Synthesis and Properties of Block Polymers.
I. Poly-α-methylstyrene–Polyisoprene–Poly-α-methylstyrene

Lewis J. Fetters and Maurice Morton

Institute of Polymer Science, The University of Akron, Akron, Ohio 44304.
Received May 23, 1969

ABSTRACT: Block polymers of polystyrene–polyisoprene–polystyrene (SIS) and poly-α-methylstyrene–polyisoprene–poly-α-methylstyrene (mSImS) have been synthesized using 1,4-dilithio-1,1,4,4-tetraphenylbutane as the initiator. Unlike previous dilithium initiators this species is capable of generating polyisoprene whose microstructure retains the high (>90%) 1,4 character necessary for elastomeric behavior. Furthermore, molecular weight measurements indicate that this initiator is capable of synthesizing block polymers possessing predictable molecular weights and narrow molecular weight distributions. Measurements of the tensile strength of SIS and mSImS block polymers of virtually identical composition and molecular weight shows that the replacement of polystyrene with poly-α-methylstyrene endows the mSImS block polymer with higher tensile strengths at comparable temperatures as well as higher temperature capability.

The "thermoplastic elastomers"[1] have aroused considerable interest in recent years and have been the subject of a number of studies.[2–4] These materials are ABA block polymers in which the A block is polystyrene while the B block is either polybutadiene or polyisoprene. Owing to the thermodynamic incompatibility of these blocks, they form separate phases in the bulk state, with the result that the lesser component, polystyrene, is dispersed in the form of minute "domains" (*ca.* 200 Å) within the rubbery polydiene. Since the polystyrene domains are glassy at ambient temperature, they form virtually rigid junctions of the elastic chain network.

Such a network structure results in an elastomer of high tensile strength. It has been shown[2,3] that the strength of these materials depends upon the ability of the glassy polystyrene domains to yield under stress and to undergo an inelastic deformation. By the same token, the strength of these polymers is markedly affected at elevated temperatures, dropping sharply above 60° due to the approach of the glass transition temperature (T_g) of the polystyrene domains. Hence it is of considerable interest to explore possibilities of finding A blocks of higher temperature capability.

It has also been shown[5] that the strength of these elastomers is markedly dependent on the perfection and purity of the ABA block structure comprising the network. Such a high degree of structural perfection has been attainable by the use of homogeneous anionic polymerization systems, specifically the organolithium systems in hydrocarbon solvents. These systems are necessary in order to attain a high 1,4 chain structure in the polydiene block, which is required for elastic behavior. Although the simplest and most versatile polymerization would be accomplished by the use of a dilithium initiator, this has not been feasible to date since these initiators have only been prepared in aliphatic ether solvents, being insoluble in hydrocarbons, and the ethers are known to lead to high 1,2 and/or 3,4 structures[6–8] in the polydienes, structures which lead to nonrubbery properties.

A good candidate for an A block with a higher temperature potential is α-methylstyrene, since the polymer is known to have a T_g of 173°.[9] Thus poly-α-methylstyrene would not only be of interest for this reason but would also offer an opportunity to study its effect on the ambient temperature behavior of the block polymer, with special reference to the stress–strain behavior of the poly-α-methylstyrene domains.

However, to synthesize an ABA block polymer where A = poly-α-methylstyrene and B = polyisoprene (*i.e.*, an mSImS polymer), the use of a dilithium initiator is required, on two counts. In the first place, α-methylstyrene has a ceiling temperature[10] of 6° (for a 1 *M* solution) and is therefore in equilibrium with a substantial amount of monomer at room temperature. In the second place, it has a very slow rate of polymerization at room temperature or below, in hydrocarbon solvents,[11] and hence requires the presence of substantial amounts of aliphatic ethers to accelerate the rate. This poses no problem if the α-methylstyrene is the *last* monomer added, since ethers can safely be present once the isoprene has been polymerized.

A variety of dilithium initiators have been prepared[12] in solvents such as tetrahydrofuran, ethyl ether, and dioxane but these are of little interest for the reasons given above. Although organic dilithium compounds

---

[1] G. Holden and R. Milkovich, Belgian Patent 627,652 (July 29, 1963).

[2] M. Morton, J. E. McGrath, and P. C. Juliano, *J. Polym. Sci., Part C*, No. 26, 99 (1969).

[3] T. L. Smith and R. A. Dickie, *ibid., Part C*, No. 26, 163 (1969).

[4] R. F. Fedors, *ibid., Part C*, No. 26, 189 (1969).

[5] M. Morton, Proceedings of the Princeton University Conference on Advances in Polymer Science and Materials, Nov 21–22, 1968.

[6] R. V. Basova and A. A. Arest-Yakubovich, *Dokl. Akad. Nauk SSSR*, **149**, 1067 (1963).

[7] A. Rembaum, R. C. Morrow, and A. V. Tobolsky, *J. Polym. Sci.*, **61**, 155 (1962).

[8] H. Morita and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **79**, 5853 (1957).

[9] J. M. G. Cowie and P. M. Toporowski, *Eur. Polym. J.*, **4**, 621 (1968).

[10] D. J. Worsfold and S. Bywater, *J. Polym. Sci.*, **26**, 299 (1957).

[11] D. P. Wyman and I. H. Song, *Makromol. Chem.*, **115**, 64 (1968).

[12] R. P. Zelinski and C. W. Strobel, U. S. Patent 3,108,994 (1963); R. P. Zelinski and H. L. Hsieh, U. S. Patent 3,078,254 (1963).

have been prepared in hydrocarbon media,[13] they are known to be insoluble as well as impure. The work described herein concerns the successful preparation of a dilithium compound of high purity, *viz.*, 1,4-dilithio-1,1,4,4-tetraphenylbutane, in a hydrocarbon medium containing a small amount of an aromatic ether, *e.g.*, anisole and its use in synthesizing the above block polymers. The success of this synthesis is based on the fact[2,14-16] that such aromatic ethers have little or no effect on the 1,4 structure of anionically prepared polydienes.

Experimental Section

High vacuum techniques were used for all solvent and monomer purifications. The basic techniques have been presented elsewhere.[2,16] The solvents used were cyclohexane, benzene, anisole, 1,2-dimethoxyethane and tetrahydrofuran. The polymerization initiators were recrystallized ethyllithium and 1,4-dilithio-1,1,4,4-tetraphenylbutane. The monomers used were styrene, α-methylstyrene, and isoprene. All polymerizations were carried out at 25° in evacuated glass reactors.

Preparation of Dilithium Initiator. The initiator 1,4-dilithio-1,1,4,4-tetraphenylbutane was prepared by the reaction of 1,1-diphenylethylene with lithium. Purification of the 1,1-diphenylethylene was accomplished using the method of Szwarc.[17a] A solvent mixture of cyclohexane and anisole (15 vol %) was used to prepare the dilithium initiator. A typical reaction employed 1–2 g of 1,1-diphenylethylene and 2 g of lithium in approximately 100 ml of solvent mixture. The reaction was allowed to proceed for 48 hr at 20°. The solution of initiator was then filtered from the lithium and its concentration determined using the method of Gilman.[17b] The concentration of lithium was found to be between 0.01 and 0.08 mmol ml^{-1}. Prior to use, the 1,4-dilithio-1,1,4,4-tetraphenylbutane was allowed to react with enough isoprene to generate a low molecular weight ($\bar{M}_n \simeq 2000$) isoprenyldilithium polymer. This was necessary since it was found that the original dilithium initiator precipitated from solution when added to the polymerization solvent (cyclohexane or benzene). The isoprenyldilithium, however, remained in solution. The initiation reaction of 1,4-dilithio-1,1,4,4-tetraphenylbutane with isoprene was apparently complete within several minutes, as evidenced by the disappearance of the red color of the initiator.

Polymer Preparation. The preparation of ABA block polymers containing isoprene and styrene using ethyllithium initiator is presented elsewhere.[2] The polymerization of the polyisoprene homopolymers was carried out in cyclohexane with the dilithium species used as the initiator. The preparation of the block polymer SIS-6[18] was accomplished in cyclohexane solution but with the use of the isoprenyldilithium. The isoprene was polymerized first, with the styrene added after the supply of isoprene was depleted. Following the procedure outlined elsewhere,[16] a small amount of tetrahydrofuran (∼0.15 *M*) was used to accelerate the crossover reaction of isoprenyllithium with styrene. Essentially the same procedure was used to prepare the block polymers of α-methylstyrene and isoprene, the main difference being that approximately 250 ml of ether was added to the polyisoprenyllithium–hydrocarbon solution (*ca.* 90 ml) prior to the addition of the α-methylstyrene. For the mSImS-1 polymer the polymerization solvents were cyclohexane and tetrahydrofuran, while benzene and dimethoxyethane were used for the mSImS-2 polymer. It was noted that dimethoxyethane will cause a faster crossover reaction than does tetrahydrofuran. The polymerization of the α-methylstyrene was then accomplished at −78°. It might be added that it was found that the addition of just 1 drop of hexamethylphosphortriamide caused a large increase in the rate of the reaction of isoprenyllithium with α-methylstyrene as well as in the subsequent polymerization of the α-methylstyrene at −78°. However, the amide was not used in the preparation of the mSImS block polymers, since it was not known whether the amide causes any termination of the active chains under the conditions used. The polymerization of α-methylstyrene was carried out at low temperature since higher temperatures (>−30°) will cause an appreciable amount of monomer to remain in equilibrium with the polymer.[10] Following the completion of the polymerization, the reaction was terminated under vacuum with methanol. Phenyl-β-naphthylamine was added as antioxidant and the polymer coagulated in methanol and dried in a vacuum oven at room temperature. Polymer yields were quantitative.

Polymer Characterization. The number-average molecular weights were measured in toluene at 37°. Hewlett-Packard high speed osmometers (502 and 503) were used with SαS-08 deacetylated acetylcellulose membranes. From the linear plot of $(\pi/c)^{0.5}$ *vs.* concentration, the molecular weights and the second virial coefficients were derived.

Gel permeation chromatograms were obtained on the Waters instrument equipped with four columns. Dilute solutions containing 0.3 wt % of the polymers in toluene were used at a flow rate of 1.0 ml min^{-1} and a temperature of 70°.

The weight-average molecular weights were determined at 30 ± 0.5° in cyclohexane and tetrahydrofuran using a Bausch and Lomb PGD (the Sofica) light scattering photometer. The photometer was calibrated against benzene with the value of 15.8×10^{-6} cm^{-1} being adopted for Rayleigh's ratio. The solutions were clarified by filtration through solvent resistant Millipore or Selas Flotronics filters of 0.45 μ pore diameter. The values of dn/dc were determined at 30° with the use of a Brice–Phoenix differential refractometer. In tetrahydrofuran the value of dn/dc for the mSImS-1 polymer was 0.180 ml g^{-1} while the value for the mSImS-2 polymer was 0.182 ml g^{-1}. In cyclohexane the value of dn/dc for the mSImS-1 polymer was 0.131 ml g^{-1}. The light-scattering measurements were made between the angles of 30 and 150° on four different concentrations per sample. Unpolarized light was used with the wavelength being 5460 Å. The molecular weights and second virial coefficients were then determined from Zimm plots.

The ultracentrifuge measurements were made on the Beckman Model E instrument at 30° using cyclohexane and tetrahydrofuran as solvents. A double sector cell was used for the run in cyclohexane while a single sector cell was used for tetrahydrofuran. Solutions containing 1 g of polymer per 100 ml of solvent were used. Both measurements were made at 48,000 rpm.

The intrinsic viscosity measurements were done at 30° in a Ubbelohde viscometer where the solvent flow time was 157.8 sec. Cyclohexane was the solvent.

High-resolution nmr spectra of the polyisoprene were used to determine the polymer microstructure. The measurements were obtained on the Varian HA100 instrument. Solutions of the polymers (20% wt/vol) were made up in carbon tetrachloride. An internal standard, tetra-

---

(13) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, Methuen & Co., London, 1967.

(14) A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.*, **40**, 73 (1959).

(15) C. E. Rogers, *Polym. Preprints*, 2 [2], 75 (1961).

(16) L. J. Fetters, *J. Res. Nat. Bur. Stand.*, **70A**, 421 (1966).

(17) (a) G. Spach, H. Monteivo, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962); (b) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

(18) The numbers used after the hyphen denote the experimental run numbers.

TABLE I
POLYMER MOLECULAR WEIGHTS AND COMPOSITION

Sample	$M_s \times 10^{-3}$,[a] g mol^{-1}	Weight % end blocks	$[\eta]$, dl g^{-1}	$M_n \times 10^{-3}$, g mol^{-1}	$A_2 \times 10^3$,[b] mol cm^3 g^{-2}
Polyisoprene-1	108			112	1.0
Polyisoprene-2	100			103	1.0
Polyisoprene-3	73			71	1.0
SIS-1[c]	14–63–14	30		89	1.1
SIS-6	20–87–20	33		131	0.97
mSImS-1	21–85–21	33	1.08	132	0.75
mSImS-2	27–66–27	45	0.78	117	0.72

[a] The predicted stoichiometric molecular weight (M_s) is based on the assumption that each initiator species contains two lithium counterions, *i.e.*, M_s = grams of monomer/0.5[initiator]. [b] Osmotic second virial coefficient. [c] This polymer was made using ethyllithium initiator, *i.e.*, M_s = grams of monomer/[initiator].

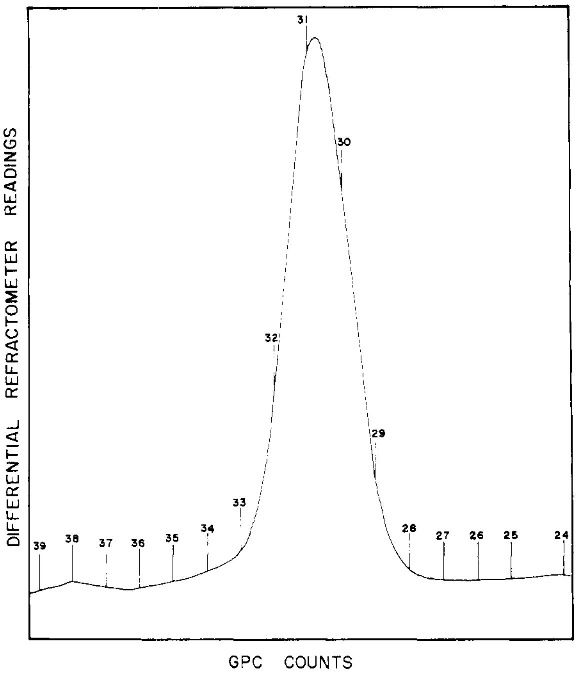

Figure 1. Gel permeation chromatogram of polymer mSImS-1.

methylsilane, was employed. The spectra were interpreted using Chen's method.[19]

For the stress-strain measurements, films were cast from tetrahydrofuran and dried under vacuum for 96 hr at 40° in order to remove all solvent. Solvent casting was used to prepare the test specimens in order to avoid the variables that can occur when molding techniques are used. Furthermore, molding of the mSImS polymers was not attempted since the possibility exists that the polyisoprene and poly-α-methylstyrene blocks will degrade at the temperature necessary (*ca.* 200°) for this operation. The test samples were stamped out of bubble-free films, using a microdumbbell die. A bench mark of 1 cm was made on the gauge section of each specimen and testing carried out on a bench model Instron tensile tester equipped with pneumatic clamps. Crosshead speed was 5 cm/min.

The glass transition temperatures of the mSImS-1 polymer were recorded on a Perkin-Elmer DSC-18 instrument. The polyisoprene had a T_g of −64° (±3°) while the value for the poly-α-methylstyrene was 154° (±3°). This value is in good agreement with the value of 156° predicted using Cowie's equation[9] relating T_g to the number-average molecular weight.

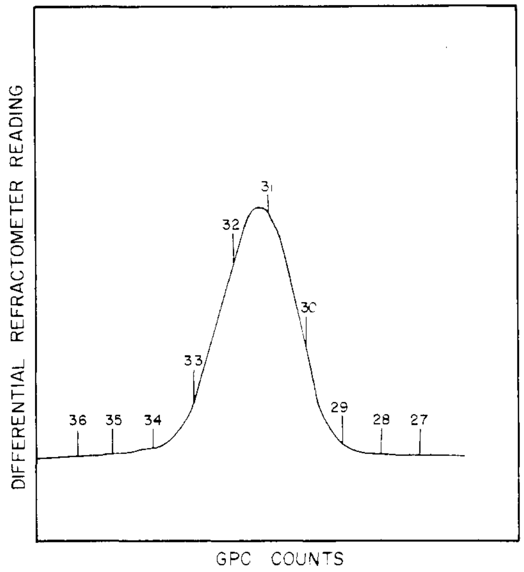

Figure 2. Gel permeation chromatogram of polymer mSImS-2.

Results and Discussion

The dilithium initiator was used to prepare several samples of polyisoprene and a polystyrene–polyisoprene–polystyrene (SIS-6) block polymer. The SIS-6 polymer was made in order that comparisons might be made with a block polymer (SIS-1) made by the use of the conventional monofunctional ethyllithium as well as the mSImS-1 polymer. The polyisoprene microstructure was found to have the composition, 65–70% *cis*-1,4, 20–25% *trans*-1,4, and the remainder 3,4. Thus the influence of anisole on the polyisoprene microstructure was minimal, as anticipated. In all of the isoprene polymerizations the volume per cent anisole was 1 or less. It was also necessary to check the number-average molecular weights of the various polymers in order that some insight might be gained into the extent of difunctionality of the initiator. These molecular weights are shown in Table I. It can be seen that the samples all possess number-average molecular weights in close accord with the predicted values. This, of course, indicates that the initiator is highly difunctional. Gel permeation chromatograms of all these samples in Table I indicated that each polymer possessed a narrow distribution of molecular weights. Of equal importance was the indication that

---

(19) H. Y. Chen, *Rubber Chem. Technol. Rev.*, **41**, 47 (1968).

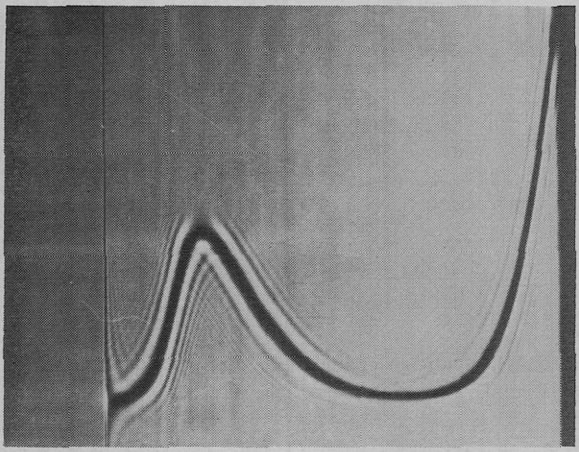

Figure 3. Schlieren pattern of polymer mSImS-1 in tetrahydrofuran. Picture taken 3 hr and 30 min after the start of the measurement.

these samples did not possess a bimodal distribution. This type of distribution would result if the initiator contained an appreciable fraction of monolithium species or if termination occurred at one of the two chain ends during the early stages of the polymerization. Figure 1 shows the gel permeation chromatogram for the mSImS-1 block polymer, while Figure 2 shows the trace obtained on the mSImS-2 block polymer.

Figures 3 and 4 are the Schlieren patterns from the ultracentrifuge for the two mSImS block polymers. Both patterns show the absence of a low molecular weight fraction of the type which could result from the presence of monolithium initiator. Hence, the data from both the GPC instrument and the ultracentrifuge are in concert with each other in that both indicate that these block polymers consist primarily of A-B-A material.

Additional characterization of the mSImS block polymers was accomplished by means of light scattering. An indication that the samples possessed a fairly narrow distribution of molecular weights can be gained by a comparison of the number-average molecular weights in Table I and the weight-average values in Table II. The measured weight-average molecular weight of a block polymer in solvents with a high refractive index should not be greatly in error as long as there is no appreciable distribution in composition and molecular weight.[20–24] Thus the weight-average molecular weights in Table II should not be too far away from the actual values.

Table II

Weight-Average Molecular Weights of mSImS Block Polymers

Sample	$M_w \times 10^{-3}$,[a] g mol^{-1}	$A_2 \times 10^3$,[a] mol cm^3 g^{-2}	$M_w \times 10^{-3}$,[b] g mol^{-1}	$A_2 \times 10^3$,[b] mol cm^3 g^{-2}
mSImS-1	141	0.70	145	0.75
mSImS-2	125	0.65		

[a] Data obtained in tetrahydrofuran. [b] Data obtained in cyclohexane.

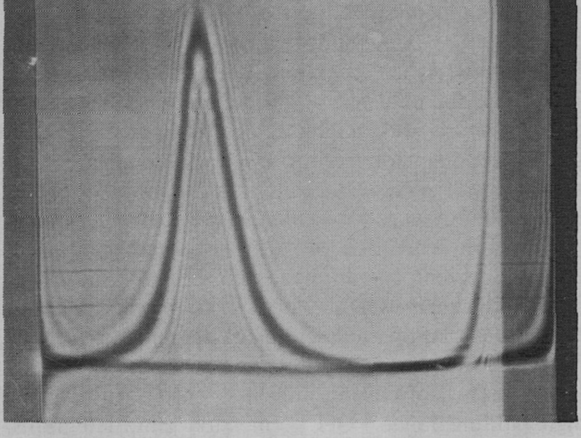

Figure 4. Schlieren pattern of polymer mSImS-2 in cyclohexane. Picture taken 4 hr and 40 min after the start of the measurement.

Another means of evaluating the efficiency of the dilithium initiator was the comparison of the tensile strengths of the SIS-6 polymer, prepared by means of the dilithium initiator, with the SIS-1 polymer, having very nearly the same composition but prepared by means of ethyllithium initiation. The stress–strain behavior of these two SIS block polymers is shown in Figure 5. As can be seen both block polymers exhibit similar properties, indicating that the dilithium initiator is capable of generating ABA block polymers free from any appreciable AB material. In this regard it has been shown[5] that in SIS block polymers, the presence of as little as 2% by weight of SI polymer causes a significant decrease in tensile strength while 5% of SI polymer will cause a drop in the tensile strength of as much as 23%.

The stress–strain data for the mSImS-1 and SIS-6 block polymers are shown in Figure 6. It is readily apparent that the mSImS-1 block polymer exhibits a markedly higher tensile strength (at 20°) than the SIS-6 polymer of equivalent composition (455 kg cm^{-2} *vs.* 260 kg cm^{-2}). Both polymer samples were synthesized using dilithium initiator obtained from the same synthesis run.

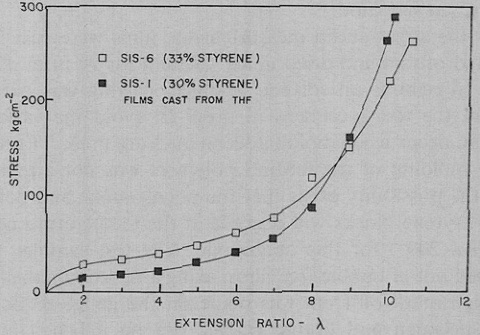

Figure 5. Stress–strain properties of polymers SIS-1 and SIS-6 at 20°.

---

(20) W. H. Stockmayer, L. D. Moore, M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16,** 517 (1955).

(21) W. Bushuk and H. Benoit, *Can. J. Chem.*, **36,** 1616 (1958).

(22) S. Krause, *J. Phys. Chem.*, **65,** 1618 (1961); **68,** 1948 (1964).

(23) D. Freyss, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B,* **2,** 217 (1964).

(24) D. N. Cramond and J. R. Urwin, *Eur. Polym. J.*, **5,** 35 (1969).

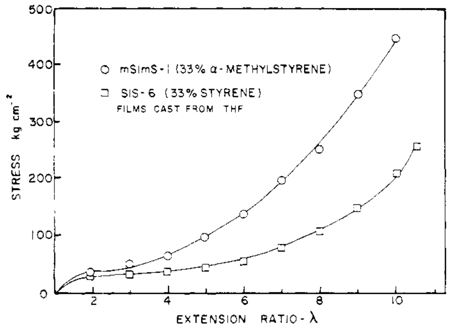

Figure 6. Stress–strain properties of polymers SIS-6 and mSImS-1 at 20°.

Thus it would seem that end blocks with glass transition temperatures higher than polystyrene not only do not detract from the tensile strength but, in fact, enhance it. It might be added that the interaction coefficient between poly-α-methylstyrene and polyisoprene is virtually the same as that of polystyrene and polyisoprene.[25] Hence the amount of phase blending in the SIS-6 and mSImS-1 block polymers should be nearly identical. It can be assumed that the effectiveness of the glassy domains (the sites of stress concentration) as energy "sinks"[2-4] is greatly dependent on the degree of phase separation. Thus the better the phase separation, *i.e.*, the less the glassy domains are diluted by the rubbery component, the greater is the energy absorbed prior to the disintegration of these domains. Some phase blending in block polymers is inevitable since absolute insolubility will occur only for infinite molecular weights or when the difference in the cohesive energies of the blocks becomes infinite. Furthermore, it is doubtful if phase equilibria are attained during film formation of these block polymers.

If the phase purity of the SIS-6 and mSImS polymers are indeed similar, then the higher strengths of the latter species imply that the poly-α-methylstyrene domains are capable of absorbing more energy than the polystyrene. This would presumably be due to the higher stress which the poly-α-methylstyrene can support at comparable temperature. It is significant, in this regard, that the per cent set at break of the mSImS-1 polymer is 90–100% compared to 40–50% for the SIS-6 polymer. For both block polymers, this inelastic deformation is completely recoverable by heating the material to the *T* of the end blocks.

Figure 7 contains the stress–strain curve for the mSImS-2 block polymer. This polymer possesses a tensile strength of 480 kg cm^{-2}. This material was observed to undergo a large amount of drawing at low elongations. Hence, this polymer was prestretched and permitted to relax for 24 hr at 20°. The sample thickness was then measured, the bench mark of 1 cm was applied, and the stress–strain measurements were performed. The other block polymers did not exhibit this drawing phenomenon. Thus, the sample thicknesses used in the calculation of the tensile strengths for these polymers were those of the unstretched films.

TABLE III
THE TENSILE STRENGTH AND ELONGATION AT BREAK AT VARIOUS TEMPERATURES FOR THE mSImS AND SIS-6 BLOCK POLYMERS

	mSImS-1		SIS-6	
Temp, °C	σ_b, kg cm^{-2}	λ^a	σ_b, kg cm^{-2}	λ^a
−60	615	4	440	5
−40	600	6	380	6.5
−20	580	7	360	8.5
0	530	8.5	345	10
10	500	9		
20	455	10	260	11
40	295	12	235	14
60	225	13	120	16
80	110	11.5	30	16
100	65	11		
115	45	12.5		
130	20	11		
145	6	4		

[a] The values of λ (extension ratio) are only approximate for temperatures other than 20°.

The temperature behavior of the SIS-6 and mSImS-1 polymers is compared in Figure 8. This figure shows plots of σ_b *vs.* temperature for the SIS-6 and mSImS-1 block polymers. Here σ_b is the breaking stress. It is apparent that for both of these block polymers, the breaking stress increases with decreasing temperature, the mSImS-1 block polymer exhibiting a significantly higher breaking stress than the SIS-6 block polymer at any comparable temperature. These values for the breaking stress at various temperatures are shown in Table III along with the values for elongation at break. In addition to exhibiting higher breaking stress than the SIS-6 polymer, the mSImS-1 material retains some strength up to temperatures 50° higher than the SIS-6

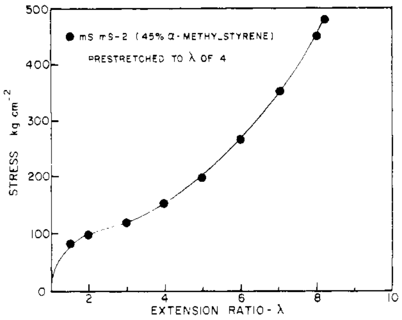

Figure 7. Stress–strain properties of polymer mSImS-2 at 20°.

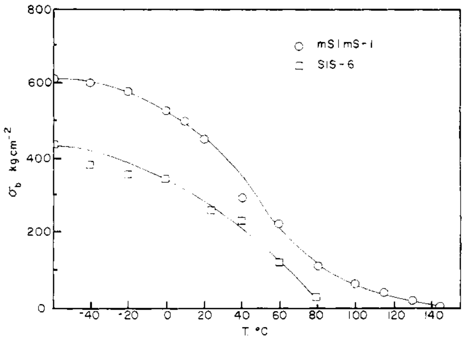

Figure 8. Effect of temperature on tensile strength of polymers SIS-6 and mSImS-1.

---

(25) P. A. Small, *J. Appl. Chem.*, 3, 71 (1953).

block polymer. Thus replacement of polystyrene by poly-α-methylstyrene endows the resultant block polymer with both greater tensile strength and higher temperature capability.

At 100° the mSImS-1 block polymer retains a tensile strength of 65 kg cm^{-2}. This polymer is thus markedly stronger than many gum rubber vulcanizates, *e.g.*, SBR[26] ~6 kg cm^{-2}, with the exception of Hevea vulcanizates. The mSImS-1 material is somewhat weaker at 100° than some carbon black filled rubbers, *e.g.*, Hevea[27] (~180 kg cm^{-2}), a 55/45 butadiene–acrylonitrile copolymer[27] (~130 kg cm^{-2}), or SBR[28] (~100 kg cm^{-2}), while on the other hand, it is stronger than such filled vulcanizates as an emulsion polyisoprene[28] (~55 kg cm^{-2}) or polyisobutylene[29] (~50 kg cm^{-2}). Thus this block polymer is comparable in breaking stress at 100° to some filled rubber vulcanizates while at ambient temperature and lower it possesses a higher breaking stress than any conventionally cross-linked filled rubber vulcanizate, including the best Hevea vulcanizates.

Acknowledgments. This work was supported in part by The Goodyear Tire & Rubber Co. and by the Air Force Materials Laboratory, U. S. Air Force, under Contract AF 33(615)-5362. The assistance of Mr. D. Hassick and Mr. R. Mate of The Goodyear Tire & Rubber Co. in the gel permeation chromatography is gratefully acknowledged. Polymer SIS-1 was synthesized by Dr. F. Schwab. The ultracentrifuge runs were kindly performed by Mr. E. Slagowski.

(26) T. L. Smith, *J. Polym. Sci.*, **22**, 99 (1958).

(27) B. B. Boonstra, *India Rubber World*, **121**, 299 (1949).

(28) A. M. Borders and R. D. Juve, *Ind. Eng. Chem.*, **38**, 1066 (1946).

(29) T. F. Lavery, F. S. Grover, S. Smith, and L. J. Kitchen, *Rubber Age*, **80**, 843 (1957).

Exchange Reactions between Lithium Alkyl and Alkenyl Aggregates in Hydrocarbon Solution

F. Schué[1] and S. Bywater

Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada.

Received June 9, 1969

ABSTRACT: The ^{7}Li nmr spectra of a number of lithium alkyls (*n*-, *sec*-, and *t*-butyl) together with lithiomethyltrimethylsilane and oligomeric polyisoprenyllithium have been measured alone and in binary mixtures in cyclopentane. All the systems showed rapid mixing of the aggregated species at room temperature if *t*-butyllithium was not one of the components. The systems containing *t*-butyllithium behaved differently. Slow mixing of *t*-butyllithium over a period of hours was observed with both *sec*-butyllithium and lithiotrimethylsilane but with polyisoprenyllithium partial exchange occurred in at most a few minutes but did not proceed further. The implications of these experiments for polymerization studies is discussed.

The physical properties of lithium alkyls in solution have a very important bearing on their initiation of polymerization. It is well known that the alkyls are associated in solution in hydrocarbons as are the active centers in polymerization.[2] In the early stages of polymerization both residual lithium alkyl and polymer lithium species will coexist. The formation of mixed aggregates can be expected under these conditions as was demonstrated for simple alkyls by Weiner and West[3a] and for the polymer systems by Morton.[3b] The behavior of lithium alkyl initiators in aliphatic hydrocarbons in particular shows a rather complex pattern. There is a period of increasing initiation rate,[4] most probably linked to reactivity differences of the various alkyl containing aggregates[5] present at different times, before reaction slows due to depletion of the reactants. The process of chain initiation might then be affected by rates of exchange of lithium-containing species between various aggregates or by the dissociation rates of these aggregates. If intermolecular exchange takes place by a dissociative process, as has been suggested,[6] these two processes are related.

The chemical shift of the ^{7}Li resonance is sensitive to the environment in the aggregates and has been used by Brown[7] to measure exchange rates between simple alkyls in a number of solvents. It is of obvious interest to extend these data to systems of interest in polymer chemistry, and for this purpose low molecular weight polyisoprenyllithium was chosen.

Experimental Section

The lithium alkyls used were supplied by the Foote Mineral Co. as solutions in heptane or pentane, with the exception of lithiomethyltrimethylsilane ($LiCH_2Si(CH_3)_3$) which was prepared as described in the literature.[8]

n-Butyllithium was used as received after removal of the solvent. The secondary and tertiary compounds were subjected to a short-path distillation to a cooled receiver. *t*-Butyllithium sublimes smoothly at 75°, *sec*-butyllithium

---

(1) N.R.C. postdoctoral fellow. Address correspondence to the Institut de Chimie, Faculté des Sciences de Strasbourg.

(2) S. Bywater, *Advan. Polym. Sci.*, **4**, 66 (1965).

(3) (a) M. A. Weiner and R. West, *J. Amer. Chem. Soc.*, **85**, 485 (1963); (b) M. Morton, E. E. Bostick, and R. Livigni, *Rubber Plastics Age*, **42**, 397 (1961).

(4) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **42**, 2884 (1964).

(5) J. E. L. Roovers and S. Bywater, *Macromolecules*, **1**, 328 (1968).

(6) G. E. Hartwell and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4625 (1966).

(7) T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

(8) J. W. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963).