Block and Graft Copolymers of Pivalolactone. 4. Triblock and Block–Graft Copolymers from Pivalolactone and Isoprene

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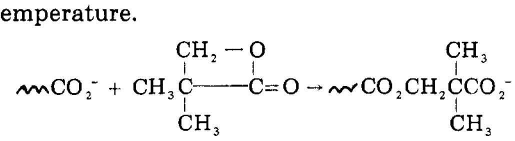
ABSTRACT: Poly(pivalolactone-*b*-isoprene-*b*-pivalolactone) triblock copolymers and poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone] block–graft copolymers have been synthesized by attaching poly(pivalolactone) segments to polyisoprenes. The triblock copolymers were made by reaction of α,ω-dilithio-*cis*-1,4-polyisoprene with carbon dioxide, conversion of the resulting lithium carboxylates to tetrabutylammonium salts, and use of salts to initiate polymerization of pivalolactone. For the block–graft copolymers, the dilithiopolyisoprene was first reacted with *s*-BuLi in the presence of tetramethylethylenediamines to introduce lithio sites randomly along the chain by metalation. The metalated polymer was then carboxylated followed by conversion of lithium carboxylates to tetrabutylammonium salts and use of the salts to initiate polymerization of pivalolactone. Both types of polymers were very strong, especially after orientation by drawing, and are highly resilient thermoplastic elastomers. Strength is ascribed to apparent "cross-linking" through crystalline domains of the poly(pivalolactone) segments, which form a separate phase in the polyisoprene major phase. The block–graft polymers have been spun into elastic fibers, which, after orientation, have shown resistance to stress decay equal to that of sulfur-cured natural rubber. From these results, it is concluded that the apparent "cross-links" formed by crystalline poly(pivalolactone) are just as effective as chemical cross-links.

Preliminary reports on grafting of poly(pivalolactone) segments to elastomeric backbones have been given recently.[2,3] These have included forming of block–graft copolymers from pivalolactone and isoprene, grafting of pivalolactone to poly[ethylene-*co*-propylene-*co*-1,4-hexadiene], and grafting to copolymers from acrylic and methacrylic acids. More complete accounts of products from ethylene–propylene copolymers[4] and acrylic acid copolymers[5] have since appeared. The present paper is concerned with a detailed description of the preparation and properties of poly[pivalolactone-*b*-isoprene-*b*-pivalolactone] and poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone].[2]

All of these products behave as though they are cross-linked. This is believed to be a consequence of rapid and almost complete crystallization of the poly(pivalolactone) segments and separation of this crystalline phase into discrete domains that act as tie points for the major rubbery phase. That poly(pivalolactone) segments do separate into crystalline domains has been demonstrated for grafted ethylene–propylene copolymers[4] and acrylic acid copolymers.[5] Poly(pivalolactone) is quite efficient in this respect because relatively short chains readily enter into domain formation. The domains also reform readily after being melted and recooled, which means they can be fabricated in the same way as conventional thermoplastic materials.

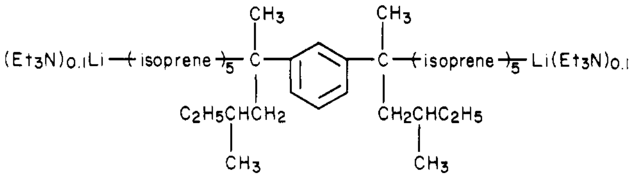
Grafting of poly(pivalolactone) has been accomplished by use of the anionic, ring-opening polymerization described by Hall.[6] In solvents of high dielectric constant, tetraalkylammonium salts initiate this polymerization at room temperature.



$$\sim\!\sim CO_2^- + CH_3\underset{CH_3}{\overset{CH_2-O}{C\!-\!\!-\!\!-\!C{=}O}} \rightarrow \sim\!\sim CO_2CH_2\underset{CH_3}{\overset{CH_3}{C}}CO_2^-$$

If the alkyl groups are bulky enough to cause good ion separation, initiation and propagation are both very rapid. Chain transfer of protons between pendent carboxylate groups permits initiation to occur at each site whether or not all are neutralized. Thus, attachment of poly(pivalolactone) grafts to an elastomeric backbone requires only that the backbone has carboxyl groups at the desired graft sites. The problem, then, reduces to the question of how to prepare a polyisoprene appropriately substituted with carboxyl groups.

Synthesis of poly[pivalolactone-*b*-isoprene-*b*-pivalolactone], the ABA triblock copolymers, required polyisoprenes containing carboxyl groups at both ends. It was also essential to have the cis-1,4 configuration to impart high strength and resilience. Products meeting both requirements could be obtained by carboxylation of polyisoprenes prepared using difunctional alkyl lithium initiators. We have used two such initiators. One is DiLi-3, which is a composition obtained from Lithcoa and is said to have a functionality slightly greater than two.[7] The second is Diplit 5.1, which we developed specifically for this work and is represented by formula I.[8,9] I was obtained by the



I

reaction of *m*-diisopropenylbenzene with *sec*-butyllithium in the presence of 0.1 equiv of triethylamine to give an addition product that was then stabilized by addition of 5 equiv of isoprene. Beinert et al.[10] have also prepared polyisoprene with lithium at each end by initiation with a *m*-diisopropenylbenzene-*sec*-butyllithium reaction product.

Synthesis of block–graft copolymers, poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone], required polyisoprenes with carboxy groups on the ends and along the chain. These were made by carboxylation of α,ω-dilithiopolyisoprenes that had first been lithiated by the method of Tate et al.[14] This method involves use of butyllithium complexed with tetramethylethylenediamine to substitute lithium for hydrogen at allylic positions in polydienes.

Experimental Section

Materials. Isoprene, cyclohexane, and tetrahydrofuran were rigorously purified by methods previously described.[8]

Pivalolactone was prepared by reaction of chloropivalic acid with sodium hydroxide according to the procedure described by

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Lorenz.[12] It was dried, degassed, distilled under reduced pressure, passed through neutral alumina, and stored cold under argon.

Argon and nitrogen were purified by passage through a reduced nickel oxide catalyst (Girdler G52) to remove oxygen and through 4 Å molecular sieves to remove water. Limits for argon were 0.9 ppm for oxygen and 0.4 ppm for water. The nitrogen used assayed for 0.4 ppm oxygen and 0.6 ppm water. Coleman instrument grade CO_2 was used for the carboxylation step. It was passed through Girdler's catalyst and then through 4 Å molecular sieves. To prevent possible diffusion of air into gas streams, reducing valves having stainless steel diaphragms were used.

Tetramethylethylenediamine (TMEDA) was distilled, bp 121 °C, from sodium at atmospheric pressure just before use.

Styrene was passed through basic alumina and stored cold. Immediately before use, a portion was treated with sufficient 1.7 N *n*-butyllithium in hexane to initiate polymerization. Pure material was obtained by vacuum distillation from the polymerizing mixture.

Initiators. DiLi-3 was obtained from Lithium Corp. of America. It is described[7] as an organolithium initiator that has an average of 2.2 carbon–lithium bonds per molecule.

Diplit 5.1 was prepared as previously described.[8,9]

α,ω-Dilithio-*cis*-1,4-polyisoprene. Polyisoprene, having carbon–lithium bonds at each end for preparation of poly(pivalolactone-*b*-isoprene-*b*-pivalolactone) copolymers, was prepared by initiation of isoprene with DiLi-3. In a typical preparation, a flask, fitted with a side arm for additions and a T tube to enable maintenance of an argon atmosphere under positive pressure, was dried by flaming it under a strong stream of argon. To the flask was added 250 mL of cyclohexane and 30 mL (20 g) of isoprene.[8] This mixture was heated to 60 °C, and 0.835 mequiv of DiLi-3 was added. This amount of initiator, assuming no destruction of active ends and complete conversion of isoprene to polymer, should give a polyisoprene having an M_n of 50 000. Shortly after addition of initiator, the polymerization proceeded vigorously and cooling was applied to keep the temperature near 60 °C for 40 min and then at room temperature for 1 h.

Pivalolactone-*b*-isoprene-*b*-pivalolactone Triblock Copolymer. The above reaction solution was diluted with 50 mL of tetrahydrofuran followed immediately by addition of 150 mL of tetrahydrofuran saturated with carbon dioxide with very vigorous agitation.[11] All of the red-amber color of the dilithiopolyisoprene faded, and a viscous solution formed. After 10 min, the mixture was heated to 60 °C for 1 h and then flushed with nitrogen to drive off unreacted carbon dioxide. To the mixture was added 0.415 mequiv of tetrabutylammonium hydroxide (TBAH), which is one-half the amount of available Li^+, and heat was applied for another 30 min. The viscosity of the solution sharply decreased during this step. Pivalolactone (PVL) (7.0 mL) was added to the solution over 3 min while the solution was heated to 60 °C and stirred constantly. After 4 min, the solution gelled. Stirring was discontinued, and the mixture was allowed to cool to room temperature. After 1 h, the polymer was thoroughly extracted with tetrahydrofuran to remove any homopolyisoprene. None was recovered. If exchange between Bu_4N^+ and Li^+ at chain ends had not occurred, 25% of the isoprene would have been recovered as homopolymer.

Caution: Unpublished work at Haskell Laboratory, E. I. du Pont de Nemours and Co., has shown that PVL caused skin tumors in mice when applied as a 25% solution in acetone for most of the life span of the mice. The time required for tumor formation was greater than that for β-propiolactone, a positive control in the test, and the extent of tumor formation was much less than that for β-propiolactone.

The residue after extraction was washed with alcohol and dried. The yield was 86%. Anal. C, 80.74; H, 9.83; O, 9.43. This analysis corresponds to 31% PVL in the copolymer as compared to 26% calculated on the basis of weight of monomers used.

Pressed films were strong and snappy, indicating substantial absence of AB polymer. If chain transfer had not occurred, AB polymer would amount to 50% of the total, and strong, resilient films would not have been obtained from mixtures containing such a large amount of this weak diblock polymer.

Salt Formation with Tetrabutylammonium Chloride. Pivalolactone-*b*-isoprene-*b*-pivalolactone triblock copolymer was prepared essentially as described above except that 300 mL of cyclohexane was used at the start, and the polyisoprene solution was diluted with only 25 mL of THF and carboxylated with 100 mL of THF saturated with carbon dioxide. The tetrabutylammonium salt of the carboxylated polyisoprene was formed by addition of 0.415 mequiv of tetrabutylammonium chloride (TBACl) dissolved in a small amount of THF. After addition of PVL, an extremely tight gel formed within 15 min. The product was extracted and precipitated as described above. No homopolymers were found, and the triblock copolymer in film form had excellent physical properties, being comparable to those described above.

Randomly Lithiated α,ω-Dilithio-*cis*-1,4-polyisoprene. α,ω-Dilithio-*cis*-1,4-polyisoprenes for block–graft copolymers were prepared by initiation with Diplit 5.1, using a procedure that has been described earlier.[8] The polyisoprenes so obtained were 92% 1,4 and 8% 3,4. Molecular weight distributions of these polymers were quite narrow, as indicated by M_w/M_n below 1.6, usually less than 1.5. A typical preparation is described below.

Since the polymer was to be carboxylated by reaction with carbon dioxide, it was prepared in equipment that would enable transfer to a carboxylating solution in which carbon dioxide was present in excess. This was done to prevent chemical cross-linking by reaction of organometallic sites with carboxylates. The equipment consisted of a reactor fitted with a sealed top having four ground glass openings. These were fitted with a stirrer, a T-tube connected to a bubbler for maintaining an argon atmosphere in the reactor, a serum stoppered inlet port, and a glass transfer tube sealed with a gum rubber sleeve. The glass transfer tube had one leg in the polymerization reactor and the other in a carboxylation reactor that will be described subsequently. The polymerization reactor was thoroughly dried by overnight heating in an oven at 150 °C and by flaming with rapid passage of argon. Argon flow was continued during attachment of the fittings, and an argon blanket was kept over the reactor throughout addition of solvent and reagents and subsequent reactions by keeping positive pressure of argon in the T-tube with excess gas being continually released through the bubbler. The reactor was charged with 2750 mL of purified cyclohexane and 450 mL (300 g) of purified isoprene. After the solution was heated to 40 °C, polymerization was initiated by adding 80 mL (8.0 mequiv) of 0.1 N Diplit 5.1 from a 100-mL hypodermic syringe. The initial red color of the initiator was rapidly discharged, and the solution turned yellow orange. The temperature of the reaction solution was kept at 45–50 °C by cooling and subsided after 1 h, after which it was heated to 57–60 °C for 2.75 h.

The polymerization solution was then cooled to 25 °C, and 7.3 mL (48.2 mmol) of tetramethylethylenediamine (TMEDA) was added. After the solution was stirred for 20 min, a 10-mL sample was removed by hypodermic syringe and decomposed in THF/alcohol to obtain polymer for analysis by gel-permeation chromatography (GPC). To the remainder was added over about 10 min 31.1 mL of 1.25 N (38.9 mequiv) *sec*-butyllithium[14] in hexane, which resulted in a change in color from orange yellow to red. After the solution was stirred for 1 h, the polyisoprene was ready for the carboxylation step.

Carboxylation of Lithiated *cis*-1,4-Polyisoprene. A 10-L resin kettle for carboxylation was set up next to the polymerization kettle and fitted with a sealed lid with three necks. One was for a four-blade stirrer, the second was for the transfer tube from the polymerization kettle, and the third was attached to a Nujol bubbler to allow blanketing gas and excess carbon dioxide to escape. Tetrahydrofuran (3500 mL) saturated with carbon dioxide was placed in the kettle. The glass transfer tube from the polymerization kettle was lowered until the leg in the polymerization kettle was near the bottom, and the leg in the carboxylation kettle was near what was to be the top of the liquid level. This latter leg had a port near the top fitted with a No. 22 needle through which nitrogen or argon flowed toward the discharge end to prevent carboxylation in the tube. This was necessary to avoid plugging of the tube. Then the polyisoprene solution was transferred by increasing argon pressure in the polymerization kettle, which forced the solution to pass through the transfer tube to the vigorously stirred contents of the carboxylation kettle. The rate of addition was adjusted to cause rapid discharge of the color of the lithiated polyisoprene and to result in dissolution of the lithium salt of the carboxylated polyisoprene.

To the lithium carboxylate solution was added 500 mL of 1.2 N sulfuric acid with vigorous stirring. Then 500 mL of methanol was added with gentle stirring to break the dispersion. The upper layer was washed with 300 mL of water, and layers again separated with addition of 300 mL of methanol. After three more such washes, the solution was dried with anhydrous magnesium sulfate, filtered under nitrogen pressure, and concentrated to 1398 g of solution (19.3% solids). Total solids were 270 g, which is 90% of the theoretical. The solid's content was determined by evaporating solvent from a weighed sample under reduced pressure at 50–60 °C.

The carboxyl content was determined by dissolving 6–20-g samples in 25 mL of tetrahydrofuran, previously neutralized to the phenolphthalein end point, and titrating to the phenolphthalein end point with 0.1 N tetrabutylammonium hydroxide in methanol.

Quantitative infrared analysis was used to check titration data. These carboxylated polyisoprenes absorb at 5.87 μm for the carboxyl group, 6.02 μm for the *cis*-1,4 double bond, and 6.10 μm for the 3,4 double bond. Absorbance of the carboxyl group bears a straight line relationship to the absorbance of either double bond, at least in the range where absorbance is 0–2. A plot of milliequivalents of carboxyl/gram of polymer as the ordinate vs. the ratio of absorbance at 5.87 μm (for C=O in CO_2H) to 6.02 μm (for cis C=C) as the abscissa gives the relationship $y = 9.26x$, from which carboxyl content is readily obtained.

Solutions of lithium salts of polyisoprene carboxylic acids were also converted to polyisoprene carboxylic acid solutions by stirring them with a 10 M excess of Amberlyst 15 ion exchange resin for 18 h. This was a convenient way to prepare samples for infrared analysis.

For the polyisoprene described here, GPC of the sample taken before carboxylation indicated an M_n of 67 000 and an M_w/M_n of 1.41. Values after carboxylation were M_n 62 000 and M_w/M_n 1.40. Titration gave 0.140–0.139 mequiv of acid/g of solids, which is 89% of the theoretical, and IR analysis indicated 0.131 mequiv of acid/g of solids (84% of the theoretical). Based on an M_n of 62 000 and 0.135 mequiv of acid/g, the calculated number of acid sites per chain was 8.4.

A second preparation using 333 g of isoprene, 89 mL of 0.1 N Diplit 5.1, 8.1 mL of TMEDA, and 34.6 mL of 1.25 N *sec*-butyllithium led to 318 g (95.5% of solids) of carboxylated polyisoprene of M_n 65 000 and M_w/M_n 1.46. Titration indicated 0.135–0.134 mequiv/g (86% of the theoretical), and IR analysis gave a value of 0.134 mequiv/g. From these numbers, the calculated number of acid sites per polymer molecule is 8.8.

Poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone]. The carboxylated polyisoprene solutions described above were combined (582 g of solids) and 92% of the acid neutralized by adding 71.1 mL of 1.03 N tetrabutylammonium hydroxide in methanol. The neutralized solution was diluted with 500 mL of THF and vigorously stirred and 388 g of PVL in 1 L of THF was rapidly added. After 23 min, the reaction mixture gelled. It was kept overnight under nitrogen. The gel was divided into approximately 250-g portions, each of which was blended with 400 mL of THF for about 5 min, followed by addition of 50 mL of 0.5 N hydrochloric acid in alcohol. The dispersion was then poured slowly into 1 L of alcohol and the precipitate isolated on a filter. This process was repeated two times. The washed polymer samples were combined, reblended in alcohol, isolated on a filter, and dried. Anal. Found: C, 77.48, 77.16; H, 10.28, 10.39. The carbon analysis indicates a PVL content of 38.5% (theoretical was 40% on the basis of materials charged).

GPC analysis gave a curve having a minor peak corresponding to a small amount of poly(pivalolactone) homopolymer and a major peak corresponding to the block–graft copolymer. Integration of the total curve gave an M_n of 62 000 with an M_w/M_n of 2.27. However, the major peak showed an M_n of 107 000 and an M_w/M_n of 1.44. Thus grafting of PVL did not result in any broadening of the molecular weight distribution.

The average molecular weight of the mixture of the two samples of polyisoprene was 63 639. The molecular weight added by the PVL was 39 839 for a total of 103 478, as opposed to 107 000 found by GPC. The average number of PVL segments (one for each carboxyl site) was 8.6 per chain from which the PVL polymer segment length was calculated to have a molecular weight of 4432.

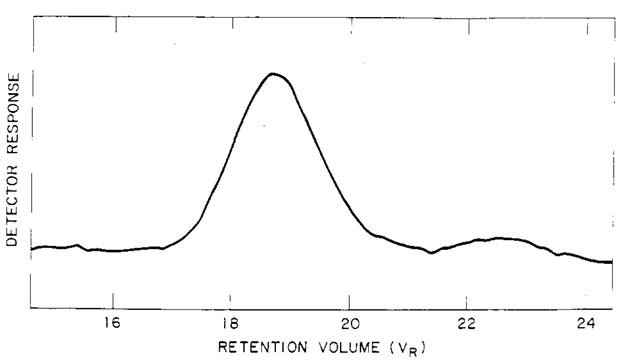


Figure 1. GPC curve for poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone]. Main peak $\bar{M}_n$ 177 000, $\bar{M}_w/\bar{M}_n$ 1.48. Minor peak $\bar{M}_n$ 5900, $\bar{M}_w/\bar{M}_n$ 1.28.

Twenty-five grams of this polymer was molded into a $^7/_8$ in. diameter spinning rod at 200 °C and melt spun at 250 °C at a wind up rate of 400 ft/min. A hand-oriented sample of fiber had a tenacity of 0.87 dN/tex (0.98 g/denier) with a break elongation of 285%.

Poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone] made from a polyisoprene of $\bar{M}_n$ 114 000 and $\bar{M}_w/\bar{M}_n$ 1.46, containing a total of 12.65 PPVL segments per polymer molecule, was prepared by the procedure described above. Analysis showed C 78.13, 78.04; H 10.42, 10.44, which corresponds to 35.75% PVL. GPC, the curve in Figure 1, showed a main peak at $\bar{M}_n$ 177 000, $\bar{M}_w/\bar{M}_n$ 1.48, and a very small peak at $\bar{M}_n$ 5900, $\bar{M}_w/\bar{M}_n$ 1.28. From percent of PVL, $\bar{M}_n$ of the polyisoprene, and the number of PPVL segments, the length of each PPVL segment was calculated to be 4992. The total weight of the PPVL segments was 12.65 × 4992 or 63 149, and addition of this number to the polyisoprene molecular weight gave 177 149 for the molecular weight of the block–graft copolymer in good agreement with the GPC value of 177 000.

Test Methods. Tensile strength and elongation were determined using an Instron Tensile Tester. The strength of the films is expressed in both mega Paschals, MPa,[13] the S.I. unit for strength, and pounds per square inch, psi, which is a more familiar term. The conversion factor is 1000 psi = 6.90 MPa. Tensile strength of fibers is given in decinewtons per tex, dN/tex (tex is the weight in grams of 10^3 m of yarn), and in grams per denier, g/denier. Stress in psi is equal to tenacity in g/d × 1.28 × 10^4 × density of the fiber. Thus, for a fiber of density of 1, 1 g/denier is equal to 12 800 psi.

DSC measurements were made on a Du Pont thermal analyzer.

GPC determination of molecular weight and polydispersity of polyisoprenes and carboxylated polyisoprenes was done on a Waters Model 200 gel permeation chromatograph equipped with four styragel columns arranged in a set to give a linear separation in molecular weight from 10^3 to 10^6. The eluting solvent was tetrahydrofuran. Calibrations were made using 272 and 17 M polybutadiene standards obtained from the Phillips Petroleum Co. GPC molecular weights of poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone] were determined on *m*-cresol solutions at 100 °C.

Results and Discussion

The effectiveness of crystalline domains of polypivalolactone (PPVL) in a matrix of polyisoprene has been studied by examination of ABA triblock copolymers, poly(pivalolactone-*b*-isoprene-*b*-pivalolactone), and ABA-*g*-A block–graft copolymers, poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone]. As will be discussed subsequently, investigations have also been made on such variations of the block–grafts as poly[isoprene-*b*-pivalolactone)-*g*-pivalolactone], BA-*g*-A, and biased polymers, which have grafts concentrated near the ends of the rubbery backbone.

ABA Triblock Copolymers. Poly(pivalolactone-*b*-isoprene-*b*-pivalolactone) triblock copolymers were made by the reaction sequence in Scheme I.

Scheme I
Synthesis of Poly[pivalolactone-*b*-isoprene-*b*-pivalolactone]

$$\text{isoprene} + \text{Li-R-Li} \longrightarrow \text{Li-polyisoprene-Li}$$

$$\text{Li-polyisoprene-Li} \xrightarrow{\text{CO}_2} \text{LiO}_2\text{C-polyisoprene-CO}_2\text{Li}$$

$$\text{LiO}_2\text{C-polyisoprene-CO}_2\text{Li} \xrightarrow[\text{2. Bu}_4\text{NOH}]{\text{1. H}^+} \text{Bu}_4\text{NO}_2\text{C-polyisoprene-CO}_2\text{NBu}_4$$

$$\text{Bu}_4\text{NO}_2\text{C-polyisoprene-CO}_2\text{NBu}_4 \xrightarrow[\text{2. H}^+]{\text{1. PVL}} \text{PPVL-polyisoprene-PPVL}$$

Table I
Orientation of Triblock Copolymer Films

$(\text{PVL})_{170}(\text{IP})_{588}$-$(\text{PVL})_{170}$[a]	tensile strength MPa	psi	% of elongation
as pressed	16.15	2340	1210
after orientation	21.6	3130	420

[a] Anal. C, 75.42; H, 9.92. PVL content calcd from C, H anal. is 46%.

Table II
High-Temperature Properties of Oriented Films of $(\text{PVL})_{170}(\text{IP})_{588}(\text{PVL})_{170}$

temp, °C	tensile strength MPa	psi	% of elongation
25	21.6	3130	420
100	12.4	1800	415

Because anything less than quantitative conversion of isoprene by the dilithio initiator to α,ω-dilithiopolyisoprene would result in an AB copolymer that could not be removed from the final product, the nature of poly(pivalolactone-*b*-isoprene) was determined first. These polymers were synthesized by the method outlined in Scheme I, except that 2-butyllithium was used in the polyisoprene-initiating step in place of the dilithio initiator. The diblock polymers obtained could be hot pressed into films, but these films were very weak. Thus, contamination of ABA triblock copolymers or block–graft copolymers with AB diblocks will lead to a dimunition of properties.

The triblock copolymers were made by Scheme I, using DiLi-3[7] as the dilithio initiator. These products consisted of a soft segment of polyisoprene, which was primarily of cis-1,4 structure, to which PPVL blocks were attached at each end. They could be pressed into films above 215 °C, and the films had good strength and very high elongation. Strength was increased and elongation decreased by orientation by drawing. This was done by stretching short of the breaking elongation, relaxing, and repeating the cycle several times. For a product composed of a polyisoprene block of $M_n \sim 40\,000$ (DP 588) and PVL segments of M_n 17 000 (46% PVL), the increase amounted to 5.45 MPa[12] or 790 psi, as is shown in Table I. Orientation also reduced the permanent set from a large number to less than 10%.

Thermal behavior of the polymer was changed by orientation. DSC measurements on as-pressed film gave a reproducible melt endotherm at 215 °C and a smaller peak at 227–230 °C. Drawn films showed only a single endotherm at 227 °C. Reheating the oriented film again gave a reproducible main peak at 215 °C and a smaller peak at 227–230 °C. After being allowed to stand for 1 week, the film showed a minor endotherm at 214 °C and a major one at 226 °C. The transitions at 215 and 226–227 °C indicate the presence of two crystalline forms. These probably correspond to the two well-known forms of pivalolactone homopolymer. Orientation apparently favors the higher melting form. It appears to be the more stable of the two, since it predominates in stored samples.

Table III
PVL Block Length in $(\text{PVL})_n(\text{IP})_{588}(\text{PVL})_n$ and Strength and Elongation Changes

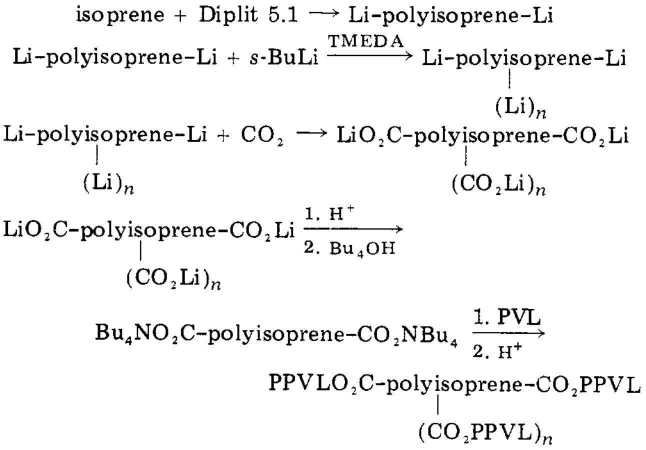
n	% PVL	tensile strength MPa	psi	% of elongation
103	34[a]	24.16	3500	765
128	39[b]	34.50	5000	485
157	44[c]	52.23	7570	285

[a] Anal. C, 78.66; H, 10.51. [b] Anal. C, 77.06; H, 10.47. [c] Anal. C, 75.67; H, 10.16

Table IV
$(\text{PVL})_n(\text{IP})_m(\text{PVL})_n$ from Polyisoprene Prepared Using Diplit 5.1

polyisoprene segment M_n	*m*	M_w/M_n	pivalolactone segment *n*	% of PVL
106 000	1560	1.53	450	46
50 000	735	1.28	166	40
50 000	735	1.28	107	30
28 000	410	1.22	95	40
48 000	705	1.32	27	10

Scheme II
Synthesis of
Poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone]



$$\text{isoprene} + \text{Diplit 5.1} \longrightarrow \text{Li-polyisoprene-Li}$$

$$\text{Li-polyisoprene-Li} + s\text{-BuLi} \xrightarrow{\text{TMEDA}} \underset{(\text{Li})_n}{\text{Li-polyisoprene-Li}}$$

$$\underset{(\text{Li})_n}{\text{Li-polyisoprene-Li}} + \text{CO}_2 \longrightarrow \underset{(\text{CO}_2\text{Li})_n}{\text{LiO}_2\text{C-polyisoprene-CO}_2\text{Li}}$$

$$\underset{(\text{CO}_2\text{Li})_n}{\text{LiO}_2\text{C-polyisoprene-CO}_2\text{Li}} \xrightarrow[\text{2. Bu}_4\text{OH}]{\text{1. H}^+}$$

$$\text{Bu}_4\text{NO}_2\text{C-polyisoprene-CO}_2\text{NBu}_4 \xrightarrow[\text{2. H}^+]{\text{1. PVL}} \underset{(\text{CO}_2\text{PPVL})_n}{\text{PPVLO}_2\text{C-polyisoprene-CO}_2\text{PPVL}}$$

A consequence of the high melting point of the crystalline pivalolactone cross-links is good retention of properties at elevated temperatures. As the data in Table II show, oriented films tested at 100 °C had roughly 60% of their room-temperature strength. Elongation at 100 °C was unchanged from that at room temperature.

The strength of these triblock copolymers varied considerably from sample to sample, probably because of the difficulties involved in reproducibly orienting films to the same degree. The copolymer described in Tables I and II had a tensile strength of 21.6 MPa, but other samples containing less PVL were stronger. The highest strength observed was 52 MPa (7570 psi) for a copolymer containing 44% PVL. These results are described in Table III and are for polymers having soft segments of $M_n \sim 40\,000$ melt pressed into films, hand oriented, and tested at 25 °C.

In addition to being melt pressed into elastic films, these polymers were melt spun into elastic monofilaments. Compositions containing 34 to 42% pivalolactone gave fibers that, after orientation, had tenacities of 0.29–0.63 g/denier at elongations of 370–430%. Since these fibers have a density approximately equal to 1, conversion of fiber tenacities into psi shows the fibers to be comparable in strength to the film strips.

Triblock copolymers have also been made using Diplit 5.1 in place of DiLi-3 as the bifunctional initiator for polymerizing isoprene. The poly(pivalolactone) blocks were attached to the polyisoprene by the same series of reactions as those in Scheme I. The products had B blocks of M_n 28000 to 100000 and 30–46% pivalolactone (see Table IV).

Block-Graft Copolymers. Poly[(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone] have been prepared by the series of reactions depicted in Scheme II.

Polymerization of isoprene with Diplit 5.1 in the first step gave α,ω-dilithiopolyisoprenes that were 92% 1,4 and had $\bar{M}_w/\bar{M}_n$ values generally in the 1.3 and 1.6 range. Isoprene polymerization was taken to as high a conversion as possible to reduce unreacted isoprene to a minimum. This is to reduce or eliminate complications that would be caused by addition of *sec*-butyllithium to isoprene in the second step to form an initiator that would form PVL homopolymer in the last step. As will be seen shortly, very little homopolymer was present in the block–graft copolymers.

To develop sites for grafting, the polyisoprene was reacted with *sec*-butyllithium in the presence of tetramethylethylenediamine (TMEDA) in a second step. TMEDA serves two functions. It reduces the viscosity of the solution and it increases the basicity of butyllithium through coordination of the lithium by the amino groups to the point where it is capable of replacing hydrogen with lithium at allylic positions in polydienes. As mentioned earlier, Tate et al.[14] used this reaction to metalate polybutadiene and polyisoprene in their preparation of polydiene polymers grafted with polystyrene. Replacement of allylic hydrogen is strongly favored over addition of the organometallic to the double bond. Salinger and Dessy[15] showed that allyl carbanions are much more stable than those of tertiary, secondary, and primary alkyl groups. Thus, even if a carbanion of a saturated grouping should form first, it would immediately exchange with allylic positions.

The lithio sites formed along the diene chain were then converted into PVL grafting sites by reaction with carbon dioxide in the third step.

It is important to prevent incursion of air or moisture during the first three steps in Scheme II. Failure to do so will result in loss of lithio sites and, therefore, of grafting sites. In the third step, it is important to maintain an excess of carbon dioxide to reduce the chance of chemical cross-linking through reaction of carboxylated sites with unreacted lithio sites. Such chemical cross-linking would result in formation of a gel that has a deleterious effect upon subsequent molding and spinning.

The efficiency of the combined lithiation and carboxylation steps, which is the percent of carboxyl groups formed per molecule of complexed *sec*-butyllithium, ranged between 60 and 90%.

The fourth step involves conversion of the carboxylate polyisoprene to tetrabutylammonium salts and use of these salts to initiate polymerization of pivalolactone. The product was shown by GPC to be the block–graft copolymer contaminated with a very small amount of pivalolactone homopolymer. The block–graft copolymer showed a Poisson molecular weight distribution (see Figure 1) with an $\bar{M}_w/\bar{M}_n$ very close to that of the parent polyisoprene. Within experimental error, the molecular weight of the block–graft copolymer as determined by GPC was the same as that calculated from the $\bar{M}_n$ of the polyisoprene plus the amount of grafted pivalolactone. It is assumed the pivalolactone homopolymer was formed as a result of a small amount of butyllithium from the lithiation step that would have been converted to butyric acid and thence to tetrabutylammonium butyrate. The $\bar{M}_n$ of this homopolymer was practically the same as the molecular weight calculated for the PPVL segments in the block–graft copolymer.

Scheme III
Biased Polymers with Polystyrene Near the Ends

$$\text{BuLi} \xrightarrow{\text{styrene}} \text{Bu-Polystyrene-Li} \xrightarrow{\text{isoprene}}$$

$$\text{Bu-polystyrene-polyisoprene-Li} \xrightarrow{\text{styrene}}$$

$$\text{Bu-polystyrene-polyisoprene-polystyrene-Li}$$

In addition to random grafting of poly(pivalolactone) segments, polymers in which grafting was concentrated near the ends of the polyisoprene chain were also examined. These were made from biased copolymers from isoprene and either styrene or 4-methylstyrene, using the reaction sequence illustrated in Scheme III. This method is a modification of Karoly's[16] procedure for preparing poly[styrene-*b*-butadiene-styrene] triblock copolymers. He describes addition of diene midway during the polymerization of styrene whereupon styrene stops polymerizing and diene polymerization begins. When the diene has been consumed, then styrene starts to polymerize again. This behavior is a consequence of the large difference in the isoprene/styrene reactivity ratio, r_1/r_2 of which has been reported to be 5.8/0.03.[17]

The product from Scheme III was then lithiated, carboxylated, converted to a tetrabutylammonium salt, and reacted with pivalolactone in the same manner as in the earlier cases. Because benzylic carbanions are more stable than allylic carbanions,[15] metalation preferentially takes place in the polystyrene part of the copolymer molecule. Thus, on average, more grafting sites are developed near the ends of the polyisoprene than along the chain.

A third variation was one in which lithio was on one end but not the other. In this case, isoprene was initiated with butyllithium to give Bu(–isoprene–)$_n$Li in the first step and then treated by the other steps as in Scheme II.

Properties of Block–Graft Copolymers. The makeup of the block–graft copolymers is complex and raises questions about what part or parts of the molecule are most responsible for strength and other properties. The factors include the PVL content, the length of the rubbery segment, the distance between grafts or soft segment length (SSL), the presence of PPVL blocks at both ends of the polyisoprene, the length of the PPVL blocks or hard segment length (HSL), and concentration of PPVL blocks near the ends of the rubbery blocks. To find out which of these are most important, the polymers were spun into fibers, and the fiber properties were studied.

For an elastic polymer to be spinnable, it must be free of gel. Otherwise melt fracture is so severe that spinning is not feasible at any temperature even at slow extrusion rates, hence the emphasis on avoidance of chemical cross-links in the carboxylation step during polymer synthesis. Our polymers spun smoothly at 250–260 °C at reasonable windup rates when the polyisoprene block had M_n of 95000 or less and M_w/M_n of 1.5 or less. At higher molecular weights and broader distributions of molecular weights, spinning was much less satisfactory.

As described earlier for ABA triblock copolymers, all of the fibers were oriented by drawing. Various heat treatments were tried on oriented fiber, but these had little detectable effect. Accordingly, the bulk of our work was done on fibers that were oriented but not annealed.

Table V
$(PVL)_n(IP)_m(PVL)_n[(PVL)_n]_o$
Variation in PVL Content[a]

% of PVL	T_B dN/tex	T_B g/denier	E_B, %
25	0.62	0.7	590
35	0.79	0.9	425
40	0.88	1.0	340
45	0.88	1.0	295
50	1.06	1.2	205

[a] $m = 588\text{-}1350$; $n = 52\text{-}254$; $o = 3.5\text{-}13.5$.

Table VI
Variation in M_n of B Block for Block-Graft Copolymers Containing 35% PVL

M_N range	T_B dN/tex	T_B g/denier	E_B, %
40000-50000	0.79	0.9	420
50000-60000	0.84	0.95	450
60000-70000	0.79	0.9	400
70000-80000	0.79	0.9	420
over 80000	0.79	0.9	440

Table VII
Variation in Number of PPVL Segments

no. of segments	T_B dN/tex	T_B g/denier	E_B, %
3-4	0.71	0.8	485
4-6	0.76	0.86	453
6-8	0.83	0.94	438
8-10	0.82	0.93	394
10-12	0.84	0.95	405
>12	0.74	0.84	390

Table VIII
Biased Block-Graft Copolymers

B block: M_n for polyisoprene	B block: M_n for styrene block	% of PVL	no. of PPVL segments	T_B dN/tex	T_B g/denier	E_B, %
44 000	416	40	6.7	0.35	0.4	405
44 000	0	40	6.7	0.35	0.4	373
76 000	832	32	8.3	0.71	0.8	360
76 000	0	35	8.6	0.66	0.75	400

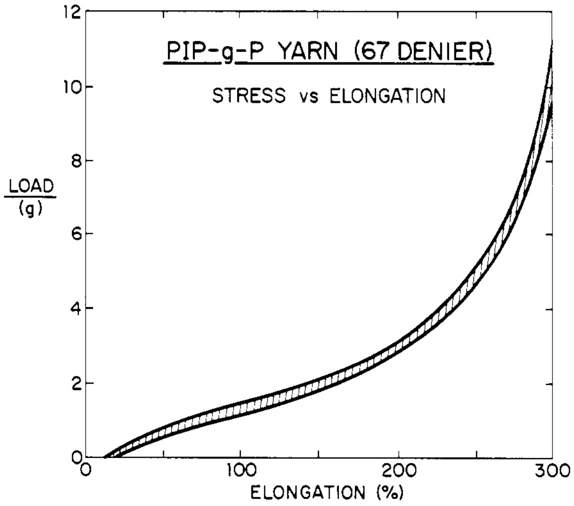


Figure 2.

Of the factors affecting properties, PVL content appears to be the most important. Table V shows data obtained on oriented fibers from polymers made from polyisoprenes of M_n 40 000–92 000, having 3.5–13.5 hard segments, with hard segment lengths of 5200–25 400. Strength is shown in S.I. units, dN/tex, and also in the more familiar grams/denier. As the data show, strength increases with PVL content, though increases obtained for amounts above 35% are only marginal. Elongation decreases regularly with increase in PVL content. The values given at each level of percent of PVL are averages of at least four different samples.

M_n of the polyisoprene part of the block–graft copolymer appears to have little effect on properties if this value is above 40 000. Table VI shows data on products containing 35% PVL varying in M_n from 40 000 to 92 000 and having 3.5 or more PPVL segments per chain. These are averages of four or more samples for each molecular weight range. Strength and elongation were the same over the entire range.

Similarly, the number of PPVL segments, and by inference the soft segment length and hard segment length, have very little influence on strength and elongation. This is illustrated by Table VII, which contains results on block–graft copolymers containing 35% PVL distributed in 3 to over 12 segments and having polyisoprene backbone lengths of M_n 40 000 to 80 000. Strengths and elongations did not vary significantly over this range of composition.

Biased polymers containing short segments of polystyrene at each end were prepared to find out if concentrating PPVL hard segments at the ends changed properties. These polymers were thought to have these segments near the ends because of the susceptibility of benzylic protons in the polystyrene part to replacement of lithium by the butyllithium–TMEDA reagent. Thus, these products have PPVL grafts on the ends and near the ends. Their properties, however, were not better than the nonbiased copolymers. Comparisons are shown in Table VIII.

The tenacities of both types of M_n 44 000 polymers were lower than expected. This result is probably related to the fact that these polymers were made early in the program before better techniques were worked out. The M_n 76 000 polymers, which were synthesized later, were near the strength range expected on the basis of the data in Table VI.

Poly[(isoprene-*b*-pivalolactone)-*g*-pivalolactone] copolymers, BA-*g*-A, also appeared to have properties roughly comparable to the ABA-*g*-A type. BA-*g*-A block–graft copolymers containing 35% PVL and having polyisoprene backbones of M_n 42 000 to 89 000 varied in tenacity from 0.6 to 1.06 g/denier at elongations of 370 to 450%. Averages for 11 different polymers were a tenacity of 0.82 g/denier and an elongation of 410%.

Since a tenacity of 1 g/denier corresponds to a strength of 12 800 psi for a fiber of density 1, these block–graft copolymers are much stronger than sulfur-cured natural rubber. In addition, they have very high resilience. This is illustrated in Figure 2, which shows the stress–strain relationship for a 35% PVL ABA-*g*-A yarn. The top curve was obtained as load was applied, and the bottom curve was generated as load was removed. The area between the curves represents work lost and amounts to 13% of the total area under the top curve. Thus, work recovered, or resilience, was 87%, which compares very favorably with sulfur-cured natural rubber.

Stress decay of ABA-*g*-A block–graft copolymers was found to be as good as or better than that of the sulfur-cured natural rubber. Decay was measured by stretching filaments 300% and noting the stress required to maintain this extension as a function of time. As is illustrated in Figure 3, stress decay for an ABA-*g*-A block–graft copolymer containing 34% PVL was no greater in a 20-h

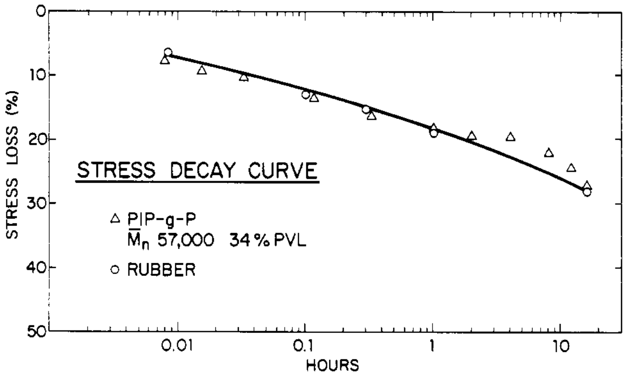


Figure 3.

period than that of strips of a sulfur-cured gum natural rubber. These data together with resilience and stress–strain behavior indicate that the crystalline cross-links in oriented ABA-*g*-A block–graft copolymers of pivalolactone and isoprene are as effective as are the chemical cross-links.

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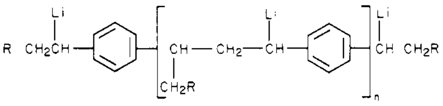

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Graph Theory and Molecular Distribution. 2. Copolycondensation of A-Group Polyfunctional Monomers with B-Group Polyfunctional Monomers

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ABSTRACT: The development in part 1, based on graph theory, is extended to the derivation of distribution functions for systems composed of different monomers bearing A-functional groups together with different monomers bearing B-functional groups (systems of order II); the A group can react only with the B group and vice versa. These distribution functions are identical with those established by Stockmayer, using generating functions.

Some years ago, in order to examine cases more general than those dealt with in previous studies,[1-6] Stockmayer[7,8] proposed a generalized distribution function for a variety of monomers bearing A-functional groups which can only react with a variety of monomers bearing B-functional groups (systems of order II[9]). The calculations involved in establishing this distribution function are tedious, particularly in the determination of Lagrangean multipliers.

Later on, Gordon and co-workers[10,11] showed that the distribution function could be calculated by using the theory of stochastic branching processes.[12] But this technique involves abstract mathematics and requires deriving probability generating functions; the method is quite general but rather difficult to use.

In the preceding paper,[13] we showed how graph theory allows one to obtain directly and readily the molecular distribution functions in the most general system of order I,[9] i.e., consisting of various monomer units with different functionalities, all sites being identical and equireactive. The purpose of this paper is to establish general molecular distribution functions in the case of order II systems by the same methods.

System Model

Consider a general system of order II[9] initially composed of *M* moles of monomers partitioned in *A* moles of A monomers (i.e., monomers bearing only functional groups A) and *B* moles of B monomers (i.e., monomers bearing only functional groups B). This type partition of the or-

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