Preparation and Properties of ABA Block Polymers of Styrene and Butadiene or Isoprene Made with sec-$C_4H_9Li \cdot 2(C_2H_5)_2O$

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Synopsis

ABA-type "tapered" block polymers were prepared from styrene (monomer A) and butadiene or isoprene, using an initiator of sec-butyllithium complexed with two molecules of ethyl ether. The stress–strain curves of polymers containing about 20–50% styrene show the usual resemblance to curves of crosslinked elastomers. The SBS polymers had higher tensile strengths than the SIS polymers. They also had slightly higher tensile strengths than comparable SBS polymers made with sec-butyllithium. The SIS polymers, however, had generally lower tensile strengths than those made with sec-butyllithium. This is probably caused by higher styrene content of the isoprene block, brought about by increased randomization of the styrene–isoprene copolymerization due to the presence of the ether. The A and B blocks become more compatible, producing loss of strength in the polymer. Infrared analyses of polydienes made with the sec-$C_4H_9Li \cdot 2(C_2H_5)_2O$ initiator showed a 6% to 8% increase in 1,2-content (for polybutadiene) or 3,4-content (for polyisoprene), compared to polymers made with sec-butyllithium. The polymer microstructures still have high (>80%) total 1,4-content, however. Thus, this amount of ether can be tolerated in the polymerization system without great loss of rubbery properties or block structure in the resultant polymers.

INTRODUCTION

Recent studies have shown that ABA-type block polymers of styrene or a substituted styrene (monomer A) and butadiene or isoprene (monomer B) exhibit stress–strain behavior similar to that of vulcanized elastomers.[1-6] These polymers are prepared with organolithium initiators in an all-hydrocarbon system. The presence of polar compounds, as alkyl ethers, in the polymerization system is detrimental in at least two respects. They reduce the high 1,4-content of the microstructure of the diene blocks,[7-9] resulting in a loss of rubbery properties. Also, in an all-hydrocarbon system, the polymerization of mixtures of styrene and diene produces "tapered" block polymers[1,3]; ethers randomize this polymerization, resulting in loss of block structure.[10-13]

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It has been found in these laboratories that small amounts of ethyl ether can be present in the polymerization of mixtures of styrene and butadiene or isoprene without producing loss of block structure. Also, the microstructure of the polydiene is not greatly altered. Specifically, ABA block polymers of these monomers were prepared with an initiator of sec-butyllithium complexed with two molecules of ethyl ether. Their stress–strain curves were compared to polymers made with sec-butyllithium.[3] The microstructures of the polydienes made with this initiator were determined and compared to polymers prepared with sec-butyllithium.

EXPERIMENTAL

Materials

The materials used were the same as those described in a previous paper and were handled in the same manner.[3] The ethyl ether was anhydrous ACS reagent grade. It was thoroughly sparged with nitrogen, stored in a bottle that was sealed with a self-sealing rubber septum, and transferred by hypodermic syringe.

The initiator solution was prepared by diluting the sec-butyllithium stock solution (Foote Mineral Company) with n-heptane and the requisite amount of ether to form a solution $0.20M$ in sec-$C_4H_9Li \cdot 2(C_2H_5)_2O$. It is known that sec-butyllithium is thermally unstable, and ethers accelerate its decomposition.[14,15] By storing the initiator solution at $-17°C$, stability could be maintained for at least several days, however. Solutions were analyzed periodically by the method of Gilman and Cartledge[16] and were discarded when the concentration of carbon-bound lithium began to decline.

Polymerizations and Polymer Evaluations

Polymerizations were run in 4-oz screw-capped bottles in the same manner as described in a previous paper.[3] Scavenger levels for the initiator were determined in the same manner as described previously.[3,17] Monomer-to-initiator ratios were chosen so that all polymers would have a total molecular weight of 100,000. Polymers were evaluated by methods described in the earlier paper.[3]

RESULTS AND DISCUSSION

It has been demonstrated that SBS or SIS block polymers prepared with sec-butyllithium have tensile strengths superior to those made with n-butyllithium initiator.[3] Presumably this is because sec-butyllithium is a very rapid initiator for styrene.[18] All alkyllithium is rapidly converted to polystyryllithium; when this is added to a diene–styrene mixture to complete the triblock polymer, no unreacted alkyllithium remains which could form AB-type block polymer. The AB polymer lowers the tensile strength of ABA polymers.[19]

Hence, *sec*-butyllithium was chosen as the initiator to be evaluated as an etherate for this study. It is known that alkyl or cyclic ethers accelerate the initiation of styrene by alkyllithiums.[20] Thus, a *sec*-butyllithium etherate should provide extremely rapid initiation for styrene.

A series of SBS polymers was prepared by the usual method of preparing a "living" polymer of styrene with the *sec*-$C_4H_9Li \cdot 2(C_2H_5)_2O$ initiator, then using this to initiate a mixture of diene and styrene.[3] The stress–strain curves were determined for these polymers and are given in Figure 1. They exhibit the usual shape, with low initial modulus but high ultimate tensiles and elongations. As the amount of styrene in the polymer increases, tensile strength increases, but ultimate elongation decreases. This follows
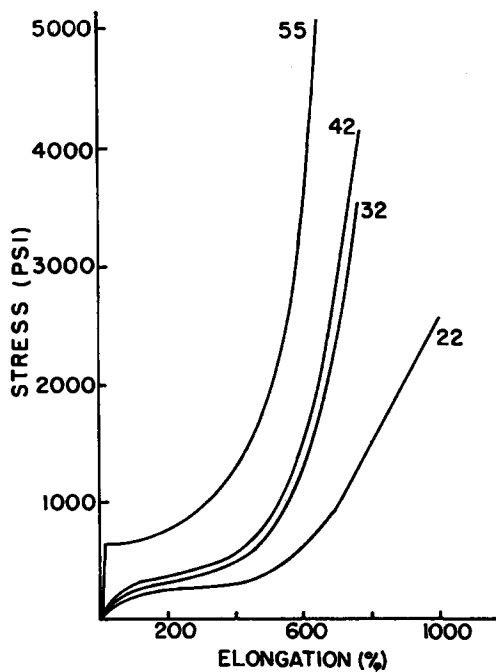

Fig. 1. Stress–elongation curves for styrene–butadiene–styrene block polymers. Numbers on curves are styrene contents of the polymers.

previous results.[3,4] The ultimate tensiles of these polymers are about equal to or even higher than comparable polymers made with *sec*-butyllithium,[3] especially at the lower styrene contents. This might be due to the presence of the ether. The "cross-over" reaction between dienyllithium and styrene to form the final styrene block is relatively slow.[21] Hence, this styrene block may be fairly polydisperse, and some of the styrene segments may be so short that the chains contribute little to the overall strength of the polymer.[19] With ether present, however, the cross-over reaction becomes rapid and the final styrene block should be nearly monodisperse.[6,22] Thus, all polymer chains should have essentially monodisperse styrene blocks at both
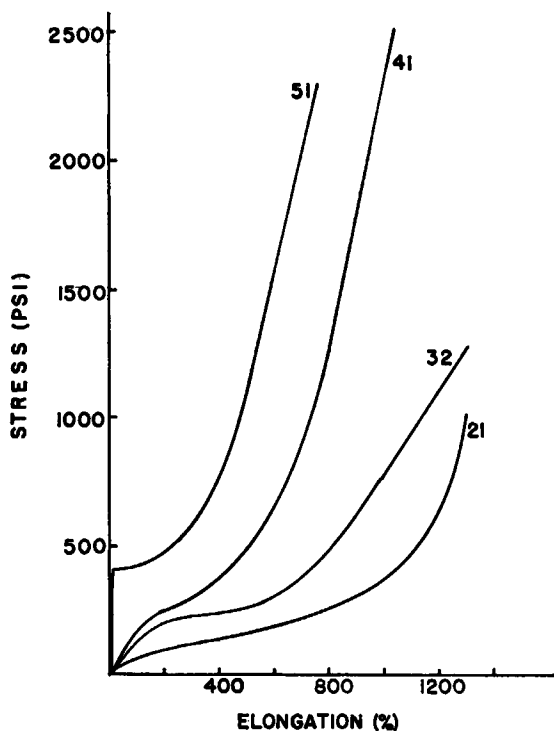
Fig. 2. Stress–elongation curves for styrene–isoprene–styrene block polymers.

ends (see above), and all should contribute equally to the strength of the polymer.

A series of SIS polymers was also prepared with the etherate initiator, and their stress–strain curves are given in Figure 2. These all have lower tensile strengths and higher ultimate elongations than comparable SBS polymers. This corresponds to previous results.[3] They also have somewhat lower tensile strengths than comparable SIS polymers made with sec-butyllithium, in contrast to results with the SBS polymers. This may be due to the amount of styrene that is incorporated in the isoprene block. Styrene copolymerizes more readily with isoprene than with butadiene in a hydrocarbon solvent with alkyllithium initiator.[23] It has been argued that this increased amount of styrene in the isoprene block decreases the incompatibility of the blocks, leading to more phase blending and thus poorer tensile strengths.[19] It will be shown in a subsequent paper than the presence of ether does introduce a considerable portion of styrene into the isoprene block.

Microstructure of Diene Homopolymers

Polydienes were also prepared with the etherate initiator, and their microstructures were determined by a modified Binder method.[24] The results are given in Table I and are compared with results from polydienes made

TABLE I

Microstructures of Polybutadienes and Polyisoprenes Prepared with sec-Butyllithium
and sec-$C_4H_9Li \cdot 2(C_2H_5)_2O$[a]

	Polybutadiene			Polyisoprene		
	Etherate		Non-etherate	Etherate		Nonetherate
Inherent viscosity	0.99	1.74	1.64	1.18	2.44	0.72	1.06
cis-1,4-content, %	36.4	39.0	40.4	63.9	65.8	68.4	68.9
trans-1,4-content, %	43.8	41.7	48.1	19.0	17.7	21.7	20.7
1,2-content, %	19.7	19.3	11.6	17.1	16.5	10.0	10.3

[a] Polymers were prepared in benzene at 50°C. Inherent viscosities were determined in toluene at 30°C. Analyses for the polymers were normalized to 100%. The 1,2-contents of the polyisoprenes were negative fractions of a per cent and were neglected.

with sec-butyllithium.[3] For both types of polymer, total 1,4-content decreased about 6% to 8%, with a concurrent increase in 1,2-content (for polybutadiene) or 3,4-content (for polyisoprene). Both polymers are, however, still high in total 1,4-addition, and thus this amount of ether can be tolerated in the polymerization system without great loss of rubbery properties in the diene block.

These results on microstructure concur with previous results on polyisoprene[9] and polybutadiene.[25] Although only two samples of each polydiene were analyzed, they showed that as polymer molecular weight increased, the cis-1,4-content of both polydienes increased slightly and trans-1,4-content decreased. This also falls in line with previous results.[3,26]

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