

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### ABA Block Copolymers of Dienes and Cyclic Sulfides

Maurice Morton<sup>a</sup>; S. L. Mikesell<sup>ab</sup>

<sup>a</sup> Institute of Polymer Science The University of Akron, Akron, Ohio <sup>b</sup> General Electric Company, Coshocton, Ohio

**To cite this Article** Morton, Maurice and Mikesell, S. L.(1973) 'ABA Block Copolymers of Dienes and Cyclic Sulfides', *Journal of Macromolecular Science, Part A*, 7: 7, 1391 – 1397

**To link to this Article:** DOI: 10.1080/10601327308060508

**URL:** <http://dx.doi.org/10.1080/10601327308060508>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## ABA Block Copolymers of Dienes and Cyclic Sulfides

MAURICE MORTON and S. L. MIKESELL\*

Institute of Polymer Science  
The University of Akron  
Akron, Ohio 44325

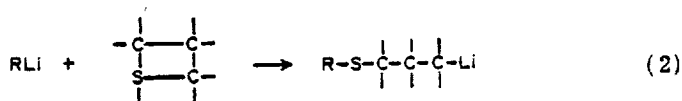
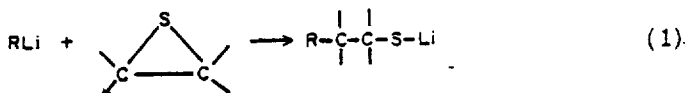
### ABSTRACT

ABA block copolymers have been synthesized in which the center block was polyisoprene or polybutadiene and the end blocks were polyethylene sulfide or polythiabutane. The latter were shown to crystallize, leading to mechanical properties analogous to those of the "thermoplastic elastomers."

Recent studies [1-3] in these laboratories have demonstrated that the organolithium-initiated anionic polymerizations of cyclic sulfides lead to "living" systems, which are therefore suitable for the synthesis of block copolymers of predetermined structure. The two types of cyclic sulfides which were found to be amenable to this type of polymerization were the thiiranes (three-membered) and the thietanes (four-membered). These investigations also showed that the polymerization of these two ring-opening systems operated via different mechanisms, i.e., the thiiranes by the propagation of a thiolate species and the thietanes by the propagation of a carbanionic chain end:

---

\*Present Address: General Electric Company, Coshocton, Ohio.



Thus, in the case of block polymerization with vinyl monomers, the thiiranes are only capable of participating in a "unilateral" way, i.e., the thiolate is incapable of initiating the vinyl monomer; while the thietanes can operate in a "bilateral" manner, i.e., they can both initiate and be initiated by vinyl monomers.

The first members of the above two series, i.e., ethylene sulfide and thiacyclobutane, are of special interest since they lead to crystalline polymers. They were therefore considered to be excellent candidates for the synthesis of ABA block copolymers, where the B block was an elastomeric polydiene, since such polydienes are also easily polymerized by organolithium initiators. Such a synthesis would therefore lead to elastomeric ABA block copolymers having crystalline end blocks, in contrast to the well-known styrene-diene-styrene block copolymers which have noncrystalline polystyrene end blocks. The latter are known to aggregate into glassy "domains" which act as virtual network junctions and lead to high-strength elastomers. Hence there is considerable interest in the mechanical properties of an analogous block copolymer having crystalline "domains."

### SYNTHESIS OF ABA BLOCK COPOLYMERS WITH CRYSTALLINE END BLOCKS

Crystalline polymers, such as the above two sulfides, would be expected to be insoluble at the ambient and lower temperatures required for the organolithium polymerization. Hence, for a homogeneous polymerization in solution, it was necessary to use a difunctional organolithium initiator, which would first form an  $\alpha,\omega$ -dilithiopolydiene and would then initiate the polymerization of the crystalline end blocks. The latter, if not too large, could be kept in "solution" by the larger, soluble center block. For this purpose the soluble dilithium initiator 1,4-dilithio-1,1,4,4-tetraphenylbutane was used, since it had been shown [4] to be an efficient initiator for anionic polymerization of dienes.

The types of block copolymers prepared and the polymerization conditions are described in Tables 1 to 3. The mixtures of solvents shown in these tables refer to the fact that a hydrocarbon solvent (hexane or benzene) was used first in order to prepare the diene center block having a high 1,4 unit structure for good rubbery properties, after which an equal amount of the more polar solvent tetrahydrofuran was added in order to speed up the polymerization of the cyclic sulfide. In all cases, 100% conversion was achieved by allowing sufficient time for the polymerization of the cyclic sulfide, which usually required several days, as compared with hours for the diene polymerization. NMR studies showed that the initiation of polymerization of the cyclic sulfides by dienyl lithium was very rapid (ca. 4 or 5 min) even at  $-40^{\circ}\text{C}$ . In the case of the ethylene sulfide, the lithium carbanions showed some tendency toward metallation, and this was circumvented by first "capping" the polydienyl lithium with propylene sulfide at  $-78^{\circ}\text{C}$ .

TABLE 1. Synthesis of Thiacyclobutane-Isoprene-Thiacyclobutane (TCB-I-TCB) Polymers

Polymer No.	Mol wt. ( $M_s$ ) <sup>a</sup> $\times 10^{-3}$	% TCB	Solvent	Temp ( $^{\circ}\text{C}$ )
I-5	10.0-59.6-10.0	22.3	Hexane/THF	-78
I-3	21.3-59.4-21.3	41.6	Benzene/THF	23

<sup>a</sup> $M_s$  = stoichiometrically predicted molecular weight.

TABLE 2. Synthesis of (Ethylene Sulfide)-Isoprene-(Ethylene Sulfide) Polymers (ES-I-ES)<sup>a</sup>

Polymer No.	Mol wt ( $M_s$ ) $\times 10^{-3}$	% Ethylene sulfide
I-18	4.4-80.0-4.4	10
I-22	10.2-83.0-10.2	20
I-15	17.0-80.0-17.0	30
I-16	26.3-80.0-26.3	40

<sup>a</sup>Polymerization temperature,  $23^{\circ}\text{C}$ . Solvent, hexane/THF.

TABLE 3. Synthesis of (Ethylene Sulfide)-Butadiene-(Ethylene Sulfide) Polymers (ES-B-ES)<sup>a</sup>

Polymer No.	Mol. wt ( $M_g$ ) $\times 10^{-3}$	% Ethylene sulfide
B-27	4.5-80.0-4.5	10
B-28	10.0-80.0-10.0	20
B-29	17.1-80.0-17.1	30

<sup>a</sup>Polymerization temperature, 23°C. Solvent, benzene/THF.

Although these polymers did not actually precipitate from solution while the end blocks were being polymerized, the solutions became increasingly turbid and were quite opaque at the end of the reaction. These "solutions" were also highly gelled, presumably because of the well-known association of the difunctional chain ends, and the gels had to be removed mechanically from the reaction vessels. After the swollen polymer gels were dried, the resulting elastomers did not swell in solvents at ambient temperatures but could only be dissolved at elevated temperatures, presumably due to the crystalline end blocks. Test films were molded from these block polymers, using a 10-min molding time and the minimum temperature required to produce clear specimens, in order to avoid any degradation of the polydiene. The molding temperatures were 100, 160, and 196°C for the TCB-I-TCB, ES-I-ES and ES-B-ES polymers, respectively. Even so, it was not always possible to form good samples from the more crystalline block polymers.

### PROPERTIES OF THE BLOCK COPOLYMERS

All of the block copolymers showed the expected temperature transitions for each block when examined by Differential Scan Calorimetry. At a heating rate of 10°/min, these showed a  $T_g$  for the polyisoprene of -56°C, a  $T_g$  for the polybutadiene of -86°C, and a  $T_m$  of 55 and ~200°C for the polythiabutane and polythiapropane, respectively. These transitions were generally similar for the blocks and their respective homopolymer controls. Further confirmation of the crystallization of the end blocks was obtained from x-ray diffraction. However, the extent of crystallization of the end blocks was definitely

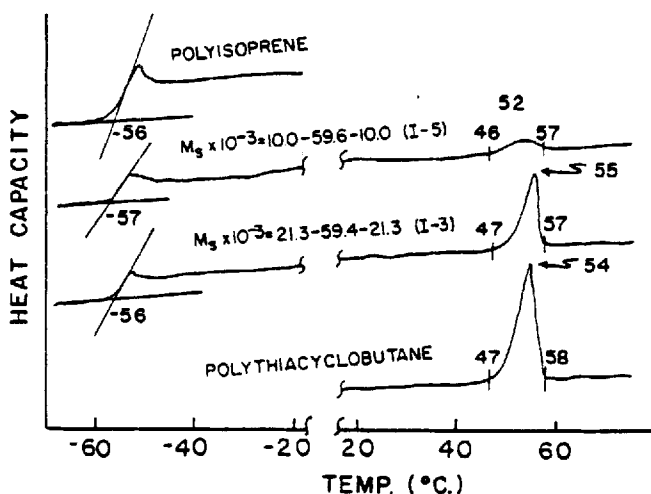


FIG. 1. DSC thermograms of TCB-I-TCB triblock copolymers. Scan rate =  $10^\circ/\text{min}$ .

affected by the amount of end blocks present. Thus, from the DSC thermograms shown in Fig. 1, it can be deduced that the end blocks of the I-5 polymer show only 15% of the crystallinity exhibited by the end blocks of the I-3 polymer, computed on the basis of the end-block content of each polymer. A similar effect on crystallinity was noted in the case of the ethylene sulfide block polymers, of the ES-I-ES and ES-B-ES types, as shown in Fig. 2 for the latter.

Although Fig. 1 shows a very good agreement between the crystal melting points of the end blocks and that of the homopolymer of polythiabutane, this was not quite the case for the ethylene sulfide, where the crystal melting point was depressed to some extent in the polymers having a low end-block content. This was undoubtedly due to the very high melting point of this polymer ( $\sim 200^\circ\text{C}$ ), where such effects would be expected to be exaggerated. In fact, a very profound difference was found between the melting temperature ( $T_m$ ) and the crystallization (or freezing) temperature ( $T_c$ ) of the ethylene sulfide end blocks, as shown in Table 4. Needless to say, this unusually high degree of supercooling was not found for the homopolymer. It should be noted that this supercooling phenomenon was still observed even when the cooling rate was as low as  $0.5^\circ/\text{min}$ . It is obvious that there are restrictions to crystallization of the end blocks which are not present in the homopolymer, and this is, of course, not really surprising.

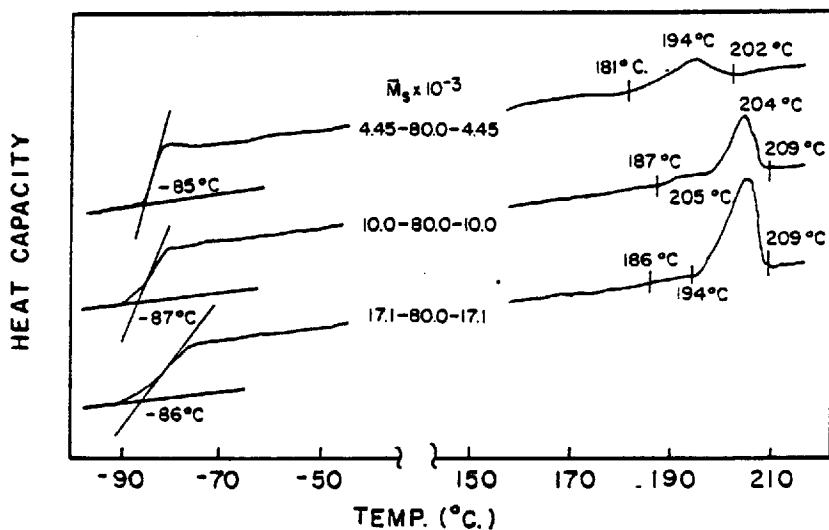


FIG. 2. DSC thermograms of ES-B-ES triblock copolymers. Scan rate =  $10^{\circ}/\text{min}$ .

TABLE 4. Solubility and Crystallization of Ethylene Sulfide Block Polymers

Polymer No.	% Ethylene sulfide	% Extracted		Melting temp ( $^{\circ}\text{C}$ )	Crystallization temp ( $^{\circ}\text{C}$ )
		$\text{C}_6\text{H}_6$	THF		
I-18	10	17.6	30.5	137-140 <sup>a</sup> 148-160	63-40
I-22	20	2.0	6.2	175-190	77-65
I-15	34	2.3	3.6	186-199	85-70
I-16	40	1.8	2.8	185-204	85-70
B-27	10	1.5	2.8	181-202	84-67
B-28	20	0.4	0.5	187-208	85-68
B-29	30	0.8	1.8	194-209	93-72

<sup>a</sup>Two  $T_m$  peaks were observed for this polymer, corresponding to the behavior of the homopolymer under the same conditions.

The effect of end-block content on degree of crystallinity is also demonstrated by the solubility data shown in Table 4 under "°% Extracted." These figures show how much of the block polymers could be dissolved at reflux temperatures in the solvents indicated. The effect of end-block content is obvious, but the large difference between the isoprene and butadiene polymers at 10% ES content is rather surprising. It correlates with the substantially lower  $T_m$  value of the 10% ES isoprene polymer, but there does not appear to be an obvious explanation for the apparently poorer crystallization of the blocks in the isoprene polymer compared to those in the butadiene polymer.

Finally, some comments are in order about the tensile properties of these elastomers. In general, the ethylene sulfide block polymers were much weaker and less extensible than the corresponding styrene-diene-styrene block polymers, demonstrating a maximum tensile strength of no more than 60 kg/cm<sup>2</sup> and an extension ratio at break of about 3 for the 30% ES polymers. (These compare with values of about 300 kg/cm<sup>2</sup> and extension ratios of 9-10 for the SDS elastomers.) However, these data are undoubtedly not reliable, especially in view of the difficulties encountered in molding homogeneous, uniform films from such a high-melting polymer. As for the thiacyclobutane block polymers, these showed no measurable strength at all, being soft rubbers of the consistency of chewing gum. However, it is probably premature to draw any conclusions from these mechanical properties until they can be more closely related to the morphology of these polymers.

#### ACKNOWLEDGMENT

This work was supported mainly under Contract F33615-69-C-1222 of the Materials Laboratory, U.S. Air Force.

#### REFERENCES

- [1] M. Morton and R. F. Kammereck, J. Amer. Chem. Soc., **92**, 3217 (1970).
- [2] M. Morton, R. F. Kammereck, and L. J. Fetters, Macromolecules, **4**, 11 (1971).
- [3] M. Morton, R. F. Kammereck, and L. J. Fetters, Brit. Polym. J., **3**, 120 (1971).
- [4] L. J. Fetters and M. Morton, Macromolecules, **2**, 453 (1969).