

## Preparation and Stress-Strain Properties of SBS and SIS Block Polymers Made with Dilithium Initiators

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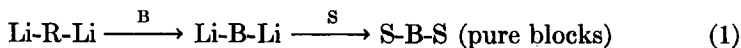
### Synopsis

ABA-type block polymers of styrene (monomer A) and isoprene or butadiene were prepared using two commercially available dilithium adducts of isoprene as initiators. One (DiLi-1) was predominantly dilithio diisoprene and contained a small amount of dimethyl ether (ether/Li > 1.0). The second (DiLi-1 C.E.) was a higher molecular weight version of DiLi-1, containing about seven isoprene units per molecule. It contained only a trace of dimethyl ether (ether/Li < 0.1). Polymers were made by charging all of the monomers at the start of the reaction. The diene polymerized first, incorporating some styrene. When the diene was consumed, the difunctional polymer chains then added a block of nearly pure polystyrene at each end. Thus an ABA-type polymer was synthesized in one step. These polymers show the usual behavior of pseudo-vulcanized elastomers. Their stress-strain curves are given. The SBS polymers had the higher tensile strengths. None had tensile strengths as high as SBS or SIS polymers made with *n*- or *sec*-butyllithium. It was shown that the diene blocks contain appreciable amounts of styrene. This leads to more compatibility between the A and B blocks; it also shortens the styrene blocks compared to the theoretical lengths of "pure" blocks. Both effects can lead to loss of tensile strength. Microstructures of the diene homopolymers made with these initiators are also given.

### INTRODUCTION

Rather extensive literature has appeared in recent years on the preparation and properties of ABA block polymers, usually involving styrene and butadiene or isoprene. These have been termed "thermolastic" polymers and have been thoroughly reviewed.<sup>1-7</sup> In most cases, these polymers were prepared with a monofunctional lithium alkyl, utilizing some type of sequential addition of the monomers to form the block polymers.<sup>8-11</sup> There has been some mention of the use of dilithium initiators for the preparation of block polymers in the patent literature, but detailed studies were not reported.<sup>12-14</sup> Block polymers can be prepared from dilithium initiators by at least two different reaction routes. These are given in the

following generalized schematic equations, for polymerizations involving styrene (S) and butadiene (B):



Recently, a detailed study was reported on an ABA block polymer of  $\alpha$ -methylstyrene and isoprene made with a specially synthesized dilithium initiator by reaction (1) above.<sup>15</sup> We wish to give an account of some studies on the preparation and properties of styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) block polymers made with two dilithium initiators which have recently become commercially available; these polymers were made by reaction (2). At present, no polymers of this type have been prepared in our laboratories via reaction (1).

## EXPERIMENTAL

### Materials

The sources and purifications of the monomers and the benzene solvent were given previously.<sup>8</sup> The initiators were two dilithium adducts of isoprene and were designated DiLi-1 and DiLi-1 C.E. The DiLi-1 was predominantly dilithiodiisoprene, with small amounts of dilithiotriisoprene and dilithiotetraisoprene present. It was dissolved in a solvent of about 92% benzene and 8% dimethyl ether. The ratio of ether/Li was slightly greater than unity. The DiLi-1 C.E. was a higher molecular weight (chain-extended) product of DiLi-1, with an average of about seven isoprene units per molecule. Its solvent was almost wholly benzene, with only a trace of dimethyl ether present. The ratio of ether/Li in this solution was less than 0.1. These materials are more fully described in product bulletins<sup>16</sup> and the patent literature<sup>17</sup> from Lithium Corporation of America. The stock solutions of these initiators were further diluted with benzene to 0.20M for use in this work. Both the stock solutions and the diluted solutions were analyzed periodically by the double titration method of Gilman and Cartledge.<sup>18</sup> They were always 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 in the previous paper.<sup>8</sup> In all of these preparations, however, all of the styrene and diene was charged at the beginning of the reaction. When the dilithium initiator is added, the diene polymerizes more rapidly at first; when its concentration is reduced to a very low level, the styrene polymerization predominates. This technique produces a polymer with "tapered" center blocks (see discussion). All polymerizations were run at 50°C for the SBS polymers and at 40°C for the SIS polymers; they are quite rapid and are usually complete in a few hours. Polymers were

isolated by coagulation in methanol containing a small amount of a phenolic antioxidant and dried in vacuo at moderate temperature ( $<50^{\circ}\text{C}$ ). Sufficient quantities of the dilithium initiator were added at the start of the polymerization to allow for the scavenger level.<sup>8,19</sup> All polymers were prepared to have a theoretical molecular weight of 100,000.

### Polymer Evaluation

Polymers were evaluated and analyzed as described in the previous paper.<sup>8</sup> Stress-strain testing was also done in the same manner, except that the Instron cross-head separation speed was 5 in/min.

## RESULTS AND DISCUSSION

When a dilithium initiator is used to prepare an ABA block polymer of styrene and a diene, all of the monomers can be charged at the start of the reaction. The diene polymerizes first, with the polymer chain growing at both ends, with incorporation of small amount of styrene.<sup>20-23</sup> When little diene remains, the styrene then polymerizes as a block of nearly pure polystyrene at each end of the polymer chain, producing an ABA block polymer in a single reaction. All polymers reported here were prepared in this way. It is assumed that the polystyrene blocks at each end of the polymer chain are equal in length. Presumably, each end of the growing diene chain should equally obey copolymerization laws, thus yielding symmetrically tapered polymer composition.

Preparation of ABA block polymers in this manner provides a convenient, one-step synthesis. It avoids the sequential addition of monomers, which requires tedious and rigorous techniques and which risks the possibility that spurious impurities in the added monomer may prematurely terminate some of the growing polymer. The disadvantage is that the diene block contains some styrene (and vice versa). The amount of styrene in the diene block increases slowly as the diene polymerizes, forming what has been termed a "tapered" block.<sup>8,9</sup> Such blocks are probably more compatible with the styrene end blocks than a "pure" diene center block would be. This leads to more phase blending of the A and B blocks, with resultant loss in tensile strength.<sup>5</sup> The results reported herein apparently reflect this phenomenon.

### SBS Polymers

Two series of SBS block polymers were prepared with the two dilithium initiators. The stress-strain curves for those made with DiLi-1 are given in Figure 1, and for those made with DiLi-1 C.E. in Figure 2. As the styrene content of the polymers increased, tensile strengths generally increased and ultimate elongations decreased. When the styrene content of the polymers reaches about 40%, the polymers exhibit a yield point at low extensions ("cold-drawing"). This has been reported by others and

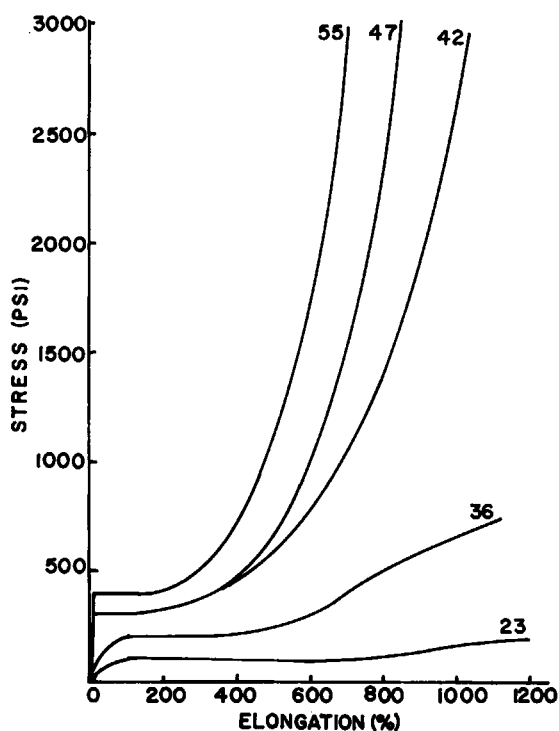


Fig. 1. Stress-elongation curves for styrene-butadiene-styrene block polymers prepared with DiLi-1 initiator. Numbers on curves are the styrene contents of the polymers.

is taken as evidence that a semicontinuous phase of polystyrene is being formed.<sup>4</sup>

Differences can be noted between these two series of polymers, however, and also between these and comparable polymers made with butyllithiums. The polymers made with DiLi-1 C.E. have better tensile strengths than those made with DiLi-1. This must reflect the amount of ether present in the initiator, since ethers randomize the copolymerization of styrene and butadiene.<sup>12,22,23</sup> Even a small amount of randomization, however, may lead to more phase blending between the blocks and hence loss of strength, as discussed above. Only small amounts of ether can be tolerated in these polymerizations without loss of block structure.<sup>24</sup>

None of these polymers had tensile strengths equal to comparable polymers made with *n*- or *sec*-butyllithium.<sup>8</sup> Some of the latter polymers had tensiles well over 4000 psi, but none of those made with the dilithium initiators reached this figure. Also, polymers made with DiLi-1 or DiLi-1 C.E., and containing about 35% styrene, had poor tensiles (<1500 psi). Comparable polymers made with the butyllithiums had tensiles of >2500 psi. Thus, the polymers made with the butyllithiums had better tensiles over all than those made with the dilithium initiators; they also required

a lower styrene content for the development of good tensile strength. These results undoubtedly reflect the presence of the ether in the dilithium initiators. They may also partly be the result of the polymerization method; with the butyllithium initiator, half of the styrene is homopolymerized to form the "living" polymer. This is then added to a mixture containing the butadiene and the remaining half of the styrene. Thus in

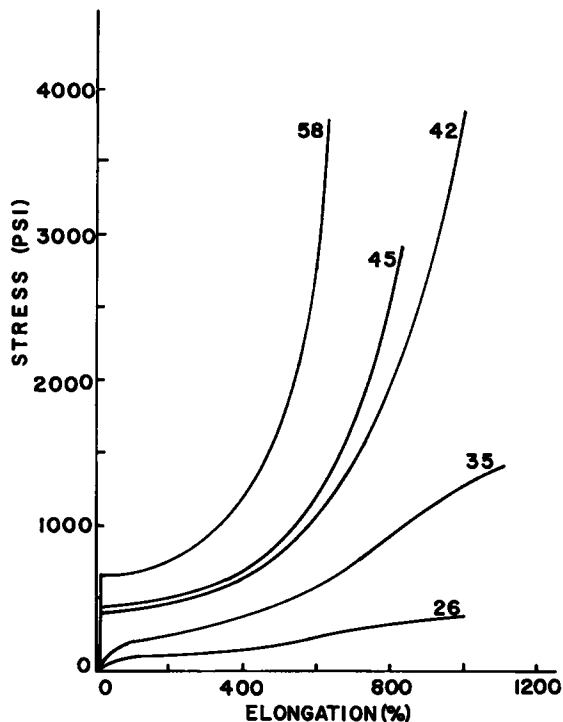


Fig. 2. Stress-elongation curves for styrene-butadiene-styrene block polymers made with DiLi-1 C.E. initiator.

the copolymerization step, there is only half as much styrene present at the start as there is in the copolymerizations done with the dilithium initiators. This should also increase the amount of styrene incorporated into the diene blocks of the polymers made with the dilithium initiators. The ramifications of this are discussed below.

### SIS Polymers

The stress-strain curves for SIS block polymers made with DiLi-1 are given in Figure 3, and for those made with DiLi-1 C.E., in Figure 4. The same general results were obtained as for SBS polymers. Tensile strengths generally increased and ultimate elongations decreased as the styrene contents of the polymers increased. As with the SBS polymers, styrene contents of nearly 40% were needed before tensile strengths of more than a few

hundred pounds were attained. However, these polymers underwent cold-drawing before elastic elongation began.

Just as with the SBS polymers, the SIS polymers made with DiLi-1 C.E. had slightly better tensile strengths than those made with DiLi-1. All of these had poorer tensile strengths, however, than the SIS polymers made with either *n*- or *sec*-butyllithium.<sup>8</sup> These effects again must reflect the increased phase blending of the styrene and isoprene blocks. It is known that styrene copolymerizes more readily with isoprene than with

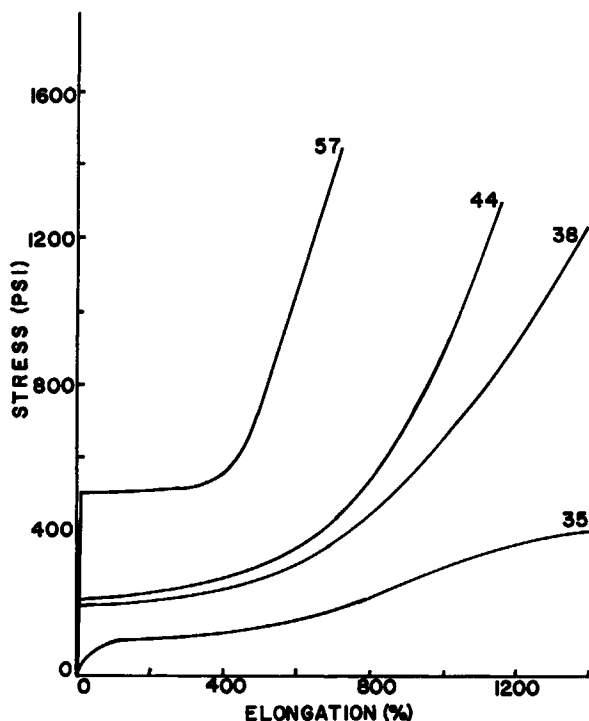


Fig. 3. Stress-elongation curves for styrene-isoprene-styrene block polymers made with DiLi-1 initiator.

butadiene in organolithium-initiated polymerizations in hydrocarbon solvents.<sup>25</sup> Thus, the isoprene blocks in these polymers actually contain a considerable portion of styrene. Hence, they become fairly compatible with the styrene blocks, resulting in rather low tensile strengths (all samples had <2000 psi tensile strength).

#### Styrene Incorporation in the Diene Blocks

The stress-strain behavior of these polymers was different from similar ones made with *n*- or *sec*-butyllithium. It was desirable to obtain data on the amount of styrene incorporated in the diene blocks; from this, the composition and size of the blocks could be determined and compared with

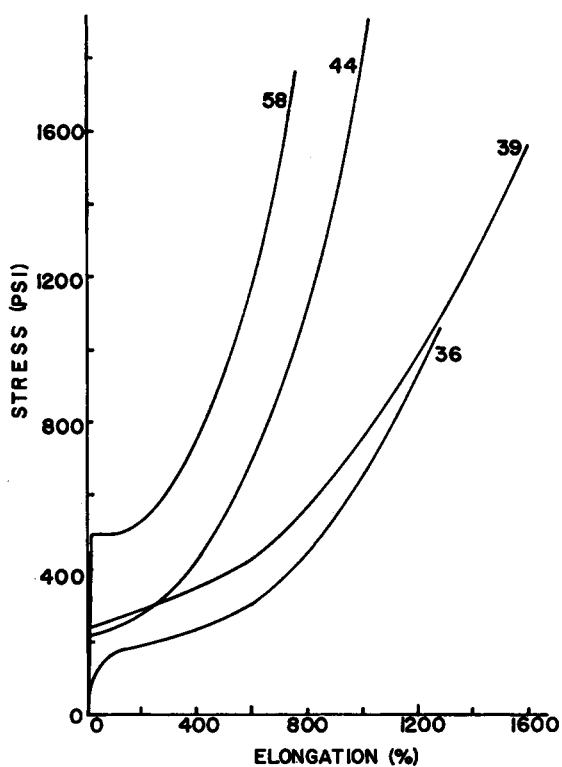


Fig. 4. Stress-elongation curves for styrene-isoprene-styrene block polymers made with DiLi-1 C.E. initiator.

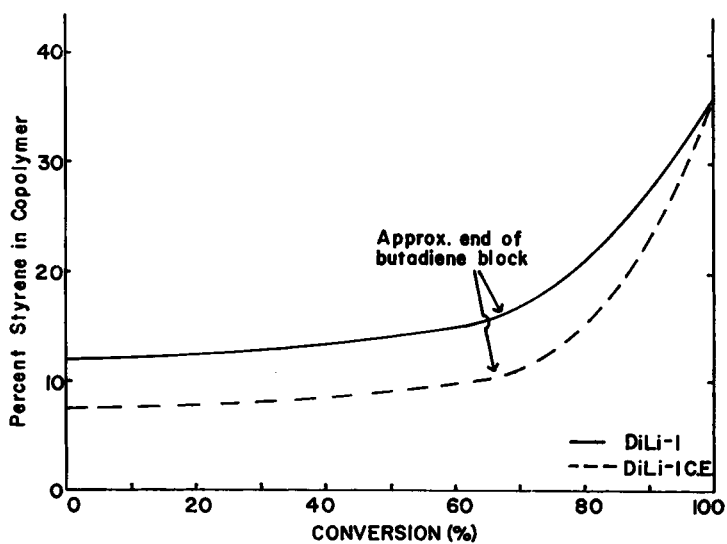


Fig. 5. Styrene incorporation in styrene-butadiene copolymerizations.

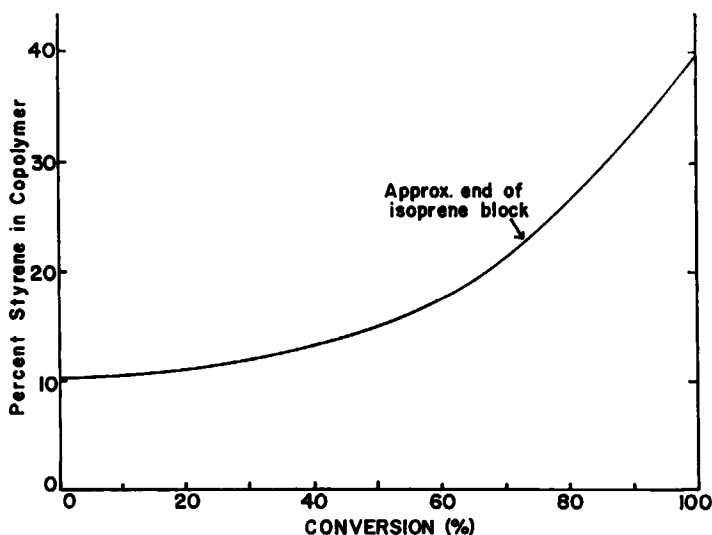


Fig. 6. Styrene incorporation in styrene-isoprene copolymerizations.

the polymers made with the butyllithiums. This might give some insight into the reasons for the different stress-strain behaviors.

Results for styrene-butadiene copolymerizations are plotted in Figure 5. It can be seen that more styrene is incorporated into the butadiene block with DiLi-1 initiator than with DiLi-1 C.E. Presumably, this reflects the amount of dimethyl ether in the initiator. The point is marked on each curve which approximates the beginning of the terminal styrene-rich blocks, as indicated during polymerization by the appearance of orange color. The polymer made with DiLi-1 contained over 15% styrene at this point; the one made with DiLi-1 C.E. had about 10% styrene. The initial polymers that were formed also differed by about 5% in their styrene contents. This difference persisted throughout the formation of the butadiene block. Thus, the blocks do contain an appreciable "tapering" concentration of styrene.<sup>3,9</sup>

The data for the styrene-isoprene copolymerizations are plotted in Figure 6. Within experimental error, styrene incorporation in the isoprene block is the same with either initiator. Styrene copolymerizes rather readily with isoprene in an all-hydrocarbon system.<sup>23,25</sup> Apparently the small amounts of dimethyl ether present do not greatly enhance this copolymerization, unlike the butadiene-styrene system. It can be noted from Figure 6 that the isoprene block actually contains about 23% styrene. This should produce considerable compatibility between the block segments, accounting for the low tensile strengths. It was noted above that polymers made with DiLi-1 C.E. had higher tensiles than those made with DiLi-1, yet the styrene analyses showed that both types of polymers have nearly the same block composition. Examination of Figures 3 and 4 shows, however, that all polymers had very low tensile (<2000 psi) and that the differences in



tensile strengths between the two sets of polymers were small. Evidently, other more subtle distinctions in polymer structure must account for the small differences in tensile strengths.

The method by which these copolymerizations are carried out produces another factor which must influence the stress-strain behavior of these polymers. Since a considerable portion of the styrene is incorporated into the diene block, the end blocks of polystyrene are considerably shorter than they would be if pure blocks were formed. For example, the SIS polymers depicted in Figure 6 were made from a 60/40 charge of isoprene/styrene. If pure blocks had formed, and if both ends of the polymer chains were symmetric, then the resultant molecular weights of the blocks would have been 20,000(S)-60,000(I)-20,000(S). Analysis showed, however, that at the onset of color, conversion was near 76%, with 23% styrene in the center block. If color change marked the separation of elastomeric and plastic blocks, the composition would approximate a 76,000 molecular weight center block (23% styrene) and 12,000 molecular weight end blocks (94% styrene).

Thus, the copolymerization of the styrene in the center block not only will cause more compatibility between the A and B blocks, but also causes the A blocks to be considerably shorter than intended. Both effects can cause loss of tensile strength, particularly at the lower styrene contents.<sup>5</sup> Similar calculations were made for the SBS polymers depicted in Figure 5, and all results are given in Table I. It can be seen that all styrene blocks are shorter than the theoretical values.

TABLE I  
Block Molecular Weights for Pure and Tapered ABA Polymers

Initiator	Block molecular weights, $\times 10^{-3}$	
	Pure	Tapered <sup>a</sup>
Styrene-Isoprene-Styrene		
DiLi-1 or DiLi-1 C.F.	20(S)-60(I)-20(S)	12(A; 94/6)-76(B; 23/77)- 12(A; 94/6)
Styrene-Butadiene-Styrene		
DiLi-1	18(S)-64(B)-18(S)	15(A; 85/15)-70(B; 15/85)- 15(A; 85/15)
DiLi-1 C.E.	18(S)-64(B)-18(S)	17(A; 87/13)-66 (B; 10/90)- 17(A; 87/13)

<sup>a</sup>Assuming that the B block ends at the color change and the A blocks begin. The ratios in parentheses represent the approximate styrene/diene ratios in the respective A and B blocks.

### Microstructure of Diene Homopolymers

Both polybutadienes and polyisoprenes were prepared with the dilithium initiators and their microstructures were determined by infrared analyses,

using a modified Binder method.<sup>26</sup> These are reported in Table II, together with comparable polymers made with monolithiumalkyls. In general, the microstructures of the various polymers are comparable. Those from the dilithium compounds tend to have slightly lower *cis*-1,4-

TABLE II  
Microstructure of Diene Homopolymers<sup>a</sup>

Initiator	Polybutadiene			Polyisoprene		
	<i>cis</i> -1,4, %	<i>trans</i> -1,4, %	1,2, %	<i>cis</i> -1,4, %	<i>trans</i> -1,4, %	3,4, %
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li	40.4	48.1	11.5	68.9	20.8	10.3
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li · 2(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	39.0	41.7	19.3	65.8	20.9	13.3
DiLi-1	37.0	48.1	15.0	64.3	21.1	14.7
DiLi-1 C.E.	38.7	48.8	12.5	65.6	20.6	13.6

<sup>a</sup> Polymerizations were run in benzene solvent at 50°C. The 1,2-contents of the polyisoprenes were negative fractions of a per cent and were neglected. All polymers have inherent viscosities of 1.0 to 1.8.

contents than polymers from *sec*-butyllithium, and slightly higher 1,2-content (for polybutadiene) or 3,4-content (for polyisoprene). Polybutadiene from *sec*-(C<sub>4</sub>H<sub>9</sub>)Li · 2(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O has a markedly higher 1,2-content than any of the others. The microstructures agree fairly well with comparable data in the literature.<sup>8,15,27</sup>

### Molecular Weight Distributions

A number of both SBS and SIS polymers were examined by gel permeation chromatography. In all cases only a single peak was seen. It was usually somewhat broader than a typical peak for an anionic polymer. This could be caused by slow-reacting impurities in the system or by leakage of traces of water into the polymerization bottles. Either situation would produce premature termination of some molecules, allowing the remainder to grow to a molecular weight higher than 100,000.

The single peak indicates that only one initiator species is present. If a monolithium species is present in the initiator, on a kinetic basis it should produce a 50,000 molecular weight AB-type block polymer. Any appreciable amount of such a polymer should appear as a separate peak or distinct shoulder on the main peak. Typical gel permeation chromatograms and a more thorough discussion of them are given elsewhere.<sup>28</sup>

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