

Styrene–Diene–Lactone Block Copolymers

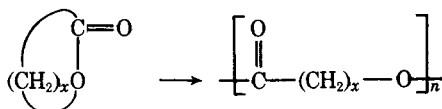
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Synopsis

By use of butyllithium as initiator and by incremental addition of monomers, block polymers of styrene, butadiene, and lactone can be prepared. Polymerization of ϵ -caprolactone involves the displacement by base on the carbonyl carbon with the formation of an alkoxide endgroup. To polymerize lactone with poly(butadienyllithium), it is best to convert the carbon–lithium chain ends to alkoxide ends first. Styrene–butadiene–lactone terpolymers of high butadiene contents are thermoplastic rubbers. They have raw tensile strength equal to S–B–S triblock copolymer. Caprolactone-containing samples have unusually good ozone resistance; those prepared with the β -lactone of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid have much improved hot tensile strength. Terpolymers of low butadiene content are clear thermoplastic resins. Polymer of 20–20–60 (styrene–butadiene–caprolactone) polymer has raw properties similar to those of balata. It has high tensile, high tear strength, and similar hardness at room temperature, but higher softening point. Polymer alloy formed by mixing styrene–acrylonitrile copolymer and styrene–butadiene–caprolactone terpolymer has high tensile strength and excellent Izod impact. It compares favorably with ABS resin made by latex graft polymerization.

INTRODUCTION

Lactones (cyclic esters) of various structures can be polymerized to yield polyesters represented by the following reaction:



The readiness of lactones to polymerize and depolymerize varies with ring size. Four-, six-, seven-, and eight-membered rings are readily homopolymerized by a variety of catalysts. Five-membered cyclic esters, such as γ -butyrolactone, exhibit little tendency to form homopolymer. Polyesters of four- and six-atom lactones depolymerize readily at 100°–150°C. Polymer of β -propiolactone (four-atom ring) degrades to acrylic acids, and poly(δ -valerolactone) (six-ring lactone) reforms cyclic esters. Polyester from ϵ -caprolactone (seven-ring lactone) does not readily depolymerize and resembles polyesters derived from higher ω -hydroxy acids.

The use of initiating species is required in most polymerizations of lactones. Active initiators include both anionic and cationic species. A wide variety of compounds is reported to initiate the polymerization of ϵ -caprolactone. Active catalysts include water,¹ aluminum alkyls,² aluminum trialkoxides,³ metal alkyls of Groups Ia, IIa, IIb, or IIIa,⁴ Grignard reagents,⁵ metal amides,⁶ alkaline earth, aluminum, or boron hydrides,⁷ alkali metal alone,⁸ metal hydrides,⁹ alcohols, amines, or amino alcohols,¹⁰ glycols in the presence of acid,¹¹ Lewis acids,¹² tin, lead, or manganese compounds,¹³ and ester interchange catalysts.¹⁴

Butyllithium is known to initiate the polymerization of dienes and vinylaromatics, and products of novel structures and properties may result by formation of copolymers and terpolymers of diene, vinylaromatic, and lactone. It has been reported that a mixture of low molecular weight polyester, high molecular weight polyester, a small amount of polystyrene, and polystyrene-polyester block copolymer were formed when ϵ -caprolactone was added to the living polystyrene initiated with sodium-naphthalene complex.¹⁵ Copolymers of pivalolactone and isoprene or butadiene have been described in recent years.^{16,17} This report concerns some of our work in the synthesis of block terpolymers of styrene, butadiene, and lactone, primarily ϵ -caprolactone, and describes the unique properties of these terpolymers.

EXPERIMENTAL

Reagents. The solvent, cyclohexane (Phillips polymerization grade), was dried by countercurrent scrubbing with prepurified nitrogen, followed by passage over activated alumina. Phillips special-purity butadiene was distilled through activated alumina and condensed in a cylinder containing Drierite. Styrene, refluxed with CaH_2 , was vacuum distilled. ϵ -Caprolactone (Union Carbide) and 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid β -lactone (Eastman Chemical) were vacuum distilled from a 2% solution of toluene 2,4-diisocyanate. *sec*-Butyllithium in heptane was purchased from Foote Mineral Company.

Polymerization. Polymerizations were carried out in unused beverage bottles which had been cleaned and air dried at 60°C. Cyclohexane was first added to each bottle under a nitrogen blanket, the prepurified nitrogen was dispensed through a fitted glass tube and purged through the solvent at the rate of 3 l./min for 3 min in an effort to remove residual amount of moisture and air. The bottle was capped with toluene-extracted self-sealing rubber gaskets and perforated metal caps having three holes. Styrene was added directly to the solvent from a calibrated syringe followed by *sec*-BuLi to initiate polymerization. To prevent any possible leakage into the bottle cap in the bath, 170 kPa (~ 1.7 atm) of prepurified nitrogen pressure was introduced into the bottle after the monomer and initiator had been added. The bottles were then tumbled in a 70°C constant-temperature bath for 40 min and cooled to below 40°C. Butadiene was then added from a calibrated dispenser. The bottles were then tumbled in the 70°C bath for 1 hr. Small amounts of ethylene oxide or ϵ -caprolactone were added and followed by the addition of ϵ -caprolactone. The bottles were again tumbled in the 70°C bath. Reactions were shortstopped with 1 phr of 2,2-methylenebis(4-methyl-6-*tert*-butylphenol). Polymers were isolated by coagulation with isopropyl alcohol, except for homopolymer of lactone, which was recovered by evaporation of diluent. All samples were vacuum dried at 60°C.

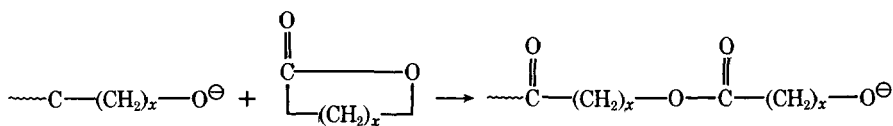
Polymer Alloys. Styrene-butadiene-caprolactone block terpolymer was blended with styrene-acrylonitrile copolymer (75/25 random copolymer, Tysil 767). Polymers were fluxed together in Brabender Plastograph rotating at slow speed (less than 10 rpm) under a nitrogen atmosphere. They were then premixed at 100 rpm for 3 min. Dicumyl peroxide was added, vacuum was applied, and polymers were mixed for an additional 7 min.

Analysis. Inherent viscosity was measured in chloroform at 25°C. Hydroxyl was determined by the perchloric acid catalyzed method,¹⁸ and carboxy content

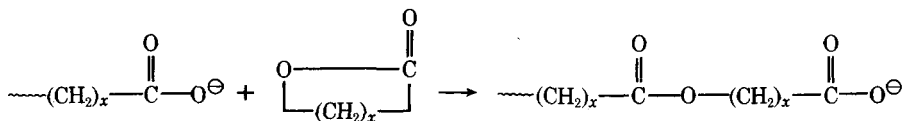
was found by titration with sodium methoxide using thymol blue as indicator.¹⁹ Soxhlet extraction was carried out using both the screen and thimble methods with acetone or cyclohexane as solvent. For polymers of this investigation the screen method is preferred because of its higher accuracy and precision. GPC analysis was performed using the Waters gel permeation chromatograph.

RESULTS AND DISCUSSION

The mechanism of anionic polymerization of lactones is most likely to resemble the mechanism for saponification of ordinary esters. Thus, it involves the second-order displacement by base on the carbonyl carbon, with the formation of an alkoxide endgroup. The alkoxide formed in the initial step would attack the carbonyl carbon of the monomer, and the lactone ring opened to regenerate the alkoxide endgroup²⁰:



Another plausible mechanism is one which allows the growing polymer to possess a carboxylate terminal group. This path would require the less common alkyl oxygen fission to occur:



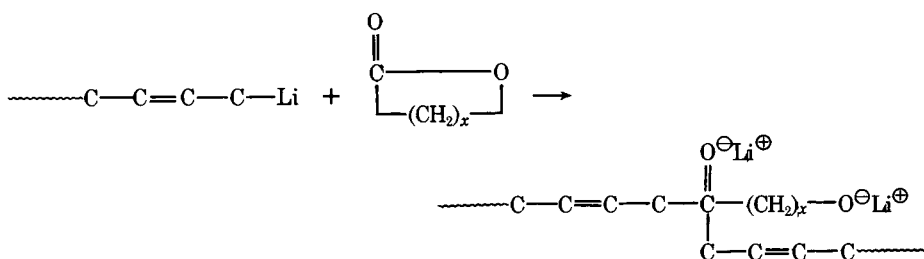
High yields of polyester are formed when butyllithium is reacted with ϵ -caprolactone. The products varied from waxy solid (mp = 55°C, η_{inh} = 0.21) to leather-like solid (mp = 67°C, η_{inh} = 1.17). ϵ -Caprolactone (25 mmoles) was added to a 4000 molecular weight polybutadiene which was initiated with butyllithium (25 mmoles) to determine the nature of the resulting endgroup. Hydroxyl content was found to be 0.38% (calculated value is 0.42%), with no measurable carboxyl group. This supports the mechanism which involves acyl oxygen cleavage. We successfully prepared polydiene-polyester and polystyrene-polyester block copolymers by using butyllithium as initiator and by polymerizing vinyl monomer first followed by addition and polymerization of lactone.²¹

It was necessary to demonstrate that a mixture of homopolymers is not formed when lactone is added to polybutadienyllithium. A solution blend of polybutadiene and polylactone was prepared from homopolymers made at the same BuLi level as the block copolymer. The dry product was a separable mixture of homopolymers with liquid polydiene covering the surface of solid polylactone. Polymer prepared by incremental addition of monomers was a homogeneous, white solid and differed greatly in appearance from the solution blend. This result suggested that the polymer was mostly a true copolymer and to verify this the solubility of the polymer was compared to that of a solution blend of poly-

lactone and polybutadiene. Acetone and cyclohexane were chosen as solvents to distinguish copolymer from mixture. Polylactone is soluble in acetone and insoluble in cyclohexane, and just the opposite is true for polydiene. A comparison of product with solution blend is given in Table I. The polymer was almost completely extracted into cyclohexane, but only a small amount was extracted in acetone. The solution blend was extracted almost equally into either solvent. The large difference in extraction behavior between product and mixture proves a true block copolymer is formed by incremental addition of diene and lactone.

Although block copolymers can be made by this procedure, we found it is much better to convert the carbon-lithium chain ends to alkoxide ends before the addition of the lactons. Reagents such as ethylene oxide, propylene oxide, epichlorohydrin, propionaldehyde, methyl isobutyl ketone, etc., can be used to react with polymer lithium to give the desired alkoxide ends.^{22,23} This modified procedure yields block copolymer at lower catalyst levels than possible with the original procedure, and furthermore it produces less homopolymer of ϵ -caprolactone (less than 7% acetone extractable from a 50/50 copolymer).

It was apparent to us then that we could simply convert polymer lithium to polymer oxylithium prior to the addition of lactone monomer by using the lactone itself as the reagent. We soon learned that lactone, such as ϵ -caprolactone, serves as coupling agent under this condition:



Thus, (styrene)_m-(butadiene)_n-Li will react with ϵ -caprolactone to form mostly the coupled product, which is a S-B-C-B-S block copolymer, in which C is a

TABLE I
Verification of Block Copolymer Formation

Filtration		
Sample	Solvent	Extracted, %
Blend ^a	acetone	54
Block ^b	acetone	8
Blend ^a	cyclohexane	40
Block ^b	cyclohexane	98
Soxhlet Extraction		
Sample	Extracted (acetone), %	Infrared of extract
Blend ^a	44	poly(ϵ -caprolactone)
Block ^b	9	poly(ϵ -caprolactone)

^a Blend of 50 parts polybutadiene and 50 parts poly(ϵ -caprolactone).

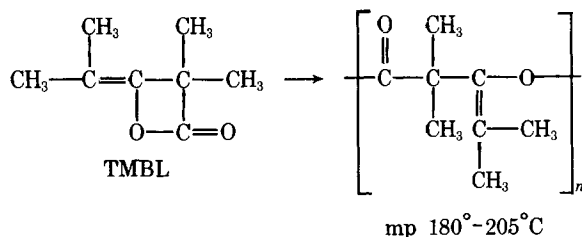
^b 50 Parts butadiene was polymerized first, and then 50 parts of ϵ -caprolactone was polymerized.

minor component, with characteristic and much discussed high raw tensile strength.²⁴ However, the coupled polymers contain alkoxide groups and can initiate the polymerization of lactone.

ϵ -Caprolactone distilled from toluene 2,4-diisocyanate yields high molecular weight block copolymers with butadiene or styrene, but undistilled lactone generally gives low molecular weight homopolymer in high yield. Isocyanate is an efficient drying agent and can react with hydroxy and carboxy compounds present in lactone monomer. We have shown that acids and alcohols function as chain transfer agents under conditions of block copolymer formation. We also found later that the lactone distilled from toluene 2,4-diisocyanate contained some of the diisocyanate which turned out to be an important ingredient in the preparation of "good" block copolymer.²⁵

The ϵ -caprolactone polymerization rate is very high, and long reaction time leads to the breakdown of block copolymer and the formation of low molecular weight homopolymer (Table II and Figs. 1 and 2).

We also polymerized other lactones such as β -propiolactone and 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid β -lactone (TMBL) with lithium alkoxide, and both were investigated in block polymer formation:



Terpolymers containing distinct segments of styrene, butadiene, and lactone received most of our attention. These polymers varied from rubbers with high raw strength, to leather-like materials, to clear, thermoplastic resins. This depends on monomer ratios as well as type of lactone used. Some of their properties and utilities are shown in Tables III to VI.

TABLE II
 ϵ -Caprolactone Polymerization Rate Study^a

Reaction time, min	Evaporation		Alcohol coagulation	
	Conv., ^b %	Inherent viscosity	Conv., ^b %	Inherent viscosity
1	98	1.23	96	1.35
3	100	1.28	97	1.44
5	100	1.22	97	1.45
10	100	1.27	97	1.46
20	100	1.15	94	1.35
40	99	1.22	94	1.40
60	97	1.18	92	1.39
180	98	1.05	87	1.23
360	95	0.93	84	1.12

^a Styrene (25 parts) was polymerized first with *sec*-BuLi in cyclohexane and then followed by 50 parts butadiene. ϵ -Caprolactone (0.3 part) was added to form coupled polymer with alkoxide sites, and then 24.7 parts ϵ -caprolactone was added at 70°C.

^b Overall conversion (minimum would be 75%).

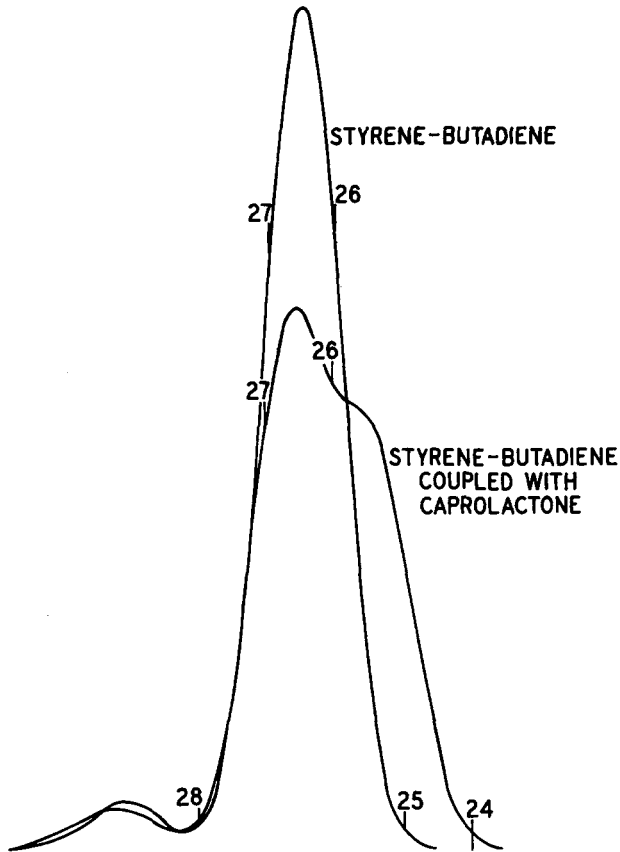


Fig. 1. Effect of caprolactone coupling on molecular weight distribution of styrene-butadiene block.

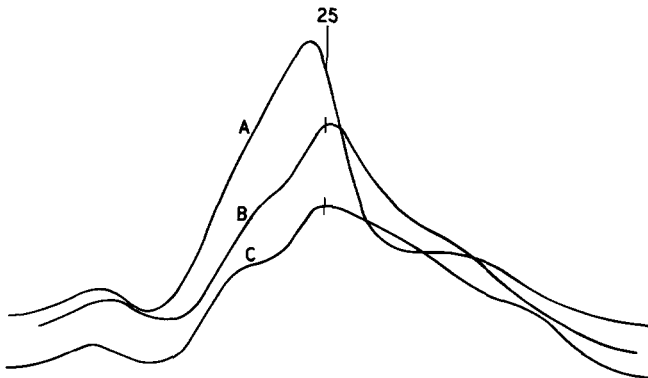


Fig. 2. Effect of reaction time on molecular weight distribution of terpolymers, alcohol coagulated: (a) 3-hr reaction time; (b) 20-min reaction time; (c) 10-min reaction time.

The data in Table III show some of these block terpolymers as thermoplastic rubber. These rubbers have high tensile strength without vulcanization similar to the S-B-S type of triblock copolymer. However, the samples containing ϵ -caprolactone have very good ozone resistance, and those containing TMBL have much improved strength at elevated temperatures. These two properties,

TABLE III
 Evaluation of Styrene-Butadiene-Lactone Block Terpolymers

Styrene-diene-lactone ratio	Inherent viscosity	Tensile			Ozone resistance	Shore D hardness
		27°C	50°C	65°C		
ε-Caprolactone (CL)						
20-20-60	2.69	4320	2560	640	good	52
25-35-40	2.13	3730	2130	510	good	43
40-35-25	1.62	3530	2830	2050	good	49
25-50-25	1.75	3630	1900	680	good	30
2,2,4-Trimethyl-3-hydroxy-3-pentenoic Acid β-Lactone (TMBL)						
15-45-40	0.60	3910	3650	3050	none	58
25-50-25	0.62	4210	1580	1630	none	43
25-60-15	1.08	4340	1920	1620	none	27
Control						
S-B-S 20-60-20	1.28	3850	1440	640	none	30

 TABLE IV
 Properties of Lactone Block Polymers of Low Butadiene Content

	Caprolactone polymers			TMBL Polymers
	60-20-20 ^a	40-35-25	45-10-45	40-35-25
Melt index, 200°C/5 kg/10 min	0.63	0.11	0.02	12.3
Flexural modulus, psi × 10 ⁻³	151	45	218	109
Tensile yield, psi	3490	—	—	2340
Tensile break, psi	—	3500	3650	—
Elongation, %	20	1720	413	87
Izod impact, ft-lb/in., notched	0.63	—	0.5	0.82
Vicat temp., °C	93	77	71	84
Shore D hardness	65	48	64	60
DTA, mp, °C	60	59	65	200

^a Styrene-butadiene-lactone ratio.

 TABLE V
 Raw Properties of a Lactone Polymer Compared to Balata

	S-B-Cl ^a	Balata
300% Modulus, psi	1350	2620
Tensile, psi	2900	3500
Elongation, %	560	380
Tear at 80°F, lb/in.	405	345
Shore A hardness at		
27°C	90.5	92.5
70°C	52.5	10.0
100°C	37	too soft
Softening point, °C	86	61

^a Styrene-butadiene-ε-caprolactone, 20-20-60.

^b Mooney machine method.

ozone resistance and improved strength at elevated temperatures, are the two most sought-after improvements on S-B-S type thermoplastic rubber. The inclusion of a high melting polyester segment such as those made from TMBL must contribute to the hot tensile strength. The good ozone resistance of polymers containing polycaprolactone blocks was unexpected. Furthermore,

TABLE VI
Properties of Polymer Alloys of ϵ -Caprolactone Block Polymer and Styrene-Acrylonitrile Copolymers

	S-B-CL (25-50-25)	S/B-CL ^a (25/50-25)
SAN/Lactone polymer	77.5/22.5	75/25
Dicumyl peroxide	0.1	0.1
Melt flow, 200°C/5 kg/10 min	0.3	0.4
Flexural modulus, psi $\times 10^{-3}$	298	249
Tensile, psi	5610	4600
Elongation, %	37	79
Izod impact, ft-lb/in., notched	11.1	15

^a S/B Block is a random copolymer.

one can obtain good ozone resistance of the S-B-S polymer by blending with a S-B-CL (such as 20-20-60) polymer to a blend containing 20% or more caprolactone. The exact mechanism of this behavior is not known at present, but it is believed to be due to the arresting of the crack growth by the highly dispersed polycaprolactone domains.

Styrene-butadiene-caprolactone block terpolymer was mixed with styrene-acrylonitrile random copolymer and a little peroxide to form polymer alloy.²⁶ Very desirable properties were obtained for a blend of 25-50-25 (styrene-butadiene-caprolactone) block terpolymer with 75-25 (styrene-acrylonitrile) copolymer (see Table VI). The polymer alloy had high tensile strength, fair melt flow, and excellent Izod impact. Tensile strength, flexural modulus, and melt flow increased while impact decreased with decreasing amount of block terpolymer in the polymer alloy. The polymer alloy compares favorably with ABS resin made by latex graft polymerization. By changing the styrene/butadiene composition so that the refractive index of this block is equal to the value of the styrene-acrylonitrile material, blends were produced having good clarity along with good properties. Results obtained from dynamic (Vibron) measurements demonstrate that the polycaprolactone and styrene/acrylonitrile form a homogeneous solid solution. It is further demonstrated that blends of the butadiene/caprolactone block copolymer with styrene/acrylonitrile copolymer then are represented as particles of polybutadiene dispersed in the polycaprolactone block-styrene/acrylonitrile solid solution.²⁶ A detailed study on the preparation of this ABS-like resin is reported by Clark and Childers.²⁷

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