

Preparation and Stress-Strain Properties of ABA Block Copolymers of α -Methylstyrene and Butadiene*

ROBERT E. CUNNINGHAM, *Research Division, Goodyear Tire and Rubber Company, Akron, Ohio 44316*

Synopsis

ABA-type "tapered" block copolymers of α -methylstyrene (monomer A) and butadiene were prepared using four commercially available dilithio initiators. Polymerizations were run at 25°C in benzene solvent, or at 40°C with butadiene dissolved in neat α -methylstyrene. Although α -methylstyrene has a rather low ceiling temperature, triblock copolymers could be made at these temperatures by using α -methylstyrene concentrations well in excess of the $[M]_e$ values at the respective temperatures. Its concentration was such that molecular weights of at least 15,000–20,000 for the A blocks could be attained. The course of the copolymerization at 40°C was followed, showing that copolymers containing about 40% α -methylstyrene could be formed in 4–8 hr, depending on the initiator used. They showed the usual behavior of triblock thermoplastic elastomers, with tensile strengths > 3000 lb/in.² at 24°C. However, because of the high T_g of poly(α -methylstyrene) (172°C), they also had tensiles of several hundred lb/in.² at 100°C, unlike comparable polymers with polystyrene end blocks, which have practically no strength at this temperature. Microstructures of polybutadienes made with these initiators are also given.

INTRODUCTION

The preparation and properties of ABA block copolymers of styrene (monomer A) and butadiene or isoprene have been well documented in recent years. However, α -methylstyrene has received relatively little attention as the monomer for the A blocks in these copolymers.^{1–5} Its polymer has a glass transition temperature of about 172°C, much higher than that of polystyrene, which is about 100°C. The tensile strength of triblock thermoplastic elastomers derives largely from the glassy end blocks. If these were poly(α -methylstyrene), such ABA copolymers should retain some tensile strength at elevated temperatures where comparable copolymers with polystyrene end blocks lose all strength.

α -Methylstyrene has a relatively low ceiling temperature, however (~60°C for neat monomer). When polymerized, it does not react to 100% conversion, but has appreciable monomer in equilibrium with active polymer chains, except at low temperatures (< -50°C).^{6,7} The monomer concentration at equilibrium, $[M]_e$, is constant, however, for a given temperature⁸; any monomer present in excess of this concentration can be polymerized.

In the few triblock copolymers reported in the literature, the α -methylstyrene blocks were prepared using reaction temperatures from 15° to -78°C to attain fairly high yield of polymer. A strong polar modifier was added to accelerate the polymerization rate, since α -methylstyrene polymerizes very slowly at these temperatures.

Hence, the diene block had to be polymerized first, using a dilithio initiator,

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to avoid loss of its high 1,4-microstructure which would occur if it were polymerized in the presence of the polar modifier.^{1,2} Temperature was then lowered and the polar modifier was added to facilitate polymerization of the α -methylstyrene blocks. These somewhat complicated techniques perhaps have discouraged more detailed investigations into the use of α -methylstyrene in triblock copolymers.

Such polymers can be made at temperatures up to at least 40°C, however, by using a large excess concentration of α -methylstyrene but polymerizing it to relatively low conversion. This is possible because of the relation between monomer concentration M and ceiling temperature.⁸ The latter increases as the former becomes more concentrated. It has been demonstrated that the ceiling temperature can be raised above 50°C by using highly concentrated monomer solutions (while still obtaining a small yield of polymer).^{7,9} Sufficiently concentrated solutions can be prepared so that poly(α -methylstyrene) with molecular weights of 20,000 or more can be made up to 40°C. These are quite adequate to serve as end blocks in triblock copolymers. They should also have narrow molecular weight distributions. Poly(α -methylstyrene) prepared at 40°C was shown to have a sharp distribution; broadening of the molecular weight distribution due to the reversibility of the reaction (depolymerization) required long reaction times.^{9a}

The ABA copolymers of α -methylstyrene and butadiene reported herein were prepared either at 25° or 40°C. In both cases, the α -methylstyrene concentrations were 2.5–3.0 moles/l. in excess of the $[M]_e$ values at the respective temperatures. With the initiator concentrations that were used, this was several times the amount of α -methylstyrene needed to form the desired end-block molecular weights (usually about 15,000–20,000).

Polymerizations were carried out in a one-step method rather than by sequential addition of monomer for each block. All of the butadiene and α -methylstyrene was present at the start of the reaction, and dilithio compounds were used as initiators. Butadiene polymerization predominates at first, incorporating a small amount of α -methylstyrene. When it is nearly exhausted, almost pure blocks of poly(α -methylstyrene) form at each end of the polymer chains, producing "tapered" ABA block copolymers, as discussed previously.¹⁰

EXPERIMENTAL

Materials

The sources and purifications of butadiene, styrene, and benzene were given previously.¹¹ α -Methylstyrene was obtained from U.S.S. Chemicals and was 98.6% pure (by gas chromatography). It was distilled in vacuo (bp 49°C at 10 mm); distillation did not appear to alter its polymerizability, so it was usually used as received.

The initiators were four developmental or commercial dilithio compounds from Lithium Corporation of America. They contained a small amount of a polar modifier. Their detailed structures will not be given here; these are available from product bulletins¹² and patent literature¹³ from the manufacturer. The manufacturer's designations, solvent, polar additive, and molar ratio of polar additive/Li are given in Table I. The stock solutions were diluted with benzene

TABLE I
Dilithium Initiators

Initiator	Solvent	Polar additive	Polar additive/Li
DiLi-1	benzene	dimethyl ether	1
DiLi-1A	benzene	triethylamine	4
DiLi-3	hexane	triethylamine	1
DiLi-4	hexane	triethylamine	1

to 0.20M for use in this work. They were analyzed periodically by the double-titration method of Gilman and Cartledge.¹⁴ They were stored under refrigerated conditions to minimize any thermal decomposition of the organolithium compounds.

Polymerizations

Polymerizations were run in 4-oz screw-capped bottles by techniques described previously.¹¹ Conditions for reactions run at 25°C were as follows: solvent, benzene; initiator, DiLi-1 (3×10^{-3} to $4 \times 10^{-3}M$); butadiene, 2.8M; α -methylstyrene, 3.7M; time, 30 hr. For reactions run at 40°C, no solvent was used; butadiene was dissolved in neat α -methylstyrene. Conditions were: butadiene, 2.8M; α -methylstyrene, 5.8M; initiator, $3 \times 10^{-3}M$.

It was observed in prior work in these laboratories and by others⁴ that the "crossover" reaction from the butadienyl anion to α -methylstyrene is quite slow. In all polymerizations, therefore, a small amount of styrene was added (about 2%, based on weight of total monomers). The "crossover" reaction from butadienyl anion to styrene is relatively rapid, compared to that of α -methylstyrene; the latter is then fairly rapidly initiated by the styryl anion. This combination appears to give a "crossover" reaction that is nearly as rapid as that obtained in the block copolymerization of styrene and butadiene (compare Fig. 1 with the similar curve for the styrene-butadiene combination in ref. 18). This relatively rapid "crossover" should product triblock copolymers with fairly narrow molecular weight distributions, as has already been shown for SBS polymers made with some of these dilithium initiators.¹⁵

Polymers were isolated by coagulation in methanol containing a small amount of a phenolic antioxidant and dried in vacuo at $\sim 50^\circ C$. They were prepared to have kinetic molecular weights of about 60,000-100,000. Their inherent viscosities indicate their actual molecular weights are in this range, since they are lower than the inherent viscosities of comparable SBS polymers of 100,000 kinetic molecular weight, reported previously.¹¹ [There is little difference between the intrinsic viscosity-molecular weight relationships, in toluene at 30°C, for polystyrene¹⁶ ($[\eta] = 1.10 \times 10^{-4}M^{0.725}$) and poly(α -methylstyrene)¹⁷ ($[\eta] = 1.08 \times 10^{-4}M^{0.71}$). Presumably, SBS and mSBmS polymers of comparable compositions and molecular weights should have similar intrinsic (or inherent) viscosities.]

Polymer Evaluation

Polymers were evaluated and analyzed as described previously.¹¹ Stress-strain testing was also done in the same manner, except that the samples were

press molded at 425°F and the Instron cross-head separation speed was 5 in./min. For tests run at elevated temperatures, the dumbbell test piece was conditioned for 10 min at the appropriate temperature before testing was begun.

RESULTS AND DISCUSSION

Polymerization at 25°C

These reactions were run in benzene solvent under the conditions given above (see Experimental). Because the polymerization rate of α -methylstyrene was quite slow, only DiLi-1 initiator, which contains dimethyl ether, was used for these studies. The initiators containing triethylamine gave polymerizations that were far too slow for practical study at this temperature (see below).

Depending on the initiator concentration, polymers containing 41%–48% (wt) α -methylstyrene could be prepared in 30 hr of reaction time. Their stress-strain properties are given in Table II. They exhibited good tensile strengths at 24°C and, in addition, had tensiles of several hundred lb/in.² at 100°C, reflecting the effect of the high T_g of the poly(α -methylstyrene) blocks. Comparable SBS block copolymers have tensile strengths of < 50 lb/in.² at this temperature. These reactions were not continued until equilibrium was attained in the α -methylstyrene polymerizations. Hence, with longer reaction times, polymers with even higher α -methylstyrene contents could be prepared.

Polymerizations at 40°C

No solvent was used for these runs; butadiene was dissolved in neat α -methylstyrene (see Experimental). All four dilithio initiators were used. Polymerizations went fairly rapidly at this temperature; butadiene was consumed in about 2 hr. Samples were not taken during this part of the polymerization, since it was known from previous work that butadiene polymerizes very rapidly with these initiators; these portions of the curves in Figure 1 are approximate. The main point of interest was in the rate of addition of the α -methylstyrene. After the red color of the α -methylstyryl anion appeared, polymerizations were stopped at various times to follow the course of the α -methylstyrene addition. These results are plotted in Figure 1. The curves exhibit the same shapes as those for the anionic copolymerization of butadiene and styrene.¹⁸ There is an initial rapid polymerization of butadiene, followed by a period of apparent dormancy before the α -methylstyrene is initiated. When this occurs, there is then another period of rapid polymerization as this monomer adds.

TABLE II
Properties of mSBmS Block Copolymers Prepared at 25°C

Initiator concn moles/l. $\times 10^3$, ^a	Inherent viscosity ^b	% mS (wt)	Tensile, psi/elong., %	
			24°C	100°C
3.0	0.96	41	2820/570	650/610
3.25	0.88	44	3600/580	875/620
3.5	0.85	46	3600/540	925/610
4.0	0.77	48	4180/540	750/430

^a DiLi-1.

^b In toluene at 30°C.

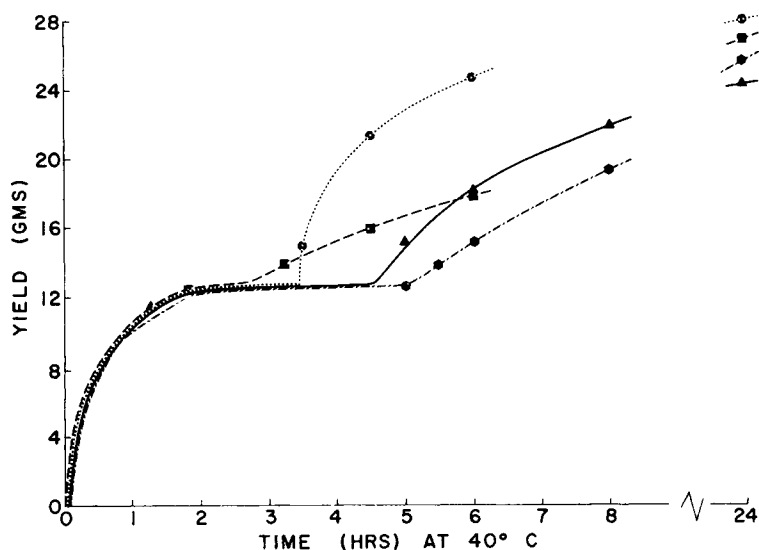


Fig. 1. Copolymer yield as a function of reaction time: (---●) DiLi-1; (---■) DiLi-1A; (—▲) DiLi-3; (- - -●) DiLi-4. Polymerization mixture contained 12 g of butadiene dissolved in 60 ml (54 g) α -methylstyrene.

The faster rate with DiLi-1 initiator, which contains dimethyl ether, is clearly shown in comparison with the other initiators, which contain triethylamine. Under the reaction conditions used, a triblock copolymer containing 40% α -methylstyrene can be prepared in about 4 hr with the former initiator; with the latter three, about 7–8 hr are required.

Copolymerizations with each initiator were also run for 24 hr, and these points are included in Figure 1. Polymers containing 50–57% α -methylstyrene were formed in this time. With still longer reaction times (48–72 hr) α -methylstyrene contents up to 70% can be achieved.

Stress-strain properties of representative polymers made with each initiator and containing about 45% α -methylstyrene are given in Table III. All initiators produced polymers with good tensile strengths (> 3000 lb/in.²) at 24°C and with strengths of several hundred lb/in.² at 100°C.

A few selected samples, made with each of the four initiators and containing various amounts of α -methylstyrene, were given stress-strain tests at 122°C. Results in Table IV show that the elastomeric polymers, with α -methylstyrene contents $\leq 45\%$, still retained tensile strengths of a few hundred lb/in.² at this

TABLE III
Properties of mSBmS Block Copolymers Prepared at 40°C^a

Initiator	Inherent viscosity ^b	Tensile, psi/elong., %	
		24°C	100°C
DiLi-1	0.72	3300/580	620/590
DiLi-1A	0.97	3380/530	830/530
DiLi-3	0.92	3600/620	820/560
DiLi-4	0.84	3200/760	470/500

^a All polymers contain $\sim 45\%$ α -methylstyrene.

^b In toluene in 30°C.

TABLE IV
 Stress-Strain Properties at 122°C

Initiator	% mS (wt)	Tensile, psi	Elong., %
DiLi-1A	30	245	460
DiLi-1	40	300	500
DiLi-3	45	415	420
DiLi-4	60	1230	100

temperature. The sample containing 60% α -methylstyrene, which presumably would form the continuous phase in this polymer, had moderate strength (1230 lb/in.²) but with low elongation (100%).

α -Methylstyrene Incorporation in the Butadiene Block

In copolymerizations run with each of the four initiators, a sample was obtained after most of the butadiene had polymerized but before the α -methylstyrene blocks began to add. These were analyzed, and in all four cases they were found to contain only 4–5% copolymerized α -methylstyrene. Thus, even though the α -methylstyrene was present in high concentration (5.8M), it had relatively little tendency to copolymerize with butadiene, especially when compared to styrene. In styrene-butadiene copolymerizations using DiLi-1, with styrene at 0.85M, the butadiene block contained about 15% styrene.¹⁰ This strong inclination for block copolymerization in the α -methylstyrene-butadiene system produces polymers with more nearly pure blocks than in the styrene-butadiene system. They therefore should have greater domain separation and hence greater tensile strengths than similar SBS polymers. Only a few such comparisons can be made from the present data for polymers made with DiLi-1 initiator. Data from Tables II and III show that the mSBmS samples have higher tensile strengths than comparable SBS polymers reported previously.¹⁰ It has also been shown that for similar triblock copolymers with a "pure" isoprene center block, those with α -methylstyrene end blocks have the higher tensile strengths.¹

Microstructure of Polybutadienes Prepared with Dilithio Initiators

Polybutadienes were prepared with the four dilithio initiators in benzene solvent, and their microstructures were determined by infrared analyses using a modified Binder method.¹⁹ Results are shown in Table V, together with data

 TABLE V
 Polybutadiene Microstructures

Initiator	Microstructure components, %		
	<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
DiLi-1	37	48	15
DiLi-1A	33	48	19
DiLi-3	33	48	19
DiLi-4	35	51	14
<i>sec</i> -C ₄ H ₉ Li	40	48	12
<i>sec</i> -C ₄ H ₉ Li·2(C ₂ H ₅) ₂ O	39	42	19

from polymers made with lithium alkyls. The polar modifiers produced some loss in *cis*-1,4 content with accompanying increase in vinyl content, compared to polymer made with *sec*-butyllithium. All have vinyl contents < 20%, however, so they still retain very good low-temperature properties, i.e., all have T_g 's below -87°C .

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