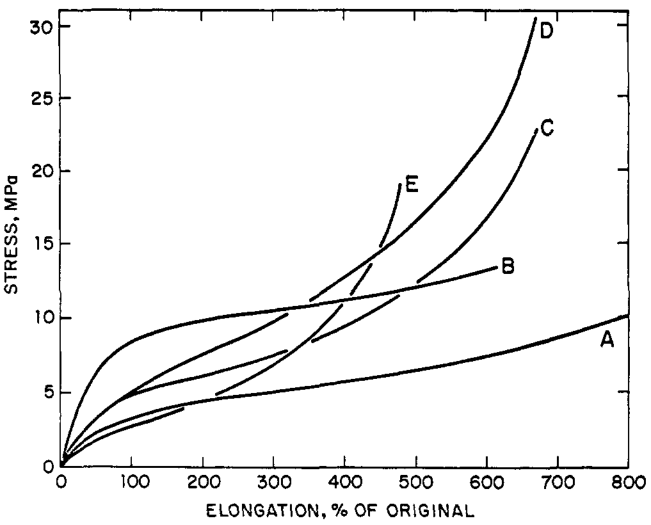

Figure 3. Stress–strain behavior of the graft copolymers identified in Table II. 1 MPa = 145 psi.

Table II
Composition and Selected Properties of Elastomeric Polypivalolactone Graft Copolymers

	Base polymer	SSL, mol wt	HSL, mol wt	Poly-PVL, wt %	T_m,[a] °C	Comp[b] set, %
A	Poly(ethyl acrylate)[c]	14 800	3700	20	195	17
B	Poly(chloroprene-*co*-methacrylic acid)[d]	3 740	1500	29	170	25
C	Poly(ethylene-*alt*-ethyl acrylate)[e]	5 000	1500	23	170	11[f]
D	Poly(ethylene-*co*-propylene-*co*-1,4,-hexadiene)-*g*-thioglycolic acid[g]	4 300	1300	26	180	23
E	Poly(ethylene-*co*-propylene-*co*-1,4-hexadiene)[h,i]					27

[a] Melting endotherm peak as determined by DSC analysis. [b] ASTM D-395, method B. All specimens were annealed 24 h at 120 °C prior to testing. [c] $\bar{M}_w \simeq 10^6$. [d] $\bar{M}_w > 100\,000$, 2.7 wt % methacrylic acid. [e] η_{inh} (0.1% in $CHCl_3$) = 2.5. [f] After 22 h at 70 °C. [g] Base polymer had the composition of sample E before addition of thioglycolic acid. Thioglycolic acid content was 2.1 wt %. [h] $\bar{M}_w \simeq 80\,000$; 55 wt % ethylene, 40 wt % propylene, 5 wt % 1,4-hexadiene. [i] Compounded and cured by conventional sulfur recipe for good compression set.

Because of the thermal integrity of the crystalline polyester tiepoint, high-temperature properties are excellent, especially in comparison to known thermoplastic elastomers. At 100 °C 65–95% of room-temperature strength at 100–300% elongation is maintained. Resistance to compression set[13] at elevated temperature is particularly good, as shown by the data of Table II. Permanent deformation is lower than that of a conventionally cured elastomer (sample E). This indicates very little network rearrangement under the combined effects of stress and temperature.

Other outstanding properties (solvent resistance, resilience, abrasion resistance, heat, and aging stability) seem related to the morphology of these unique graft copolymer systems, and will be the subject of further publications.

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(13) In this important test a specimen is held under 25% compression, heated 70 h at 100 °C, cooled, and allow to relax, and permanent deformation is expressed as a percent of the original 25% compression.
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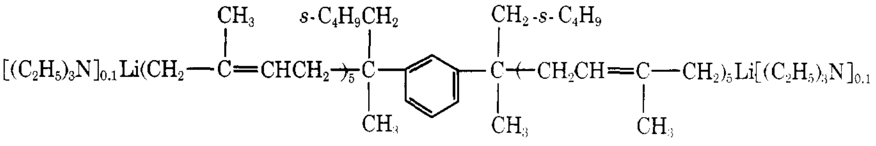
Block and Graft Copolymers of Pivalolactone. II. ABA and ABA-*g*-A Copolymers with Dienes

Introduction of crystalline tie points[1] by use of pivalolactone (PVL) as the A block monomer in ABA triblock copolymers and ABA-*g*-A block-graft copolymers has demonstrated that thermally reversible cross-linking by interchain crystallization can be just as effective as chemical cross-linking. We have found that such compositions, in which the B segments are a polydiene, are unusually strong and have exceptionally stable cross-links.

The ABA products have been made from α,ω-dithio-*cis*-1,4-polydienes obtained by polymerization of isoprene or butadiene with a difunctional lithium initiator. The base polymer was prepared by polymerization of the diene in cyclohexane solution under strictly anhydrous conditions using an amount of difunctional initiator calculated to give the desired molecular weight. Polymerizations were carried out at 60 °C and were usually complete in less than 2 h. Then the reaction mixture was diluted with tetrahydrofuran and through it was bubbled a vigorous stream of dry carbon dioxide.[2] Excess carbon dioxide was removed, tetrabutylammonium hydroxide in methanol was added, and the polymer was precipitated in ethanol. The precipitated polymer was washed with ethanol, and the ethanol was removed and redissolved in tetrahydrofuran. Pivalolactone was added whereupon polymerization proceeded almost immediately and eventually gelled the solution. The gel was broken up in ethanol, acidified with acetic acid, washed well with ethanol, and dried to give PVL–isoprene–PVL triblock copolymer.

Block-graft copolymers were made by post-lithiating α,ω-dilithio-*cis*-1,4-polydienes by reaction with *n*-butyllithium at 55–60 °C or *sec*-butyllithium at 25 °C in the presence of tetramethylethylenediamine.[3] This method has been used earlier to introduce dilithio sites at allylic positions along a polydiene chain.[4] The lithiated polydiene was carboxylated by adding this solution to vigorously stirred tetrahydrofuran through which dry carbon dioxide was bubbled. This involved transfer of the polymer solution from the flask in which it was prepared through a dry tube into a second flask containing tetrahydrofuran. Conversion of carboxylated salts to tetrabutylammonium salts and use



$$[(C_2H_5)_3N]_{0.1}Li(CH_2-\overset{CH_3}{C}=CHCH_2)_5\underset{CH_3}{\overset{s\text{-}C_4H_9CH_2}{C}}-C_6H_4-\underset{CH_3}{\overset{CH_2\text{-}s\text{-}C_4H_9}{C}}(CH_2CH=\underset{CH_3}{C}-CH_2)_5Li[(C_2H_5)_3N]_{0.1}$$

I

of the salts to polymerize pivalolactone was done as described above.

Difunctional initiators used include DiLi-3,[5] which was obtained from the Lithium Corporation of America, and a new product we have made designated as Diplit 5.1 (I). DiLi-3 is made by addition of *sec*-butyllithium to divinylbenzene in the presence of triethylamine and has a functionality slightly over 2. We have made Diplit 5.1 (I) by addition of *sec*-butyllithium to *m*-diisopropenylbenzene in the presence of 0.1 equiv of triethylamine followed by addition of 5 equiv of isoprene. I is, within experimental accuracy, bifunctional.

ABA triblock copolymers containing 35–45% of pivalolactone were made from polyisoprenes of $M_n \sim 40\,000$ prepared using DiLi-3. Films pressed from these polymers at 215 °C and higher were tough and elastic. Strips cut from these films could be cold drawn when subjected to stress and became stronger and more elastic. When stretched and then relaxed and stretched again through a number of cycles, they became oriented and increased greatly in strength. Examples of properties of oriented films are given in Table I. Fibers melt spun at 215 °C and hand drawn were also strong and very elastic. A triblock copolymer containing 42% PVL had a tenacity (breaking stress) of 0.63 g/d[7] and an elongation at break of 430%.

Block-graft copolymers were made from polyisoprenes prepared using Diplit 5.1 as the initiator. These were compositions containing 15–50% PVL distributed as 5–18 segments per isoprene chain, with each segment having a DP of 12–90. The segments were attached to polyisoprene backbones of $\bar{M}_n$ = 35 000–90 000. The polymers could be melt-spun into fibers at 240–280 °C, which, after orientation by hand drawing, had tenacities as high as 1–1.5 g/d with elongations at break of 150–450%. Highest strengths were obtained with compositions having 35% PVL and higher. Typical values are given in Table II.

Table I
Properties of Pivalolactone–Isoprene ABA Triblock Copolymers

PVL		Tensile strength, MPa[6]	Elongation at break, %
Wt %	DP		
34	103	24.15	765
39	111	34.5	485
44	121	52.23	285

Table II
Properties of Block–Graft Copolymers

PVL Wt %	Polyisoprene $\bar{M}_n$	PVL segments		T_B, g/d	Elongation at break, %
		No.	DP		
25	60 000	4	60	0.4	660
35	53 000	4.8	60	0.6	400
35	52 000	6.1	46	0.9	480
35	75 000	11	37	0.9	450
35	92 000	11	47	0.9	430
40	57 000	6.6	57	1.0	440
41	60 000	18	32	0.8	300
49	67 000	13	48	1.68	160
50	59 000	6.5	90	0.85	210
51	60 000	18	49	1.38	170

Fibers protected against oxidation with phenyl-β-napthylamine were examined for cross-link stability by a long-term stress-decay test. This involved keeping the fiber extended 300% and noting decrease in stress with time. In 20 h, stress dropped about 20%. Since this decrease was the same as obtained with a control of sulfur-cured gum natural rubber, it can be inferred that the crystalline cross-links are comparable in stability to chemical cross-links.

A more detailed account will be published later.

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(7) Stress and moduli of fibers are customarily expressed in grams per denier (g/d). Denier is the weight in grams of 9000 m of the fiber.
(8) Contribution No. 2304.

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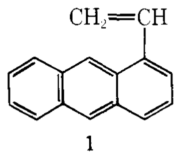
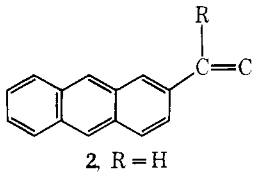
1. Polymerization of Vinylanthracene Monomers

The polymerization of 9-vinylanthracene has been studied by a number of authors[1-5] and a review article has been published[6] on this unique monomer. The 1- and 2-vinylanthracenes are also known but there has been very little published on their polymerization characteristics.[3,5,7] One universal conclusion that can be drawn from all these investigations is that high molecular weight, soluble polyvinylanthracenes cannot be synthesized by standard free radical or ionic polymerization procedures.

From a review of the above publications, the maximum degree of polymerization (dp) achieved in the polymerization of 1- and 2-vinylanthracene has been in the range of 5–20. The polymers were reported to possess the conventional 1,2 structures. In the case of 9-vinylanthracene, higher molecular weights have been claimed, dp ~ 25–35, but the polymers were reported to be mixtures of both 1,2 and 1,6 structural units:



1



2, R = H
3, R = CH_3

The intrinsic problems associated with achieving high molecular weight products from free radical and ionic poly-