30 °C). The details of the preparation and characterization of typical copolymers are given in Table I (Supplementary Material).

Carboxylation of Isobutylene Copolymers. Carboxylation and grafting of pivalolactone to the IB copolymers was carried out by a procedure similar to that previously described for polyisoprene.[4] All of these experiments were carried out in the same manner. The details are given in Table II (Supplementary Material). A description of the preparation of the polymer designated by entry 4 in Table II follows:

All glassware was heated at 125 °C before assembly and then with a heat gun after assembly, with nitrogen passing through the system. In a 1-L resin kettle equipped with a magnetic stirrer, a hose connector connected to a nitrogen bubbler, and a syringe adapter were placed 620 mL of purified cyclohexane and 40.00 g of a copolymer of IB and 4-methylstyrene (10.62 mequiv based upon an estimated equivalent weight of 3765 per aromatic residue [Table I, no. 5]). The mixture was heated and stirred until the polymer was dissolved. To the resulting solution at room temperature were added via syringe 5.80 mL (4.47 g, 76.86 mequiv) of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) freshly distilled from sodium and 38.0 mL of 1.05 N *sec*-butyllithium in hexane (38.57 mequiv). An excess of the alkyllithium was used in order to consume water and/or other active hydrogen-containing contaminants. The orange-brown solution was allowed to stir for 1 h at room temperature and was then transferred via a glass or stainless steel U-tube under nitrogen back-pressure into a flask containing 1200 mL of vigorously stirred anhydrous tetrahydrofuran that had been saturated with anhydrous carbon dioxide. Vigorous bubbling of carbon dioxide through the solution was continued during the introduction of the lithiated polymer solution. Stirring was continued until the color was completely discharged and then for several additional hours. The excess carbon dioxide was pulled off under mild vacuum, and the mixture was transferred to a large separatory funnel equipped with a paddle stirrer. Six hundred milliliters of 1.2 N aqueous sulfuric acid (720 mequiv (6.2 times the total number of milliequivalents of base that had been added)) was added, and the mixture was stirred vigorously for 5 min. Reagent grade methanol (600 mL) was added with gentle stirring, and the aqueous layer was drawn off and discarded. The organic layer was then stirred vigorously ten times with 200-mL portions of water, each washing being followed by the addition of 200 mL of reagent grade methanol with gentle stirring to aid in phase separation. (After the fourth washing, the pH of the aqueous phase had leveled at 6–7.) Emulsification and accompanying difficulty in separation of the two phases increased as the washings progressed. Cyclohexane was added as needed to help break the emulsion. After the final wash, the polymer solution was transferred to a weighed flask equipped with a Dean–Stark separator and refluxed until no more water was removed. In some runs, the water was removed at this point by drying the solution with $MgSO_4$ followed by filtration. Solvent was distilled off until the volume of the polymer solution was about 600 mL. One hundred twenty milliliters of dry tetrahydrofuran was then added.

The percent solid content of the polymer solution was found to be 6.74% by carefully weighing a 5-mL sample of the solution in a small aluminum dish and evaporating it to dryness, eventually in a vacuum oven at 75 °C. The equivalent weight per acid group of the polymer was determined to be 8173 by dissolving a carefully weighed 4-mL portion of the polymer solution in anhydrous tetrahydrofuran that had been neutralized to the phenolphthalein end point with 0.101 N tetra-*n*-butylammonium hydroxide in methanol and then titrating to the same end point with the same base. (An equivalent weight of 3765 per aromatic unit had been calculated for the IB copolymer from the UV spectrum. Thus about half of the aromatic residues were carboxylated.)

Grafting Pivalolactone (PVL) to Isobutylene Copolymers. All of these experiments were carried out in about the same manner. Details are recorded in Table III (Supplementary Material). The following description, employing the carboxylated IB–4-methylstyrene copolymer whose preparation has just been described, is typical (Table III, no. 4).

To 541.0 g of the solution from the preceding section (containing 36.46 g of carboxylated polymer) was added 3.60 mL of 1 N tetra-*n*-butylammonium hydroxide in methanol. (This quantity of the hydroxide should convert about 80% of the acid groups to tetra-*n*-butylammonium carboxylate groups.) After the resulting solution had been stirred for 0.25 h, 24.0 mL of purified pivalolactone was added via syringe. This quantity was calculated to give a graft copolymer containing 40 wt % pivalolactone. Within 0.75 h at room temperature, the stirred solution had gelled. It was allowed to stand at room temperature for about 18 h. Vigorous stirring of the reaction mixture with 700 mL of tetrahydrofuran in a blender gave a smooth suspension. To this suspension was added a solution of 30 mL of concentrated aqueous HCl in 100 mL of 95% ethyl alcohol, and vigorous stirring in the blender was continued for 8 min. Two liters of 95% ethyl alcohol was added, stirring was continued for another 5 min, and the coagulated polymer was isolated by filtration and washed on the

Table IV
Preparation of Poly(isobutylene-*co*-4-methylstyrene) with 1.23×10^{-2} mol of Isobutylaluminum Dichloride in Methyl Chloride at -78 °C[a]

mole ratio of monomers (IB:4-MeSty)	yield of, polymer, %	mole ratio of monomers in polymer	$\bar{M}_v$ (inh visc)	$\bar{M}_w/\bar{M}_n$ (GPC)
74:1	97	54:1	173 000	18.82
49:1	96	41:1	125 000	14.55
37:1	89	29:1	83 000	10.07
25:1	89	22:1	70 000	9.01
15:1	94	13.5:1	62 000	6.54

[a] Table I, entries 11 and 13–16.

filter with additional alcohol. The polymer was washed four times in the blender with 800 mL of ethyl alcohol and then dried in a vacuum oven at 70 °C; 61.0 g (100%). Unreacted hydrocarbon polymer was removed by 18-h stirring of this product with 2 L of cyclohexane, followed by filtration and drying. The resulting cyclohexane-insoluble, colorless, granular, spongy polymer weighed 59.0 g. According to elemental analysis, it contained about 39 wt % pivalolactone.

A clear, colorless elastomeric film was pressed at 210 °C. A small strip of this material, after exercising, exhibited a tenacity-at-break of 32.2 MPa (4665 psi) and an elongation of 218%.

Discussion

Isobutylene Copolymers. A brief study of the cationic copolymerization of IB with styrene and methyl-substituted styrenes was made since the resulting materials offered potential for the generation of sites suitable for the grafting of pivalolactone chains to a poly-IB backbone[6] (copolymerizations of IB with styrene and α-methylstyrene have been studied previously[7,8]). The comonomers used included 4-methylstyrene, "vinyltoluene" (a mixture primarily of 3- and 4-methylstyrenes in approximately equal amounts), styrene, α-methylstyrene, and α,4-dimethylstyrene. Most of the work was done with 4-methylstyrene and the vinyltoluene mixture.

Catalyst–solvent combinations included diethylaluminum chloride + *tert*-butyl chloride in methyl chloride or heptane, ethylaluminum dichloride in methyl chloride or heptane, and isobutylaluminum dichloride in methyl chloride. All of these copolymerizations were carried out at -78 °C, and the mole ratio of IB to the styrene ranged from 10:1 to 150:1. The products obtained varied from viscous liquids to stiff semisolids at the low and high molecular weight extremes, respectively, but most of them were clear, colorless, slightly tacky elastomers. The number of moles of IB per mole of methylstyrene in the copolymer was estimated by ultraviolet spectroscopy by comparing the height of the aromatic absorption at about 268 nm in the copolymer with the corresponding peak height of a sample of poly(4-methylstyrene) (ultraviolet spectra of the polymers were determined in cyclohexane solution). The mole ratios estimated in this fashion correlated rather well with the mole ratios of monomers used in the polymerizations.

Of the catalyst–solvent combinations examined, the diethylaluminum chloride–*tert*-butyl chloride–methyl chloride system was preferred, since it consistently gave higher molecular weight copolymers with 4-methylstyrene and vinyltoluene (e.g., Table I, nos. 3, 6, and 7). The initiating species here is presumably the *tert*-butyl cation alone or the ion pair:

$$(C_2H_5)_2AlCl + (CH_3)_3CCl \rightarrow [(CH_3)_3C]^+[(C_2H_5)_2AlCl_2]^-$$

Ethylaluminum dichloride, although somewhat more convenient since its use does not require a cocatalyst, generally gave lower molecular weight copolymers under comparable conditions than were obtained with the diethylaluminum chloride–*tert*-butyl chloride combination. Isobutylaluminum dichloride, like ethylaluminum dichloride, initiated copolymerization without the addition of a cocatalyst. The 4-methylstyrene copolymers made with this initiator in methyl chloride were of relatively high molecular weights but also had broad molecular weight distributions. In a series of 4-methylstyrene copolymer preparations with constant concentrations of isobutylene and isobutylaluminum dichloride in methyl chloride, molecular weights decreased and molecular weight distributions became narrower with increasing proportions of 4-methylstyrene (Table IV). These effects are probably the result of chain transfer by the growing copolymer chain on the methyl group of 4-methylstyrene. With all of the catalysts studied, reproducibility in molecular weight and in molecular weight distribution was difficult to achieve.

Fractionation of a 4-methylstyrene–IB copolymer (produced by ethylaluminum dichloride initiation) showed that the 4-methylstyrene units were distributed rather evenly over fractions of increasing molecular weight (Table V). It was also evident that the very broad molecular weight distribution of the unfractionated polymer is in large part due to a substantial low molecular weight fraction.

A comparison of the ^{13}C NMR spectrum of a copolymer of IB and 4-methylstyrene with that of a homopolymer of 4-methylstyrene indicates that there are few, if any, adjacent 4-methylstyrene units in the copolymer; i.e., they are not arranged in blocks. How evenly they are distributed up and down the polymer chain was not determined. (We are indebted to D. W. Ovenall of this Laboratory for determination and interpretation of the ^{13}C NMR spectra.)

The IB–copolymers of α,4-dimethylstyrene prepared with alkylaluminum halide catalysts were unique in this

Table V
Fractionation of Poly(isobutylene-*co*-4-methylstyrene)[a]

			from GPC			
	wt %	ratio IB:4-MeSty (by UV)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_v$
unfractionated	100	77	16 000	285 000	17.45	222 000
fraction 1	17.07	45	1 800	57 000	32.72	29 000
fraction 2	29.62	63				
fraction 3	14.98	63	58 000	288 000	5.0	232 000
fraction 4	4.90					
fraction 5	6.03	38	61 000	278 000	4.55	222 000
fraction 6	3.77					
fraction 7	2.50					
fraction 8	6.52	42	65 000	247 000	3.81	199 000
fraction 9	7.10					
fraction 10	7.49	57	85 000	352 000	4.14	289 000

[a] The copolymer fractionated was that described in entry 1 of Table I. Fractionation was carried out by using a Du Pont belt fractionator. The polymer was dissolved in cyclohexane and precipitated by addition of increments of 1-butanol.

study in that they yielded mixtures of noncompatible copolymers. For example, the initiation of a 68:1 molar mixture of IB and α,4-dimethylstyrene with a combination of diethylaluminum chloride and *tert*-butyl chloride in methyl chloride gave good yields of a cloudy, tacky material of relatively high molecular weight ($\bar{M}_v$ = 122 000) (Table I, no. 20). Stirring of this material with cyclohexane followed by centrifuging gave an insoluble residue that contained 35–50 mol % α,4-dimethylstyrene. The cyclohexane-soluble fraction (which constituted the majority of the sample) contained only one aromatic residue for every 177 IB residues, quite different from the 1:68 ratio of the monomers in the reaction mixture. Terpolymers of IB and 1:1 mixtures of α,4-dimethylstyrene and 4-methylstyrene obtained by initiation with the same catalyst system were also cloudy, but after removal of a small quantity of an insoluble material in similar fashion, the bulk of the copolymer contained an appreciable proportion of the intended number of aromatic residues (Table I, no. 23).

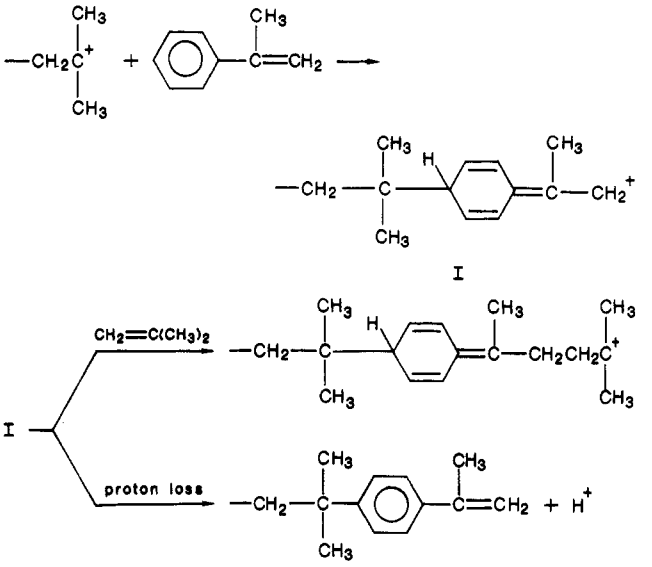
Carboxylation of Isobutylene Copolymers. The lithiation and carboxylation of the IB copolymers were carried out essentially as described previously for the preparation of poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone)] (see Scheme I)[4] (essentially no carboxylation occurred when an IB homopolymer was subjected to the carboxylation procedure described in this paper). The extent of carboxylation was determined by titration of the carboxylated polymer using a calibrated solution of tetra-*n*-butylammonium hydroxide. This gave the equivalent weight per carboxy group, or the soft-segment length (SSL), listed in Tables II and III.

With the IB copolymers derived from ring-methyl-substituted styrenes, carboxylation was no doubt occurring primarily on the benzylic methyl group. Although the intention was to carboxylate all of the aromatic units in the copolymers, the measured carboxylation efficiencies in the ring-methyl-substituted styrene–IB copolymers fell mostly in the 40–60% range. With the styrene–IB copolymers, which have one benzylic hydrogen per aromatic residue, carboxylation also occurred, but the efficiency averaged only about 22% (range 17–28%), no doubt a reflection of the relatively few reactive hydrogens and their crowded environment (e.g., Table II, no. 13). In these styrene–IB-derived polymers, the points of attachment of the polypivalolactone segments are directly on the polymer backbone, in contrast to the ring-methyl-substituted styrene-derived materials.

Surprisingly, appreciable carboxylation also occurred with α-methylstyrene–IB copolymers (e.g., Table II, no. 14) (the carboxylation efficiencies in the few experiments carried out with α-methylstyrene–IB copolymers ranged from 26 to 39%). This probably results from the presence of allylic hydrogens, which could arise during the copolymerization of α-methylstyrene and IB via occasional attack by the growing cationic polymer chain on the styrene monomer as depicted in Scheme II. Evidence for the end-group unsaturation required by this scheme has been reported by Okamara.[8] Aromatic ring lithiation, and carboxylation, although of low probability, would also be possible in these copolymers.

Growth of Poly-PVL Segments. The grafting process was also carried out essentially as described previously for the preparation of poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone] (see Scheme I.)[4] Initiating carboxylate anionic sites were generated by reaction of the carboxylated IB copolymer with tetra-*n*-butylammonium hydroxide. The addition of PVL resulted in an exothermic

Scheme II
Presumed Ring Attack by the Growing Cationic Chain in α-Methylstyrene–Isobutylene Copolymerizations



polymerization. The carboxylate ends of the graft segments were finally converted to carboxylic acid groups by an acidification prior to isolation. GPC and extraction studies suggested that little nongrafted hydrocarbon polymer and pivalolactone homopolymer were obtained.

From elemental analysis, the percent PVL contents of the graft copolymers were determined. These were usually found to be close to the intended percents. From these values and the determined equivalent weights per carboxyl group in the backbone polymers (SSL), the hard-segment lengths (HSL), i.e., the average molecular weights of the grafted PVL chains, were determined. (It was assumed that in the anionic growing of the PVL chains, all of the carboxylated sites were utilized, and that all of the grafts were of equal length.)

The properties of the graft copolymers are given in Table III. Strips cut from films obtained by hot-pressing had tenacities-at-break ranging from 5 to 20 MPa. Oriented strips exhibited up to threefold increases in tenacity over unoriented material (orienting of film strips and fibers was done by subjecting a sample to repeated cycles of stretching, short of the breaking point, followed by relaxation). The tenacities- and elongations-at-break given in Table III are for oriented material, except where otherwise noted.

Structure–Property Relationships. The IB–PVL graft copolymers prepared in this study ranged from sticky semisolids for products containing small amounts of PVL, through a rubbery thermoplastic range as the PVL content was increased from 10 to about 60%, to hard, nonelastic, thermoplastic solids for PVL contents greater than 60%. The rubbery thermoplastic materials were of prime interest in this study, and a brief examination was made of the relationships between some of the structural parameters and properties, primarily the tenacity-at-break, of both pressed film strips and melt-spun fibers.

A perusal of the data in Table III shows an obvious positive relationship between tenacity and PVL content. Specifically for a series of grafts derived from the same carboxylated backbone (constant SSL), the tenacity more than tripled as the PVL content was increased from 9 to 56% (Table III, nos. 6–8). (In these specific cases, of course, the HSL was also increasing proportionately with the PVL content.) A concomitant decrease in elongation also occurred. Although it is less clear-cut, the data in

Table VI
Melt-Spun Fibers from IB–PVL Graft Copolymers

comonomer (entry from Table III)	backbone $\bar{M}_v$ (from inh visc)	SSL	% PVL	HSL	spinning temp, °C	T_B/E_B[a]
1. 4-MeSty (3)	82000	9493	36.1	5366	252	0.29/256
2. vinyltoluene (14)	150000	10641	33.3	5316	270	0.32/64
3. α-MeSty + α,4-DiMeSty (17)	110000	10646	34.5	5606	255	0.33/186
4. α-MeSty + 4-MeSty (18)	80000	10565	36.0	6017	260	0.42/211
5. Sty + α-MeSty (19)	70000	10580	38.2	6527	250	0.27/217

[a] T_B = tenacity-at-break in decinewtons per tex; E_B = elongation-at-break (%).

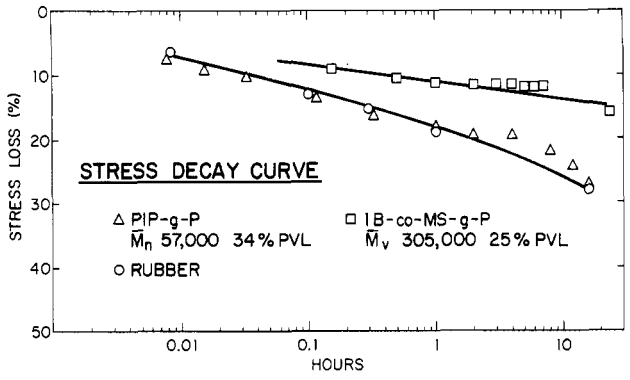


Figure 1. Stress-decay curve.

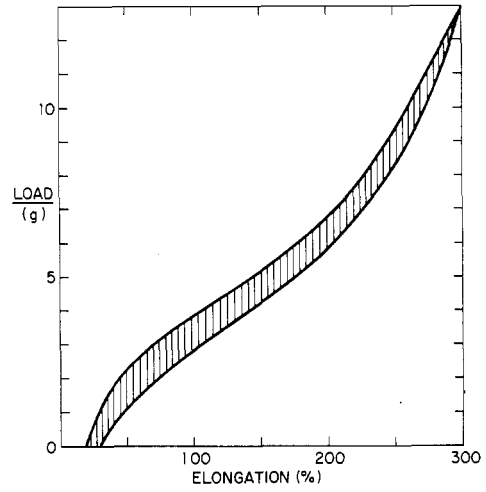


Figure 2. Stress vs. elongation for poly(isobutylene-*co*-methylstyrene)-*g*-pivalolactone.

Table III suggest that tenacity, in general, also increases with backbone viscosity molecular weight ($\bar{M}_v$). This trend is evident in the data for a series of polymers containing about 40% by weight PVL, but with varied $\bar{M}_v$ (Table III, nos. 1, 2, 4, 5, 7, and 10–12). From this series and other examples not in Table III, it appears that the tenacity reaches a maximum at $\bar{M}_v \cong 200000$, after which it levels out or decreases somewhat with further increase in $\bar{M}_v$.

Although it is not evident in the limited data given in Table III, a statistical analysis of the data from a series of 4-methylstyrene–IB-backbone-derived grafts showed a negative dependence of tenacity upon SSL and a positive dependence upon HSL. (The statistical analysis also confirmed the positive dependencies of tenacity upon PVL content and backbone $\bar{M}_v$. We are indebted to J. M. Minor of Du Pont's Engineering Department for the statistical analysis.) Intuitively, these results are logical: higher tenacity should be favored by more cross-links per chain (i.e., shorter SSL) and by longer grafted chains (i.e., higher HSL). The statistical analysis also suggested little or no dependence upon backbone polydispersity, but the conclusion is probably not significant since the data analyzed were from a group of polymers based upon backbones with relatively high polydispersities. The suspected major consequence of relatively high backbone polydispersities on the properties of the graft copolymers is a lower order of tenacity due to the presence of significant quantities of relatively low molecular weight backbone material. IB–PVL graft copolymers were consistently weaker than poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone] with comparable structural parameters, no doubt because of low molecular weight poly-IB fractions.

Many of these copolymers were melt-spinnable at 240–280 °C to elastic fibers of moderate strength. The properties of representative oriented fibers from selected copolymers containing 34–38% PVL are listed in Table VI. Although the backbones of these copolymers were based upon several different styrene comonomers, the tenacities were comparable (0.27–0.42 dN/tex), suggesting that the identity of the styrene comonomer used for the generation of graft initiation sites is unimportant. As noted above with film strips of these materials, the melt-spun fibers consistently exhibited lower tenacities than fibers of isoprene–PVL block–graft copolymers with comparable parameters.

Although generally somewhat weaker, fibers of IB–PVL grafts exhibited considerably better stress-decay behavior than the isoprene–PVL block–graft copolymers. In Figure 1, comparative stress-decay data for an IB–PVL graft copolymer containing 25% PVL (Table III, no. 13), a sulfur-cured natural rubber, and an isoprene–PVL block–graft copolymer are given. These data were obtained by stretching each fiber to 300% and maintaining that elongation while observing the decrease in stress over time. For the IB–PVL graft, which had not been previously treated with an antioxidant, the stress dropped 11% in the first hour, followed by only 5% additional drop over the next 22 h. The sulfur-cured natural rubber and the isoprene–PVL block–graft copolymer, which had been compounded with relatively large amounts of an antioxidant, showed a loss in stress of over 20% in less than 20 h. The outstanding stress-decay behavior of IB–PVL graft copolymers is presumably due to the absence of autoxidatively sensitive aliphatic unsaturation in the polymer backbone. The vulnerability of natural rubber and synthetic isoprene polymers to autoxidation and the resulting adverse effect on properties are well-known.

In Figure 2 is plotted the stress–strain behavior for a fiber of this same IB–PVL graft copolymer (i.e., Table III, no. 13) on stretching to 300% (upper curve) followed by releasing to zero load (lower curve). The work lost in this cycle, as indicated by the area between the curves compared with the total area under the top curve, was only 15%.

Registry No. (IB)(PVL)(vinyltoluene) (terpolymer), 62722-39-8; (IB)(PVL)(4-MeSty) (terpolymer), 62694-45-5; (IB)(PVL)(α-MeSty)(α,4-diMeSty) (quaterpolymer), 104715-91-5; (IB)(PVL)(α-MeSty)(4-MeSty) (quaterpolymer), 62694-76-2; (IB)(PVL)(Sty)(α-MeSty) (quaterpolymer), 104715-92-6; $(C_2H_5)_2AlCl$, 96-10-6; $(CH_3)_3CCl$, 507-20-0; $C_2H_5AlCl_2$, 563-43-9; $(H_3C)_2CHCH_2AlCl_2$, 1888-87-5; $(H_3C(CH_2)_3)_4NOH$, 2052-49-5.

Supplementary Material Available: Details of the preparation and characterization of the isobutylene copolymers (Table I), carboxylation of the isobutylene/methylstyrene copolymers (Table II), and grafting of pivalolactone to the carboxylated isobutylene/methylstyrene copolymers (Table III) (13 pages). Ordering information is given on any current masthead page.

References and Notes

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Model Copolymerization Reactions. Determination of the Relative Rates of Addition of Styrene and Acrylonitrile to the 1-Phenylethyl Radical

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ABSTRACT: 1,1′-Azobis(1-phenyl[1-^{13}C]ethane) (1) was prepared in 15% overall yield, starting from [1-^{13}C]acetic acid (99 atom %). Analysis of end-group concentrations in styrene–acrylonitrile copolymers prepared with 1 as initiator allows accurate determination of the relative rates of addition of these monomers to the 1-phenylethyl radical. We obtain $k_S/k_A = 0.20 \pm 0.02$, a result consistent with the penultimate model treatment of the styrene–acrylonitrile copolymerization by Hill, O'Donnell, and O'Sullivan.

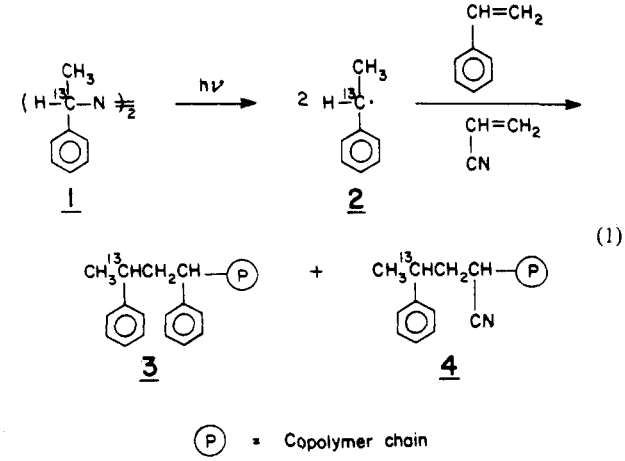
Introduction

Much of what is known about the addition of alkyl radicals to olefins has been learned from studies of radical copolymerization. In 1944 Mayo and Lewis outlined a kinetic framework for the prediction of copolymer composition, in which two kinetically distinct macroradicals compete for two olefinic comonomers.[1,2] Their "terminal" kinetic model quickly became the standard treatment of radical copolymerization, and the reactivity ratios derived from it now number in the thousands.[3] The success of the terminal model in predicting copolymer compositions has led to its widespread acceptance and to a belief that macroradical reactivity is governed in most systems only by the identity of the terminal comonomer unit.

There are good reasons to question this view. First of all, it was pointed out as early as 1946 that deviations from the predictions of the terminal model should be detected most readily in measurements of *sequence*, rather than *composition*.[4] Because sequence measurements even now are not routinely accessible, stringent tests of the terminal model have been applied only in a relatively small number of copolymerization systems. Second, the terminal model does not provide a satisfactory description of the *overall rate* of radical copolymerization. Until recently it was thought that the problem lay in inadequate treatment of the termination step, but rate measurements by Fukuda and co-workers have shown that, in the copolymerization of styrene and methyl methacrylate, it is the propagation rate constant that does not conform to the predictions of the terminal model.[5]

Problems of this kind have prompted us to renew investigation of the factors that control reactivity in radical addition to olefins. We have shown recently that the addition of primary alkyl radicals to styrene and acrylonitrile is sensitive to the nature of substituents placed γ to the radical center and that the magnitude of the effect is remarkably similar to that inferred from an application of the penultimate kinetic model to the copolymerization of these monomers.[6,7] But primary radicals are hardly realistic models of the macroradicals responsible for the growth of copolymer chains. We report in this paper a method by which one can assess the reactivity of the 1-phenylethyl radical, a plausible model of styryl-terminated macroradicals.

The method uses 1,1′-azobis(1-phenyl[1-^{13}C]ethane) (1) as a source of the 1-phenylethyl radical (2). Photolysis of 1 in a mixture of styrene and acrylonitrile leads to free radical copolymerization and to the formation of the two chemically distinct ^{13}C-enriched end-group diads 3 and 4 (eq 1). Four distinct diads are expected if end-group



stereochemistry is taken into account. Careful integration of the corresponding ^{13}C NMR signals allows determination of the relative end-group concentrations and thereby a calculation of the monomer reactivity ratios for 2. We describe these experiments in the present paper. Bevington and co-workers have reported the use of ^{13}C-en-

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