

Preparation and Stress-Strain Properties of ABC Triblock Copolymers of α -Methylstyrene, Butadiene, and Styrene

A few descriptions of ABA triblock copolymers of α -methylstyrene (monomer A) and butadiene or isoprene have appeared in the literature.¹⁻⁶ Because of the high T_g of the poly(α -methylstyrene) end blocks (172°C), they retain some tensile strength at elevated temperatures (up to at least 100°C) where similar copolymers with polystyrene end blocks lose all strength.

It has been shown that block copolymers of styrene and α -methylstyrene exhibit a single T_g , which is intermediate between that of the two homopolymers (100°C for polystyrene).⁷⁻¹⁰ These T_g 's ranged from 127° to 155°C, depending to some extent on copolymer composition and molecular weight. This was taken as evidence that the blocks were compatible and formed a single phase. Blends of the homopolymers, or block copolymers with incompatible blocks, form two phases which exhibit their respective T_g 's.

This suggested that it might be possible to prepare a triblock thermoplastic elastomer with an ABC block structure, in which the A and C blocks would be polystyrene and poly(α -methylstyrene). If these were compatible, they could form a single species of glassy domains rather than separate A and C domains. Such species should have a T_g higher than that of polystyrene; if so, the ABC copolymers ought to have better retention of tensile strength at elevated temperatures ($> \sim 70^\circ\text{C}$) than ABA copolymers with polystyrene end blocks.

A patent described "pure" ABC block copolymers, in which "living" polystyrene was used to initiate butadiene; after the latter had polymerized, temperature was lowered below 15°C and α -methylstyrene, together with a strong polar modifier as dimethoxyethane, as added.¹¹ These ABC copolymers were shown to have fairly good tensile strengths at 80°C; no evidence was shown of possible blending of the polystyrene and poly(α -methylstyrene) end blocks.

This paper reports a few "tapered" ABC copolymers, prepared by initiating a butadiene-styrene mixture with "living" poly(α -methylstyrene). Previously it was shown that the end blocks were compatible and formed a composite glassy domain with a T_g of $\sim 150^\circ\text{C}$.¹² The syntheses and stress-strain properties of these polymers are discussed herein.

EXPERIMENTAL

Materials

The sources and purification of benzene, styrene, butadiene, α -methylstyrene, and diethyl ether have been given previously.^{6,13,14} Toluene was A.C.S. Reagent grade and obtained from Fisher Scientific Company; it was used as received. The *sec*-butyllithium was obtained from Foote Mineral Company; it was handled and stored as described previously.¹⁴

Polymerizations

The "living" poly(α -methylstyrene) was prepared in toluene solution. Since α -methylstyrene has a low ceiling temperature ($\sim 60^\circ\text{C}$), it does not react to 100% conversion, but has appreciable unreacted monomer in equilibrium with active polymer chains except at low temperatures ($< -50^\circ\text{C}$). To attain a high yield of poly(α -methylstyrene), it was polymerized at -17°C . The "living" polymer solution was prepared by the same technique described previously.¹³ α -Methylstyrene polymerizes very slowly at low temperatures, but diethyl ether strongly accelerates the reaction; the initiator used was *sec*- $\text{C}_4\text{H}_9\text{Li} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$. With this system, yields of poly(α -methylstyrene) were $> 90\%$ in 48 hr reaction time.

It has been shown that this initiator can be used to make triblock copolymers of styrene and butadiene with excellent tensile strengths.¹⁴ The polybutadiene center blocks have total 1,4 content $> 80\%$, so the copolymers retain good low-temperature properties.^{6,14}

The ABC block copolymers were prepared by techniques described previously.¹³ Polymerizations were run at 50°C . The polymers were isolated by coagulation in methanol containing a small amount of phenolic antioxidant, and dried *in vacuo* at $\sim 50^\circ\text{C}$.

Polymer Evaluation

Polymers were analyzed and evaluated by previous methods.¹³ Gel permeation chromatograms were not determined on these polymers. Since they were prepared by techniques used to make SBS polymers which had narrow molecular weight distributions and little or no homopolymer or diblock copolymer,¹⁵ it is believed that they contain little poly(α -methylstyrene) or diblock copolymer. Variations in stress-strain properties are probably due to molecular weight differences in the polymers, as discussed below. Styrene content was determined by measuring the absorption of a cyclohexane solution of the polymer at 268 μm . The total of styrene plus α -methylstyrene was determined at 262 μm , and the α -methylstyrene content by difference. Samples for stress-strain tests were press molded at 425°F. For tests run at elevated temperatures, the dumbbell test piece was conditioned for 10 min at 100°C before testing was begun.

RESULTS AND DISCUSSION

Results of stress-strain tests at 24 and 100°C for representative polymers are given in Table I.

The copolymers exhibit the behavior of triblock thermoplastic elastomers. They had fair to excellent tensile strengths at 24°C, but all had tensiles of several hundred psi at 100°C. Comparable polystyrene-polybutadiene-polystyrene (SBS) block copolymers have tensile strengths <50 psi at the latter temperature. This retention of some strength at 100°C supports the previous finding that the polystyrene and poly(α -methylstyrene) end blocks are compatible, and that this composite glassy domain must have a T_g well above 100°C.¹² These polymers have strengths at 100°C similar to ABA block copolymers of α -methylstyrene and a diene,^{1,6} indicating the T_g of the composite glassy blocks must not be greatly different from the T_g of poly(α -methylstyrene). Experimental determinations showed the respective T_g 's were $\sim 150^\circ\text{C}$,¹² and $170^\circ\text{--}183^\circ\text{C}$.^{7,9,10}

Several of the polymers listed in Table I have inherent viscosities >1.6. They had rather poor tensile strengths at 24°C, although they did retain strengths of several hundred psi at 100°C. Previous experience with SBS samples in this laboratory showed that those with inherent viscosities > ~ 1.5 compression molded rather poorly, and usually had less tensile strength than polymers with lower inherent viscosities. This may account for the low tensile strengths (at 24°C) of some of the ABC samples in Table I. Conversely, a few ABC polymers with inherent viscosities <1.0 had high tensile strengths at 24°C, but were very poor at 100°C. Additional studies will be done to define the effect of the polymer's inherent viscosity on its tensile strength.

No clear conclusions can be made on the effect of the polystyrene and poly(α -methylstyrene) contents on tensile strength, particularly at 100°C. It is well established that the total content of the glassy end blocks in triblock copolymers greatly influences their tensile strengths.¹³⁻¹⁶ With ABC-type copolymers, for a given total A + C content, the proportions of A and C can be varied widely. The amount of poly(α -methylstyrene) in the copolymer should govern its strength at elevated temperatures. However, the styrene content must be sufficient to produce molecular weights of at least 8000 for the polystyrene segments, or domain formation will not occur.¹⁶ Thus, there would be maxima and minima for the contents of both aryl monomers in these copolymers, if best tensiles

TABLE I
Properties of mSBS Block Copolymers

Styrene	Percent		Inherent Viscosity	Tensile(psi)/Elong(%)	
	α -Methyl-Styrene	Total End Blocks		24°C	100°C
14	19	33	1.82	2275/790	>380/900 ^a
15	19	34	1.94	2500/770	440/900
16	21	37	1.66	1900/450	>945/700 ^a
15	23	38	1.99	1715/440	685/760
22	17	39	1.07	4200/700	329/920
17	23	40	1.71	2610/580	800/730
30	20	50	1.16	4600/775	>705/800 ^a
28	28	56	1.35	3675/375	>1725/700 ^a
25	35	60	1.49	3110/360	1615/740

^a Samples elongated to limit of instrument without breaking. Inherent viscosities were determined in toluene at 30°C.

are to be attained at both ambient and elevated temperatures. More detailed studies of these variations will be undertaken.

There was some unreacted α -methylstyrene monomer present during the butadiene-styrene copolymerization. Although reaction conditions were such that this monomer was now above its ceiling temperature and could not homopolymerize, it could copolymerize with either of the added monomers, particularly styrene. However, unpublished work in these laboratories, as well as published data show that α -methylstyrene and styrene anionically copolymerize poorly, even in the presence of diethyl ether.^{17,18} Styrene polymerization strongly predominates. Because of the concentrations of monomers used herein, it is felt that little if any α -methylstyrene was incorporated in the styrene block.

The author wishes to thank the Goodyear Tire and Rubber Company for permission to publish these results. Inherent viscosities were determined by V. A. Bittle. Analyses of copolymer compositions were done by J. D. Daugherty. This is Contribution No. 588 from the Research Laboratories of the Goodyear Tire and Rubber Company.

References

1. L. J. Fetters and M. Morton, *Macromolecules*, **2**, 453 (1969).
2. Polymer Corporation, Ltd., Brit. Pat. No. 1,191,605, 13 May 1970.
3. G. Karoly, in *Block Polymers*, S. L. Aggarwal, Ed., Plenum, New York, 1970, p. 153.
4. T. Shimomura, H. Nagata, Y. Murakami, H. Sanno, and T. Inoue, U.S. Patent No. 3,819,767, 25 June 1974.
5. B. C. Roest and H. A. J. Schepers, U.S. Patent No. 3,925,512, 9 December 1975.
6. R. E. Cunningham, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
7. M. Baer, *J. Polym. Sci.*, **A2**, 417 (1964).
8. P. Black and D. J. Worsfold, *J. Appl. Polym. Sci.*, **18**, 2307 (1974).
9. D. J. Dunn and S. Krause, *Polym. Lett.*, **12**, 591 (1974).
10. L. M. Robeson, M. Matzner, L. J. Fetters, and J. E. McGrath, in *Recent Advances in Polymer Blends, Grafts, and Blocks*, L. H. Sperling, Ed., Plenum, New York, 1974, p. 281.
11. Polymer Corporation Ltd., Brit. Pat. No. 1,189,767, 29 April 1970.
12. G. S. Fielding-Russell and P. S. Pillai, *Polymer*, **15**, 97 (1974).
13. R. E. Cunningham and M. R. Treiber, *J. Appl. Polym. Sci.*, **12**, 23 (1968).
14. R. E. Cunningham and M. L. Wise, *J. Appl. Polym. Sci.*, **16**, 107 (1972).
15. R. D. Mate and M. R. Ambler, *Separation Sci.*, **6**, 139 (1971).
16. M. Morton, L. J. Fetters, F. C. Schwab, C. R. Strauss, and R. F. Kammereck, *Fourth International Synthetic Rubber Symposium*, No. 3, Rubber and Technical Press, London, 1969, p. 70.
17. D. P. Wyman and I. H. Song, *Makromol. Chem.*, **115**, 64 (1968).
18. W. Kampf and H. Weber, *Z. Angew. Makromol. Chem.*, **26**, 155 (1972).

ROBERT E. CUNNINGHAM

Goodyear Tire and Rubber Company
Akron, Ohio 44316

Received June 15, 1977

Revised July 29, 1977