Synthesis and Properties of Block Polymers. II. Poly(α-methylstyrene)–Poly(propylene sulfide)–Poly(α-methylstyrene)

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ABSTRACT: Block polymers of poly(α-methylstyrene)–poly(propylene sulfide)–poly(α-methylstyrene) (mSPSmS) have been synthesized using ethyllithium as the initiator and phosgene to couple the active lithium thiolate chain ends. Molecular weight measurements and gel permeation chromatograms indicate that this coupling technique is capable of producing block polymers possessing predictable molecular weights and narrow molecular weight distributions. Measurements of the tensile strength of the mSPSmS block polymers revealed that these materials possess somewhat lower tensile strengths than do the corresponding block polymers made from poly(α-methylstyrene) and polyisoprene.

The first systematic investigation of the anionic polymerization of episulfides was undertaken by Sigwalt, *et al.*[1,2] Concentrating their efforts on propylene sulfide as a model compound for three-membered cyclic sulfides, these workers found that in the absence of air, moisture, and other proton-releasing compounds, the anionically initiated polymerization of episulfides proceeds without inherent termination or transfer reactions. Thus, polythioethers with number-average molecular weights up to 3×10^5 g mol^{-1} were prepared. Of equal importance, the molecular weight was predictable from the relative amounts of monomer and initiatior used in the polymerization. Propylene sulfide has also been used in the preparation of block polymers with butadiene and isoprene.[3,4] Both di- and monofunctional initiators were used. As was the case for the homopolymerization of propylene sulfide, the number-average molecular weights were governed by the ratio of monomer to initiator.

Triblock polymers of the general description ABA, where A represents an amorphous plastic, and B a rubbery material, have become the subject of intensive study in recent years.[5,6] The synthesis and physical properties of polystyrene–polybutadiene–polystyrene (SBS),[7] polystyrene–polyisoprene–polystyrene (SIS),[7,8] and poly(α-methylstyrene)–polyisoprene–poly(α-methylstyrene)[9] (mSImS), have been investigated. It was therefore of interest to study the properties of ABA block polymers where A represents poly(α-methylstyrene) and B is poly(propylene sulfide) (mSPSmS). The mode of synthesis involves the sequential polymerization of α-methylstyrene and propylene sulfide, initiated by ethyllithium, and the subsequent coupling by phosgene of the "living" AB block polymers. The coupling step is necessary since the active chain end of poly(propylene sulfide) will not react with α-methylstyrene.

Experimental Section

High-vacuum techniques were used throughout for all solvent and monomer purifications. The basic procedures have been presented elsewhere.[10] The solvent used was tetrahydrofuran (THF) while the polymerization initiators were recrystallized ethyllithium, *n*-butyllithium, 1,4-dilithio-1,1,4,4-tetraphenylbutane, and lithium ethanethiolate. The monomers used were α-methylstyrene and propylene sulfide.

Ethyllithium was prepared from ethyl chloride and lithium sand under high-vacuum conditions. The crude ethyllithium was recrystallized using the procedures presented elsewhere.[11] The purified initiator was dissolved in *n*-hexane and the solution distributed under vacuum into ampoules.

***n*-Butyllithium** (Foote Mineral Co.) in *n*-hexane solution was used as received.

Lithium ethanethiolate was prepared by the reaction of *n*-butyllithium with excess ethanethiol (Eastman Organic Chemicals) in THF at -78° under high-vacuum conditions. Ethanethiol was dried and degassed over P_2O_5 for 2 hr. After completion of the reaction (10 min) excess ethanethiol, butane, and THF were distilled off until a pressure of 10^{-6} mm was attained. The remaining lithium ethanethiolate was dissolved in fresh THF, filtered, and distributed into ampoules. The colorless solution was stored at -20°. A test polymerization with styrene produced no polymer, indicating the absence of *n*-butyllithium.

1,4-Dilithio-1,1,4,4-tetraphenylbutane was prepared by the reaction of 1,1-diphenylethylene (Aldrich Chemical Co.) with excess metallic lithium (wire form, Lithium Corp. of America) in THF at 25° under high-vacuum conditions.[12,13] A reaction time of 4 hr was sufficient for a quantitative yield. 1,1-Diphenylethylene had been purified by degassing and stirring over CaH_2 for 48 hr and subsequent purging with

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(1) S. Boileau and P. Sigwalt, *C. R. Acad. Sci., Paris*, **252**, 882 (1961).

(2 S. Boileau, G. Champetier, and P. Sigwalt, *J. Polym. Sci., Part C*, (16) 3021 (1967).

(3) A. Gourdenne and P. Sigwalt, *Eur. Polym. J.*, 3, 481 (1967).

(4) A. Gourdenne in "Block Polymers," S. Aggarwal, Ed., Plenum Press, New York, N. Y., 1970, p 277.

(5) *J. Polym. Sci., Part C*, (26) 1–200 (1969).

(6) "Block Polymers," S. Aggarwal, Ed., Plenum Press, New York, N. Y., 1970.

(7) M. Morton, J. E. McGrath, and P. C. Juliano, *J. Polym. Sci., Part C*, 99 (1969).

(8) M. Morton, L. J. Fetters, F. C. Schwab, C. R. Strauss, and R. F. Kammereck, Fourth International Synthetic Rubber Symposium, Rubber & Technical Press, Ltd., London, 1969, p 70.

(9) L. J. Fetters and M. Morton, *Macromolecules*, **2**, 453 (1969).

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

(11) M. Morton, A. Rembaum, and J. L. Hall, *J. Polym. Sci., Part A*, 1, 461 (1963).

(12) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, 47, 477 (1914).

(13) G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962).

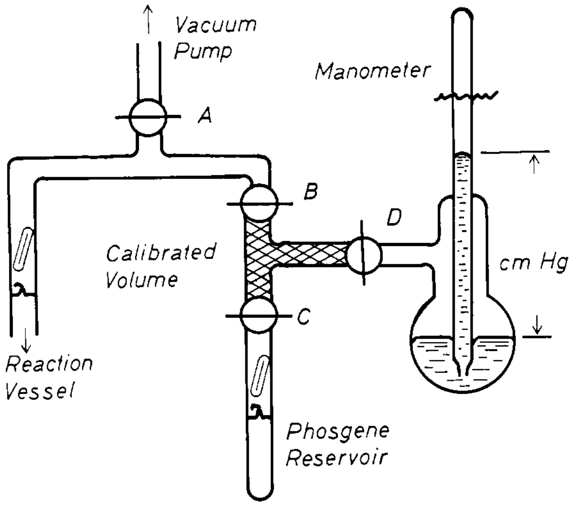

Figure 1. Apparatus for the measurement of small quantities of gaseous phosgene.

5 mol % *n*-butyllithium. The deep red solution of the active dianion was filtered under vacuum and distributed in ampoules. When stored at −20°, the initiator maintained its activity for at least 6 months.

2-Methylthiacyclopropane (propylene sulfide) (Aldrich Chemical Co. Batch No. 29081), $n^{20}\mathrm{D}$ 1.4762 (lit.[1] $n^{19}\mathrm{D}$ 1.4770), was fractionally distilled on a spinning band column at atmospheric pressure. The center fraction, bp 76–76.5° (lit.[14] bp 76–77°), had a purity of >99% as determined by gas–liquid partition chromatography, and was degassed and stirred over freshly pulverized calcium hydride until incipient polymerization (~3 hr). From there the material was flash distilled into ampoules of appropriate size. Ampoules containing propylene sulfide were sealed off at −196° to avoid pyrolysis of vapor at the constriction. The ampoules were stored at −20°.

α-Methylstyrene (Eastman Organic Chemicals) was given a preliminary drying over calcium hydride. The monomer was then distilled into a flask and exposed to butyllithium. From there the monomer was distilled into ampoules of appropriate size. The ampoules were then stored at −20°.

Phosgene (Matheson Coleman and Bell) was purified by degassing and flash distillation (three times) in a temperature gradient of −78 to −196°. The gas was then collected in ampoules such that each ampoule contained approximately 3×10^{-4} mol of phosgene at a pressure of 600 mm.

Ethyl bromide (Aldrich Chemical Co.) and **allyl bromide** (Matheson Coleman and Bell) were dried over phosphorus pentoxide, degassed, and flash distilled into ampoules.

Polymerization of Propylene Sulfide. This monomer was polymerized in THF at 25°. The initiation temperature was 25° when lithium ethanethiolate was used while a temperature of −78° was employed for the other initiators. The polymerization time was 20–24 hr for all samples. The polymerizations were terminated by the addition of either ethyl bromide or allyl bromide. This termination procedure was used in order to avoid the unstable[15,16] mercaptan chain end.

Block Polymerization of α-Methylstyrene and Propylene Sulfide. The α-methylstyrene was polymerized for 12 hr at −78° in THF using recrystallized ethyllithium as the initiator. The propylene sulfide was then added and, following the rapid disappearance of the red color, the mixture was elevated to a temperature of 25° and the polymerization completed. After 24 hr had elapsed the reaction vessel was sealed to the high-vacuum line and phosgene added by means of the apparatus shown in Figure 1.

In a typical coupling reaction, the reaction vessel containing the "living" polymers was sealed to the high-vacuum line through a break-seal equipped with a glass-coated magnetic hammer. Stopcocks A, B, C, and D were then opened and the section was evacuated until a pressure of 10^{-6} mm was attained. Then stopcock B was closed and phosgene was allowed to flow from the reservoir into the measuring device by careful manipulation of stopcock C, until a predetermined pressure was reached. By closing stopcock C and D, a certain volume of phosgene, at the given pressure and temperature, was trapped between B, C, and D. This quantity of gas was transferred into the reaction vessel by closing stopcock A, crushing the break-seal, cooling the reaction vessel to −196°, and then opening stopcock B.

The volume between B, C, and D had been calibrated, by weight measurement of the corresponding volume of mercury, before assembly of the high-vacuum line. The pressure in the measuring device could be increased or decreased by heating or cooling of the phosgene reservoir, respectively. Purified phosgene was used in ampoules containing approximately 3×10^{-4} mol of the gas to minimize hazards in case of accidental breakage of the reservoir.

In order to measure the exact stoichiometric amount of phosgene it was necessary to express a given molar quantity, equal to the number of moles of initiator, in pressure units. This was accomplished by making use of the van der Waals relation. The factor $^1/_2$ arises from the stoichiometry of the reaction

$$p(\mathrm{atm}) = \frac{(n/2)RT}{V - (n/2)b} - \frac{(n/2)^2 a}{v^2}$$

$$p(\mathrm{atm})76.0 = p(\mathrm{cm})$$

where $R = 0.082$ (l. atm/deg mol), T = temperature (°K), V = volume of measuring device (l.), n = number of moles of initiator, $b = 0.0833$ (l./mol), and $a = 10.45$ (l.^{2} atm/mol^2). The van der Waals constants a and b were obtained from published data.[17] For amounts of initiator of less than 2×10^{-4} mol, the volume correction, $(n/2)b$, in the van der Waals expression becomes negligible.

After collecting the gas, the reactor was sealed off and the coupling reaction allowed to proceed for 24 hr at room temperature under stirring. The block polymers were then isolated by slowly pouring the polymer solution into a tenfold volume of methanol. This precipitation (from THF) was repeated twice. After drying at reduced pressure and room temperature for 72 hr, the polymers were weighed and prepared for further instrumental analysis. The polymerization yield was quantitative in all cases.

The composition of the block polymers was determined from the known amounts of monomers added, assuming quantitative polymerization of each monomer. An independent compositional analysis was made from nmr data using the phenyl proton absorption at τ 3.0 and the combined absorption peaks of methylene and methine protons next to sulfur at τ 7.25 as a measure for the amount of poly(α-methylstyrene) and poly(propylene sulfide), respectively, present in the copolymer. Figure 2 shows the nmr spectra of poly(α-methylstyrene), poly(propylene sulfide), and mSPSmS in carbon tetrachloride. Area measurements were carried out both by instrumental integration and by means of a planimeter.

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(14) F. K. Beilstein, "Handbuch der organischen Chemie," Vol. 17, Part 2, 1952, p 15.

(15) R. S. Nevin and E. M. Pearce, *J. Polym. Sci., Part B*, 3, 487 (1965).

(16) P. Sigwalt, *Chim. Ind.*, **96**, 909 (1966).

(17) J. E. Haggenmacher, *J. Amer. Chem. Soc.*, **68**, 1123 (1946).

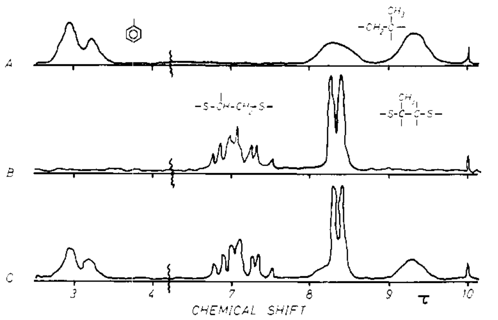

Figure 2. The nmr spectra of poly(α-methylstyrene) (A), poly(propylene sulfide) (B), and the mSPSmS block polymer (C).

Instrumental Analysis

Number-average molecular weights were determined in toluene at 37°. Hewlett-Packard 502 and 503 osmometers were used with S&S-08 deacetylated cellulose–triacetate membranes. The molecular weights were calculated from the linear plot of π/c *vs.* concentration.

Gel permeation chromatograms were obtained on a Waters Ana-Prep instrument equipped with five columns. These columns had permeability ranges of 2–5 ($\times 10^3$) Å, two columns with 5–15 ($\times 10^3$) Å, 1.5–5 ($\times 10^4$) Å, and 5–15 ($\times 10^4$) Å. Solutions containing 0.25 wt % of the polymers were used at a flow rate of 1.0 ml min^{-1} and a temperature of 45°.

Gas–liquid partition chromatographic analyses were carried out using an Aerograph A-700 instrument equipped with a 10-ft column of 15% silicone rubber SE30 on 45–60 mesh Chromosorb W. Helium was used as carrier gas at a flow rate of 80 ml/min. The column temperature was kept at 160°. A heat conductivity detector was employed in the chromatograph.

Nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument (60 Mc). Chemical shift values are expressed in τ units, using tetramethylsilane as internal reference standard.

The stress–strain properties were measured at 20° on a bench model Instron tensile tester equipped with pneumatic clamps. Cross-head speed was 5 cm/min. The test samples were stamped out of bubble free, solvent-cast films (tetrahydrofuran or benzene), using a microdumbbell die of $^1/_{10}$ in. width.

Results and Discussion

The reactions between organolithium compounds and the cyclic sulfides have been described elsewhere.[18–20] Bordwell[18] demonstrated that both alkyl- and aryllithium reagents could effect a fast elimination reaction yielding olefins and lithium mercaptans. At low temperatures (−78°) in THF it was shown[20] that the reaction between propylene sulfide and ethyllithium consists *exclusively* of the elimination of propylene and the concurrent incorporation of the sulfur atom onto the attacking carbanion. Thus, for this reason, the crossover reaction between the poly(α-methylstyryllithium) species and propylene sulfide was carried out at −78°. The remainder of the polymerization was carried out at 25° since the propagation step in the polymerization of propylene sulfide is extremely slow at low temperatures.

TABLE I
MOLECULAR WEIGHTS OF POLY(PROPYLENE SULFIDE)

Initiator	$M_s \times 10^{-4}$,[a] g mol^{-1}	$M_n \times 10^{-4}$, g mol^{-1}	$A_2 \times 10^3$,[b] mol cm^3 g^{-2}
n-Butyllithium	9.0	9.1	0.70
n-Butyllithium	5.3	5.5	0.61
Ethyllithium	45.5	47.0	0.53
Lithium ethanethiolate	6.4	6.65	0.50
1,1-Dilithio-1,1,4,4-tetraphenylbutane	9.1	9.15	0.72

[a] The predicted stoichiometric molecular weight is based on the relation: M_s = grams of monomer/n. For the dilithium initiator M_s = grams of monomer/0.5n, where n = number of moles of initiator. [b] Osmotic second virial coefficient.

Prior to the preparation of the mSPSmS block polymers, propylene sulfide was allowed to react with various organolithium initiators in order to determine whether lithium-based polymerizations were capable of generating poly(propylene sulfide) of predictable molecular weight. The results of the polymerization of this thiirane in THF are compiled in Table I. A comparison of the number-average molecular weights, M_n, and the stoichiometric molecular weights, M_s, shows excellent agreement.

These results demonstrate that the polymerization proceeds without termination or chain-transfer reactions, as has been observed by Sigwalt[16] in studies of polymerizations initiated by organosodium compounds. The use of the lithium alkylthiolate instead of alkyllithium as the initiator is advantageous in that the former compound does not react with THF at room temperature and is thus easier to handle experimentally.

In contrast to the bifunctional polymerization of propylene sulfide using sodium naphthalene as initiator,[16] the polymerization of the monomer using the dilithium initiator was found to lead to gel formation after a relatively short reaction time. Upon termination of the reaction, the solution viscosity dropped, thus indicating that the cross-links responsible for the gelation were not of a permanent nature. In the absence of published information about the exact nature of associated lithium alkylthiolate species and their degree of

TABLE II
COMPOSITION AND MOLECULAR WEIGHTS OF mSPSmS BLOCK POLYMERS

Wt % α-methylstyrene Projected	Found[a]	M_s ($\times 10^{-3}$), g mol^{-1}	M_n ($\times 10^{-3}$), g mol^{-1}
20.3	20.2 ± 1.8	8–66–8	84
30.1	29.9 ± 1.0	13–62–13	83
39.0	38.9 ± 0.8	17–55–17	90

[a] By nmr analysis. Confidence limits at p = 0.95.

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(18) F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Amer. Chem. Soc.*, **74**, 1082 (1954).
(19) B. M. Trost and S. Ziman, *Chem. Commun.*, 181 (1969).
(20) M. Morton and R. F. Kammereck, *J. Amer. Chem. Soc.*, **92**, 3217 (1970).

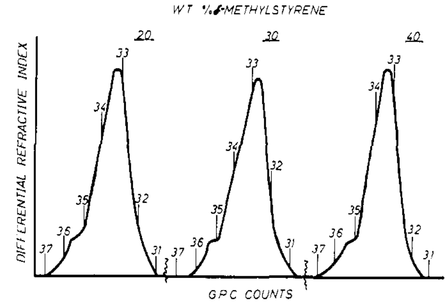

Figure 3. Gel permeation chromatogram of the mSPSmS block polymers.

association in THF, it can be assumed that the lithium thiolate group not only associates with itself but also with bivalent sulfur atoms located in the polymer chain or in the monomer. It was found that tetrahydrothiophene in amounts of 5–10 vol % was effective in the partial disruption of the gel. This compound, which provides a "monomeric" bivalent sulfur, does not polymerize or react irreversibly with the active chain ends.

Utilizing the phosgene coupling technique, three block polymers of poly(α-methylstyrene)–poly(propylene sulfide)–poly(α-methylstyrene) were synthesized. Table II shows the compositional data on these polymers. The number-average molecular weights obtained by osmometry (M_n) are in good agreement with the theoretical stoichiometric molecular weights (M_s). Similarly, the analysis of the α-methylstyrene content indicates that the synthetic procedures employed in the preparation of the block polymers exert an adequate control on the compositional parameters.

The polymers were further characterized by gel permeation chromatography. Figure 3 shows chromatograms of the mSPSmS block polymers prepared by coupling active mSPS polymers. The sharpness of the peaks suggest a narrow molecular weight distribution of the polymers, which is in accord with measurements on poly(propylene sulfide) prepared under anionic conditions by Sigwalt, *et al.*,[1] and poly(α-methylstyrene) prepared by similar procedures. Furthermore, it indicates a fast crossover reaction from active poly(α-methylstyrene) to propylene sulfide. The chromatograms show, however, small amounts of polymers with molecular weights lower than that of the main peaks. These lower molecular weight polymers are presumably uncoupled poly(α-methylstyrene)–poly(propylene sulfide) chains.

The method of synthesizing triblock polymers by coupling monofunctional diblock polymers has a severe disadvantage in that it demands a precise stoichiometry and a high efficiency of the coupling reaction. The coupling of active carbanionic polymers is facilitated by slow addition[21] of the terminating agent since the color of the active chain ends can be used as an indicator to determine the rate of addition and the amount of coupling agent. For functional groups which do not absorb in the visible portion of the spectrum, *e.g.*, alkyl thiolates, the amount of initiator employed at the start of the polymerization serves as a measure for the amount of terminating agent. However, the latter method does not take into account small losses of active functional groups which may occur during the initiation, polymerization, and crossover reaction in the preparation of diblock polymers. Furthermore, the method has to contend with experimental errors arising from the measurement of initiator concentration, plus experimental errors involved in measuring small amounts of phosgene.

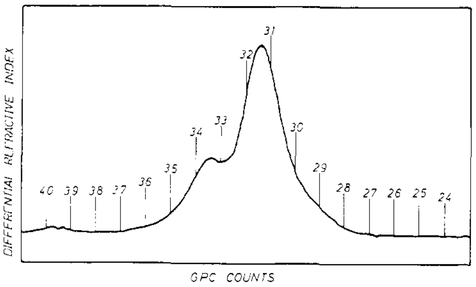

Figure 4. Gel permeation chromatogram of Kraton 1101.

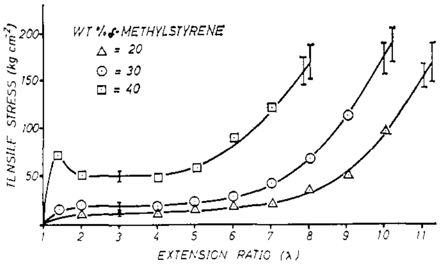

Figure 5. Stress–strain properties of mSPSmS block polymers.

In view of these shortcomings, the degree of coupling achieved in these mSPSmS block polymers must be regarded as satisfactory. This can be demonstrated by a comparison of the gel permeation chromatograms of Figure 3 with that of Figure 4 which is a chromatogram of a commercial block polymer,[22] Kraton 1101. This block polymer is reportedly[23] synthesized by a coupling reaction between an alkyl dihalide and the active carbanionic chain end of a polystyrene–polybutadiene block polymer. The shoulder at counts 33 and 34 is presumably the result of uncoupled diblock material. The amount of this diblock polymer was estimated from the gpc curve to account for 27% of the material—considerably more than the roughly 5% of diblock found in the mSPSmS polymers. The purity of the mSPSmS polymers is equivalent to that of a triblock polymer of poly(4-vinylbiphenyl) and polyisoprene prepared by coupling diblock polymer with phosgene.[21]

The stress–strain properties of the mSPSmS block polymers were measured on clear films cast from THF and benzene. The results of these measurements are shown in Table III and Figure 5. It can be seen that the stress–strain properties of this material are qualitatively similar to those of SBS, SIS, and mSImS triblock polymers. The 300% moduli (σ_λ = 4) increase with "filler" content, *i.e.*, amount of poly(α-methylstyrene). At an α-methylstyrene content of 40%, the stress–strain curve (Figure 5) shows a drawing region with a high

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(21) J. Heller, J. F. Schimscheimer, R. A. Pasternak, C. B. Kingsley, and J. Moacanin, *J. Polym. Sci., Part A-1*, 7, 73 (1969).

(22) Shell Chemical Co.

(23) British Patent 1,014,999 (Shell Chemical Co., May 13, 1963).

Table III

Physical Properties of mSPSmS Block Polymers

Wt % α-methylstyrene	Stress at 300% elong. σ ($\lambda = 4$),[a] kg cm^{-2}	Tensile strength σ_b,[a] kg cm^{-2}		Strain at break λ_b	% set (at break)
		THF	Benzene		
20	13.7 ± 0.3	155 ± 12	170 ± 20	11	5
30	19.2 ± 0.3	167 ± 4	190 ± 15	10	5
40	52.0 ± 2.0	160 ± 14	175 ± 15	8	5

[a] Confidence limits at $p = 0.95$.

initial modulus and a yield point at $\lambda = 1.4$. The elongation at break (λ_b) decreases with increasing proportion of α-methylstyrene.

The tensile strength (σ_b) of mSPSmS polymers is considerably lower than that of any SBS, SIS,[7,8] or mSImS[9] polymer of comparable molecular characteristics. This may be due to the presence of diblock impurities in the former. We have previously reported[8] that a drastic decrease in tensile strength occurred upon deliberate addition of small amounts (2–5%) of diblock polymers to either SBS or SIS systems. This effect was explained as arising from the fact that diblock polymers are not participating in the three-dimensional network and are thus unable to support stress. It is, however, unlikely that the presence of the diblock polymer is completely responsible for the lower tensile strengths of the mSPSmS polymers as compared to the SBS, SIS, and mSImS materials. An additional controlling factor of the dynamic mechanical properties, stress–strain properties and stress–relaxation properties of block polymers is the morphology of the material.[24] However, no detailed information is presently available concerning the morphology of these mSPSmS polymers. Thus, it is currently not possible to comment on the poly(α-methylstyrene) domain size and its influence on the stress–strain properties of these mSPSmS polymers.

Films cast from THF appear to have a lower tensile strength than those cast from benzene; however, the data are not statistically different. Both THF and benzene are good solvents for either poly(propylene sulfide) or poly(α-methylstyrene). Similarly, the scatter of tensile strength data does not permit any conclusions about the specific dependence of this property on molecular or compositional parameters, *e.g.*, α-methylstyrene content.

The strain at break for the mSPSmS block polymers compares favorably with those values reported for SIS, SBS,[7,8] and the mSImS[9] block polymers. However, the per cent set values at break for the mSPSmS block polymers are markedly lower, *ca.* 5%, than those found for the SIS, SBS,[7,8] and the mSImS[9] block polymers. For the block polymers containing polystyrene[7,8] the set at break ranged from 20 to 50% while values of *ca.* 100% were recorded when the terminal blocks were poly(α-methylstyrene).[9] The low values for the per cent set at break for the mSPSmS block polymers are in accord with the relatively low tensile strengths exhibited by these materials.

The tensile strengths of the mSPSmS polymers compare favorably with those obtained[25,26] from sulfur vulcanized terpolymers of propylene sulfide–ethylene sulfide–allyl thioglycidyl ether. The tensile strengths of these vulcanized materials ranged from *ca.* 100 to 150 kg cm^{-2} at elongations of 300–390%. However, the elongation at break of the mSPSmS polymers ranged from 700 to 1000%.

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(24) J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci., Part C*, 117 (1969).

(25) S. Adamek, B. B. J. Wood, and R. T. Woodhams, *Rubber Age*, **96**, 581 (1965).

(26) R. H. Gobran and M. B. Berenbaum in "Polymer Chemistry of Synthetic Elastomers," Part 2, J. P. Kennedy and E. Tornquist, Ed., Interscience, New York, N. Y., 1969, Chapter 8, pp 838, 839.