

Preparation and Stress-Strain Properties of ABA-Type Block Polymers of Styrene and Isoprene or Butadiene

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Synopsis

Several series of ABA-type "tapered" block polymers of styrene (monomer A) with isoprene or butadiene were prepared with the use of *n*-butyllithium or *sec*-butyllithium as initiators in benzene solution. The stress-strain curves of the raw polymers are reported, showing that many of them behave at ambient temperature like vulcanized elastomers. These polymers consist, however, of completely linear chains, with no chemical crosslinks between them; they are thermoplastic, can be easily molded, and are soluble in common solvents. Hence, they may be classed as pseudo-crosslinked elastomers. Better stress-strain properties are obtained from polymers made with *sec*-butyllithium than with *n*-butyllithium; in turn, polymers from butadiene have better properties than those from isoprene. Stress-strain curves most closely resembling those of crosslinked elastomers are obtained in general from polymers containing about 30-45% styrene. It was found that AB-type block polymers have very poor tensile strengths and low elongations. The microstructures of polybutadienes and polyisoprenes of various molecular weights, prepared in benzene solvent with alkylolithium initiators, were also determined and compared with literature data for like polymers prepared in cyclohexane solvent.

The advent of anionic polymerization techniques, particularly those arising from lithium-based initiators, has made possible the preparation of many novel block polymers.¹⁻⁴ Recently, it has been demonstrated that ABA-type block polymers of styrene (monomer A) with butadiene or isoprene may exhibit behavior of crosslinked elastomers, even though the polymer molecules are perfectly linear and have no chemical crosslinks between them.⁵⁻⁹ Such polymers are thermoplastic and can be easily molded at elevated temperatures to form intricate shapes, yet at ambient temperatures behave as though they were vulcanized rubbers. It was of interest in our laboratories to prepare block polymers of this type and study their physical properties as a function of their composition. This paper reports the stress-strain curves for a number of styrene-butadiene-styrene and styrene-isoprene-styrene block polymers, which clearly show their behavior as pseudo-crosslinked elastomers.

EXPERIMENTAL

Materials

Benzene was used as the solvent for all polymerizations. It was A.C.S. reagent grade, and was passed through a silica gel column and stored under nitrogen until used. The heptane used to dilute the alkyllithium solutions was Phillips Petroleum Company's "pure" grade. It was washed successively with concentrated H_2SO_4 , potassium carbonate solution, and distilled water, then distilled and stored over Drierite in a nitrogen atmosphere until used. Butadiene was Phillips Petroleum Company's "rubber" grade, and was analyzed at 99.5% butadiene by gas chromatography. It was distilled from the cylinder directly into the benzene solvent when the polymerization solutions were prepared. Isoprene was obtained from the Goodyear synthetic rubber plant at Beaumont, Texas; it had a minimum purity of 97.6%, and was usually over 98%. It was given a simple flash distillation to remove inhibitor prior to polymerization. Styrene was obtained from Sinclair-Koppers, and had a minimum purity of 99.5%. It was used as received.

Both *n*- and *sec*-butyllithium were obtained from Foote Mineral Company in hexane solution. The *n*-butyllithium was about 1.6*M*, and the *sec*-butyllithium, about 1.24*M*. Both were diluted with heptane before use to either 0.20 or 0.30*M*, stored under nitrogen, and transferred by hypodermic syringe.

Polymerizations

Most polymerizations were run in 4-oz., screw-capped bottles. The polymerization solutions were made up so that a bottle contained 20 g. of monomer. (Thus, for example, to prepare a polymer containing 40% styrene, the solution would contain 8 g. of styrene and 12 g. of diene.) One-half the requisite amount of styrene (4 g. for the above example) was first polymerized to form a polystyryllithium. Thus a solution of styrene in benzene (4 g. of styrene in 20 ml. of solution for the above example) was prepared and passed through a water-cooled silica gel column into 8 oz. bottles, all operations being done under nitrogen. The solution was then given a final sparging with nitrogen, and sufficient alkyllithium solution was added to impart a concentration of 0.20 mmole alkyllithium/20 g. of total monomer in the final polymerization bottle (giving a calculated molecular weight of 100,000 to the final ABA polymer). The red color of the styryl anion would appear at once. The bottles were capped with perforated metal screwcaps, which were lined with a self-sealing rubber gasket, and a polyethylene gasket which was next to the solution. They were polymerized for 1-2 hr. in a chilled water bath and were then allowed to stand at least 18 hr. at ambient temperature before subsequent use to insure fairly complete polymerization of the styrene.

A solution was then prepared from the diene and the remaining half of the styrene (12 and 4 g., respectively, following the above example) in

80 ml. total volume with benzene as the solvent. A quantity sufficient to charge several polymerization bottles was prepared and passed through a water-cooled silica gel column into a receiver flask. Then 80 ml. portions were measured into 4 oz. bottles, all operations being done under a nitrogen atmosphere. Trace impurities still remain in this solution which could destroy some of the polystyryllithium, however, forming low molecular weight polystyrene and increasing the molecular weight of the resultant ABA block polymer. These impurities are removed by scavenging them with alkyllithium by a technique previously described.¹⁰ Several bottles of the styrene–diene solution were polymerized with small but different levels of alkyllithium. A point is found at which no polymerization would occur, but the next incrementally higher level of alkyllithium would give polymerization, usually to nearly 100% yield. This point is termed the scavenger level¹⁰ and was generally quite reproducible for a given lot of solvent and monomers.

Thus, after the 80 ml. portion of the styrene–diene solution was charged to the polymerization bottle, it was sparged 30 sec. with nitrogen, and the scavenging level of alkyllithium was then added, a flow of nitrogen being maintained through the bottle. After allowing the alkyllithium to react for a short time, 21 ml. (which allows for the dilution by the alkyllithium solution) of the polystyryllithium solution was added (by syringe), and the bottle was capped with a metal screw cap, lined with a polyethylene gasket. The red color of the styryl anion disappeared as soon as the solution was syringed into the diene–styrene mixture and reappeared again when all the diene had polymerized and the final block of styrene began to form (see below). Bottles were tumbled in a water bath, at 50°C. for butadiene polymers and 35°C. for isoprene polymers, usually for 18 hr. Polymers were coagulated in methanol containing a phenolic antioxidant and allowed to soak for 24 hr. They were then cut up and soaked another 24 hr. or more in fresh methanol and antioxidant, then dried in a vacuum oven at moderate temperature (<50°C.).

Some polymers were prepared in larger quantities by running the polymerizations in a 4-liter resin kettle, using the same general techniques as above. The polystyryllithium was prepared in a water-jacketed 500-ml. separatory funnel, from which the solution was drained under nitrogen directly into the resin kettle which contained the diene–styrene solution. The scavenger level for this solution was obtained through separate bottle polymerizations. The resin kettle was cooled by a water bath, and good temperature control was maintained. Polymer was isolated as above.

Polymer Evaluation

Inherent viscosity of the polymers was measured in toluene at 30°C. with 0.25 g. of polymer in 50 ml. of toluene. Gel in these polymers was quite low, usually less than 3%. The styrene content of the styrene–butadiene copolymers was determined by measuring the absorption of a

chloroform solution of the polymer, at 260 $m\mu$. For the styrene-isoprene copolymers, styrene content was determined by NMR.¹¹

Samples of the polymers were molded to ~ 0.060 in. thickness at about 300°F. for 1 min. The mold was cooled under pressure with tap water, so the rate of cooling was fairly rapid. All samples molded readily. Dumbbells measuring 0.10 in. in width and 0.8 in. in length over the narrowed section were cut from the samples. Stress-strain tests were made at 25°C. with an Instron tester at a crosshead separation speed of 2 in./min. Duplicate test pieces were run for all polymers.

RESULTS AND DISCUSSION

The technique used to prepare the block copolymers reported here produces what have been termed "tapered" block polymers.⁵ It is well known that polymerization of a mixture of styrene and butadiene or isoprene with lithium or organolithiums results in essentially a block polymer.¹²⁻¹⁵ The diene polymerizes first, incorporating a small amount of styrene. As the diene concentration decreases, more styrene enters the polymer, of course, but even at the point of final exhaustion of the diene, the polymer formed up to this time contains only a few per cent styrene. After all diene has been consumed, then the remaining styrene polymerizes as a block of pure polystyrene. Thus, the diene segment contains a low but "tapering" concentration of styrene. This amount of styrene does not seem to interfere greatly with the elastomeric behavior of the diene

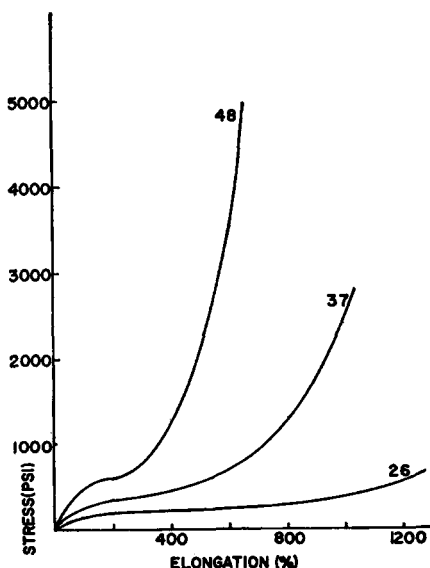


Fig. 1. Stress-elongation curves for styrene-butadiene-styrene block polymers prepared with *n*-butyllithium initiator. Numbers on curves are styrene contents of the polymers.

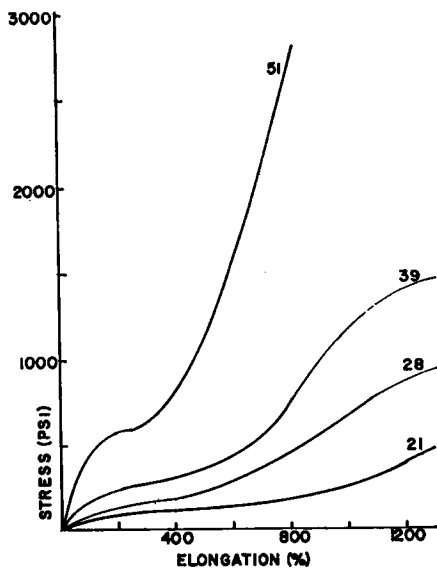


Fig. 2. Stress-elongation curves for styrene-isoprene-styrene block polymers prepared with *n*-butyllithium initiator.

polymer, which has a high 1,4-addition structure. Thus, by preparing a polystyryllithium and using this "living" polymer to initiate a mixture of diene and styrene, an essentially block polymer is formed, which has an ABA block structure, with the B segment (diene) containing a small amount of monomer A (styrene). All polymers reported here were prepared so that the A blocks are of nearly equal size.

A series of styrene-butadiene-styrene block polymers was prepared with *n*-butyllithium as the initiator, and their stress-strain curves are given in Figure 1. As the amount of styrene in the polymer increases, tensile strengths increase but ultimate elongations decrease. Also, the initial resistance to flow becomes greater, resulting in a humplike appearance in the first portion of the stress-strain curve. At styrene contents of less than 20%, polymers have very low tensile strengths, and elongation also begins to decrease. Polybutadiene of about the same molecular weight as these block polymers had a tensile strength of only a few hundred pounds per square inch and very low elongation. Likewise, AB-type block polymers containing up to 33% styrene had very poor tensile strengths and elongations, showing the necessity of styrene blocks on both ends of the polymer chains.

A series of styrene-isoprene-styrene block polymers was prepared with *n*-butyllithium initiator, and their stress-strain curves are given in Figure 2. Here, a good tensile strength is obtained only with the polymer containing 51% styrene; the remaining polymers have low tensile strengths. Likewise, AB-type block polymers made from these monomers have very poor tensile strengths, and polyisoprene of molecular weight similar to the ABA

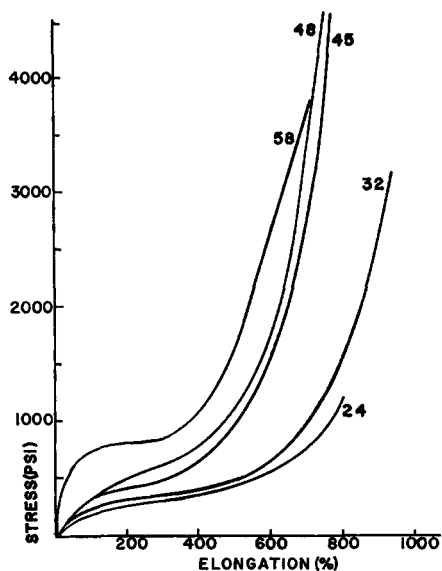


Fig. 3. Stress-elongation curves for styrene-butadiene-styrene block polymers prepared with *sec*-butyllithium initiator.

block polymers was so soft that it could not be molded into a test piece. At comparable styrene contents, styrene-isoprene-styrene block polymers have lower tensile strengths than styrene-butadiene-styrene block polymers.

It has been shown that *n*-butyllithium is a slow initiator for styrene, and at the styrene/initiator ratios used in this work, the possibility exists that unreacted *n*-butyllithium may remain after all the styrene has been converted to polystyryllithium.¹⁶ If such a mixture were used to initiate a diene-styrene mixture, the unreacted *n*-butyllithium would initiate some AB-type block polymer, which would form along with the expected ABA-type polymer. This paper, as well as the work of others,⁵ has shown that AB-type polymers have very little tensile strength. Thus, it might be expected that an ABA polymer which contained some AB polymer would have diminished tensile strength. On the other hand, it has been demonstrated that *sec*-butyllithium is a very rapid initiator for styrene, forming a polymer which is almost monodisperse.¹⁶ A polystyryllithium formed in this manner should, when used to initiate a styrene-diene mixture, produce all chains of ABA type, with all A blocks of nearly equal size. All chains in such a polymer would contribute to the strength of the polymer, and it might be expected to have a higher tensile strength than a comparable polymer made with *n*-butyllithium.

Hence, it was of interest to prepare ABA-type polymers with *sec*-butyllithium as the initiator and to test their properties. The stress-strain curves of a series of styrene-butadiene-styrene block polymers made with *sec*-butyllithium are given in Figure 3. A number of these polymers had excellent tensile strengths at good elongations. In the intermediate range

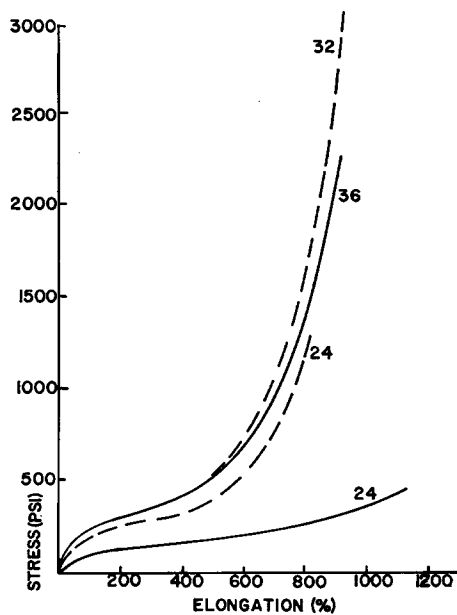


Fig. 4. Stress-elongation curves for styrene-butadiene-styrene block polymers: (—) prepared with *n*-butyllithium initiator; (- -) prepared with *sec*-butyllithium initiator.

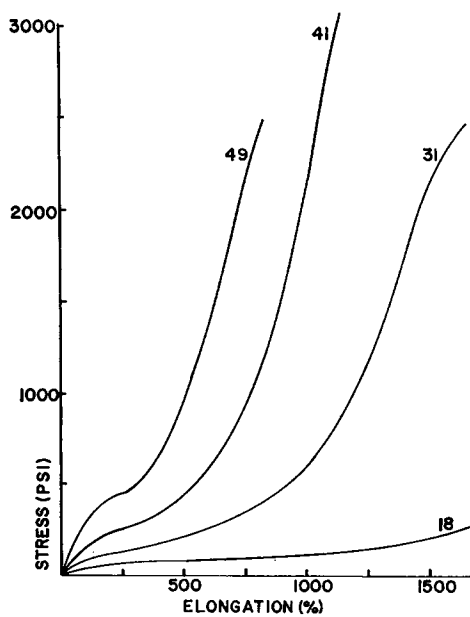


Fig. 5. Stress-elongation curves for styrene-isoprene-styrene block polymers prepared with *sec*-butyllithium initiator.

of styrene contents, these polymers did have better tensile strengths than comparable ones made with *n*-butyllithium. For comparison purposes, two pairs of their stress-strain curves are plotted to the same scale in Figure 4. At styrene contents below about 20%, polymers made from either initiator have very poor tensile strengths. Also, as the styrene contents approach about 50%, the properties of the polymers from either initiator become equal. This might be expected, since at this point, the polymers may begin to take on the characteristics of polystyrene, and the properties of this rigid glassy polymer would overshadow those of the elastomeric segments. In the intermediate range of composition, however, from about 30 to 45% styrene, where the polymers show their closest

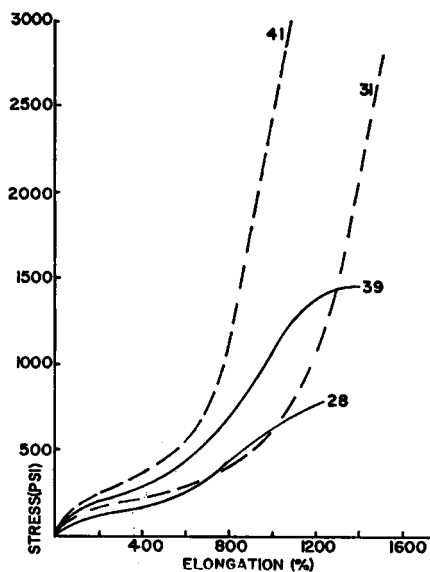


Fig. 6. Stress-elongation curves for styrene-isoprene-styrene block polymers: (—) prepared with *n*-butyllithium initiator; (--) prepared with *sec*-butyllithium initiator.

behavior to crosslinked elastomers, those made with *sec*-butyllithium do have the better tensile strengths.

Similarly, a series of styrene-isoprene-styrene block polymers was prepared by using *sec*-butyllithium initiator, and their stress-strain curves are given in Figure 5. Several of these have good tensile strengths and the improvement in tensile strength over the polymers made with *n*-butyllithium was even more marked than for the styrene-butadiene-styrene polymers. Two pairs of such polymers are reproduced to the same scale in Figure 6 for comparison purposes. Again, polymers with less than about 20% styrene or more than about 50% styrene had comparable properties, regardless of the initiator from which they were made. In the intermediate range of composition, however, *sec*-butyllithium is definitely the preferred initiator for the preparation of polymers with superior tensile strengths.

TABLE I
Properties of Various ABA Block Polymers

	Initiator	Inherent viscosity	Styrene, %	Stress-strain data	
Styrene-butadiene-styrene	<i>n</i> -C ₄ H ₉ Li	1.78	26	Fig. 1	
	"	1.41	37		
	"	1.38	48		
	" " " " " "	<i>sec</i> -C ₄ H ₉ Li	1.61	24	Fig. 3
		"	1.03	32	
		"	0.96	45	
		"	1.22	48	
"		0.73	58		
Styrene-isoprene-styrene	<i>n</i> -C ₄ H ₉ Li	1.32	21	Fig. 2	
	"	1.10	28		
	"	0.74	39		
	" " " " "	"	0.85	51	
		<i>sec</i> -C ₄ H ₉ Li	1.12	18	Fig. 5
		"	1.31	31	
		"	0.90	41	
"	0.79	49			

Properties of the various polymers are given in Table I. As noted above, polymerizations were carried out so as to produce a final polymer of about 100,000 molecular weight. Differences in the inherent viscosities of the polymers reflect the various relations of inherent viscosity to molecular weight of the respective homopolymers; e.g., for a given series of ABA-type polymers of fixed molecular weight, the higher the styrene content, the lower should be the inherent viscosity of the polymer. This is generally followed by the series listed in Table I; exceptions are probably caused by spurious impurities which destroyed small amounts of the alkyllithium or polystyryllithium and, thus, raised the molecular weight of the final polymer. Over a moderate range of molecular weights (as measured in terms of inherent viscosity), no gross effect was found on the stress-strain properties of either AB or ABA block polymers by changes in molecular weight.

In the course of this work, a number of butadiene and isoprene homopolymers were prepared, with a wide range of inherent viscosities. This afforded an opportunity to compare results on the microstructure of these polydienes, prepared in benzene, with the results of Hsieh, whose polymers were prepared in cyclohexane.¹⁷ The microstructure of various polymers, determined by a modified Binder¹⁸ method, at various inherent viscosities is given in Figure 7. At low inherent viscosities, agreement between the various structures is good for the polymers made in either solvent. The major difference lies in the change in *cis*-1,4 content of polyisoprene as the inherent viscosity increases. Hsieh reports over 80% *cis*-1,4 structure at an inherent viscosity of 6 (highest reported), while this work shows *cis*-1,4 content of slightly over 70% at this inherent viscosity, with a further

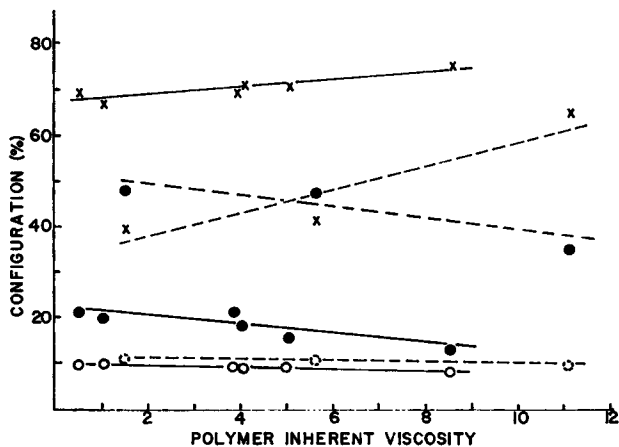


Fig. 7. Microstructure of polydienes initiated with butyllithiums in benzene: (—×) *cis*-1,4-polyisoprene; (—●) *trans*-1,4-polyisoprene; (—○) 3,4-polyisoprene; (- -×) *cis*-1,4-polybutadiene; (- -●) *trans*-1,4-polybutadiene; (- -○) 1,2-polybutadiene.

increase to only about 75% at an inherent viscosity of 8.5. A somewhat similar result was obtained with polybutadiene. For both polymers, this lower *cis*-1,4 content is reflected by a correspondingly higher *trans*-1,4 content, since vinyl contents for both polymers were low in all cases. The general trends of the data are the same for both polydienes, made in either solvent, however. The results of this work supports Hsieh's data that aromatic solvents produce polydienes of lower *cis*-1,4 content than aliphatic solvents, for lithium-initiated polymerizations.

SUMMARY

Block polymers of styrene and isoprene or butadiene can be conveniently prepared with organolithium initiators. A two-block polymer (AB-type) has very poor tensile strength and low elongation. Three-block polymers, or ABA-type, in which styrene forms the A blocks, exhibit in the proper composition range stress-strain behavior like vulcanized elastomers. Tensile strengths of 3000 to nearly 5000 psi may be attained, with high elongations, from the raw, unfilled polymer. The necessity of having polystyrene blocks at both ends of the polymer chains in order to achieve these properties is thus demonstrated. These ABA-type block polymers are, however, thermoplastic, can be easily molded, and are soluble in common solvents. The role of the styrene blocks in the behavior of these polymers is not clear at this point, and in fact it may be of a dual character. They may form small aggregates of polystyrene which serve as anchors at the end of the chains and prevent slippage of the elastomeric segments as they are elongated. They may also serve as reinforcing agents for the elastomeric segments.

Better stress-strain properties are obtained from polymers made with *sec*-butyllithium than *n*-butyllithium, presumably because all of the chains

of such polymers are of the ABA-type, with no AB-type chains present. Also, higher tensile strengths are obtained from butadiene polymers rather than isoprene polymers. In general, the ABA block polymers containing from about 30% to 45% styrene have stress-strain curves that exhibited the closest resemblance to those of crosslinked elastomers.

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Résumé

De nombreuses séries de polymères séquencés du type ABA de styrène (monomère A) avec l'isoprène ou le butadiène ont été préparées en utilisant le *n*-butyllithium ou le *sec*-butyllithium comme initiateurs en solution benzénique. Des courbes tension-élongation de ce polymère brut sont rapportées, montrant que beaucoup de ces polymères se comportent à température ambiante comme des élastomères vulcanisés. Ces polymères consistent toutefois en des chaînes complètement linéaires sans ponts chimiques entre eux; ils sont thermoplastiques, peuvent être facilement moulés et sont solubles dans les solvants ordinaires. De là, il résulte qu'ils peuvent être classés comme des élastomères pseudopontés. Des propriétés tension-élongation améliorées sont obtenues au départ des polymères, fabriqués avec le *sec*-butyllithium plutôt qu'avec le *n*-butyllithium et en retour au départ de polymère de butadiène plutôt que de polymères d'isoprène. Les courbes de tension-élongation ressemblent plus fortement à celles des élastomères pontés obtenus en général au départ de polymères contenant de 30 à 40% de styrène. On a trouvé que les polymères séquencés du type AB ont des forces de tension très faibles et de faibles élongations. Les microstructures des polybutadiènes et polyisoprènes de différents poids moléculaires préparés dans le benzène avec des initiateurs alcoyllithiens, ont également été déterminées et comparées avec les résultats de la littérature pour des polymères semblables préparés en solution dans le cyclohexane.

Zusammenfassung

Verschiedene Reihen von sogenannten "tapered" Blockpolymeren vom ABA-Typ aus Styrol (Monomeres A) und Isopren oder Butadien wurden unter Verwendung von *n*-Butyl-Lithium oder *sec*-Butyl-Lithium als Starter in Benzol-Lösung hergestellt. Die Spannungs-Dehnungs-Kurven der rohen Polymeren werden beschrieben, sie zeigen, dass sich viele von ihnen bei Raumtemperatur wie vulkanisierte Elastomere verhalten. Diese Polymeren bestehen jedoch aus völlig linearen Ketten ohne jede chemische zwischenmolekulare Vernetzung. Sie sind thermoplastisch, lassen sich leicht verformen und sind in den gebräuchlichen Lösungsmitteln löslich. Sie können daher als pseudoquervernetzte Elastomere klassifiziert werden. Die mittels *sec*-Butyl-Lithium hergestellten Polymeren besitzen bessere Spannungs-Dehnungs-Eigenschaften als die mittels *n*-Butyl-Lithium gestarteten und ebenso Butadien-Polymere bessere als Isopren-Polymere. Polymere mit einem Styrolgehalt von 30% bis 45% zeigen im allgemeinen Spannungs-Dehnungs-Kurven, die besonders stark denen vernetzter Elastomere gleichen. Es wurde gefunden, dass Blockpolymere vom AB-Typ eine sehr geringe Zugfestigkeit und niedrige Elongation aufweisen. Die Mikrostrukturen von Polybutadienen und Polyisoprenen mit verschiedenen Molekulargewichten, dargestellt in Benzol-Lösung mit Alkyl-Lithium-Startern, wurden ebenfalls bestimmt und mit Literaturdaten ähnlicher, in Cyclohexan-Lösung hergestellter Polymerer verglichen.

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