routines. Whether there is any fundamental gain in efficiency by this procedure is doubtful, however, since much additional computation has to be performed in evaluating **C** and in forming the product **CAC**. Lin and Schurr[3] have actually carried out such a scheme in the treatment of dynamic light scattering from the beads-springs model. However, they chose to symmetrize the problem by transforming **H** to $\mathbf{A}^{1/2}\mathbf{H}\mathbf{A}^{1/2}$, where $\mathbf{A}^{1/2}$ is a symmetric matrix such that

$$\mathbf{A}^{1/2}\mathbf{A}^{1/2} = \mathbf{A} \tag{8}$$

They calculate $\mathbf{A}^{1/2}$ by a trigonometric-series procedure.

On the other hand, Lodge and Wu[4] use a scheme in which they factor **A** as

$$\mathbf{L}^{\mathrm{T}}\mathbf{L} = \mathbf{A} \tag{9}$$

where **L** is a triangular (nonsymmetric) matrix which consists entirely of ones and zeros and has only two diagonals different from zero. They then transform **HA** to $\mathbf{LHL}^{\mathrm{T}}$, which is again symmetric, and diagonalize this. Since the elements of **L** are so simple, this would appear to be the fastest of the symmetrizing schemes for numerical computation; in fact, Fong and Peterlin chose to use it in their actual calculation of eigenvalues. For many purposes, for example, calculation of the dynamic viscosity, the eigenvalues are sufficient. However, in some cases the eigenvectors of HA are also needed (for example, in ref 5 and 6); however then their normalization constants will cancel out of the final results if used with a consistent definition of the matrix **M**. (Dr. Peterlin has, in fact, recognized this in his more recent paper.[6])

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Radical Copolymerization of Sulfur Dioxide and Styrene. 3.[1] Evidence for the Occurrence of the Depropagation of Growing Styryl Radicals

MASASHI IINO, HO HUU THOI, SUMIO SHIOYA, and MINORU MATSUDA*

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan.

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One of the most characteristic features of the copolymerization of SO_2 with olefins is the low ceiling temperature[2,3] (the temperature above which the copolymerization does not occur). It has been proposed that two depropagations occur concurrently with propagation in the copolymerization of SO_2 and olefins:

$$\sim CH_2CH(R)SO_2\cdot \rightarrow \sim CH_2CH(R)\cdot + SO_2 \tag{1}$$

$$\sim SO_2CH_2CH(R)\cdot \rightarrow \sim SO_2\cdot + CH_2{=}CH(R) \tag{2}$$

In an earlier study,[4] we have investigated the depropagation of growing sulfonyl radicals, expressed by eq 1. The evidence for the occurrence of the latter depropagation, which consists of the elimination of an olefin molecule from a polymer radical containing the end group $\sim SO_2CH_2CH(R)\cdot$, was reported by Bristow and Dainton.[5,6] They have shown by infrared spectroscopic measurement that, at a temperature near the ceiling temperature, the copolymerization of SO_2 with either *cis*- or *trans*-2-butene is accompanied by geometrical isomerization, which occurs via reaction 2. Nowadays it is well accepted that the depropagation[2] expressed by eq 2 occurs during copolymerization of SO_2 with olefins such as propylene, ethylene, butene, hexene, etc., in which, because the olefins do not homopropagate under conditions suitable for polysulfone formation, poly(olefin sulfone)'s having a regular alternating 1:1 composition are formed.[7]

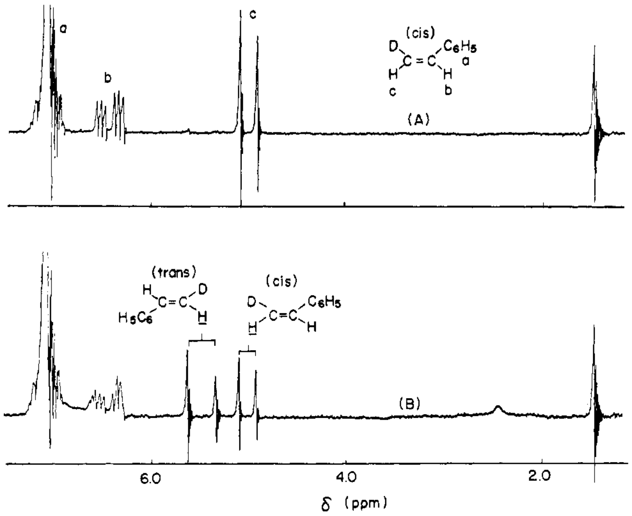


Figure 1. ^{1}H-NMR spectra of the reaction mixture: (a) before reaction, (b) after 120 min at reaction temperature 65 °C.

However, in the copolymerization of SO_2 with vinyl monomers such as styrene[8] and vinyl chloride,[9] in which polysulfones of variable composition are formed, evidence for the occurrence of depropagation of the growing radical endings has not been achieved so far. It is still a controversial problem. Walling[10] and Cais et al.[11,12] have assumed that this depropagation is involved in their proposed mechanisms for the SO_2–styrene copolymerization. The thermal decomposition of poly(styrene sulfone) at high temperature[13,14] (above 200 °C) to yield SO_2, styrene, and its dimer suggests the occurrence of this depropagation. In contrast, we have not taken into account this depropagation in our copolymerization model proposed for SO_2 and styrene[15] or vinyl chloride[16] copolymerization. Unlike olefins, the vinyl monomers can homopropagate; i.e., the $\sim SO_2CH_2CH(R)\cdot$ radical can react further with vinyl monomers to produce the radical of structural formula $\sim SO_2(CH_2CHR)_nCH_2CH(R)\cdot$, which is not expected to undergo depropagation over the range of copolymerization temperature investigated.

In the present paper, we report evidence for the occurrence of depropagation of the growing styryl radical by following the cis–trans isomerization of *cis*-β-deuteriostyrene by NMR during copolymerization with SO_2.

Experimental Section

cis-β-Deuteriostyrene was prepared from phenyldeuterioacetylene[17] by the method described in the literature.[18] The crude *cis*-β-deuteriostyrene was purified by preparative GLC (5 mm × 3 m column, GE-SE-30).

Polymerization was carried out in a NMR sample tube and stopped at times as desired by placing the tube in a precooled methanol bath. ^{1}H-NMR measurements were performed at room temperature and at 60 MHz. Polymerization rate was determined gravimetrically by carrying out the copolymerization of undeuterated styrene with SO_2 under the same experimental

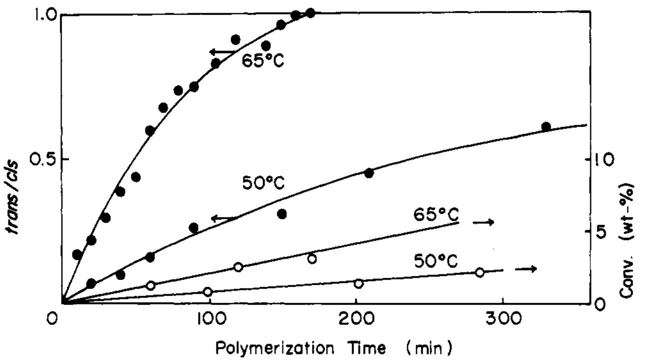
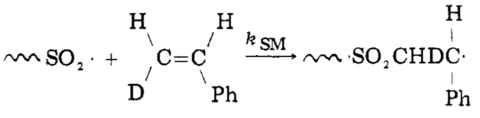


Figure 2. Cis–trans isomerization of *cis*-β-deuteriostyrene during the radical copolymerization of SO_2 and *cis*-β-deuteriostyrene: (●) Ratio of trans/cis isomers, (○) time–conversion curves for the copolymerization.

conditions. 2,2′-Azobis(isobutyronitrile) (AIBN) was used as an initiator (5×10^{-2} M). Feed composition of styrene was 8 mol %.

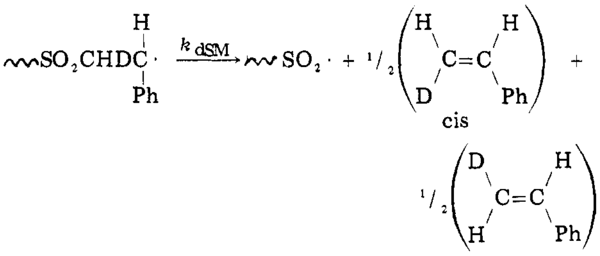
Results and Discussion

If the depropagation of growing styryl radical with the structural formula $\sim\!\sim SO_2CH_2CH(Ph)\cdot$ occurs, cis–trans isomerization of *cis*-β-deuteriostyrene will take place as follows:



(3)

cis-β-deuteriostyrene



(4)

trans

Namely, the growing styryl radical which is formed by the addition of a sulfonyl radical to *cis*-β-deuteriostyrene (eq 3) may undergo depropagation (eq 4) to produce both cis and trans isomers.

The NMR spectra shown in Figure 1a,b provide evidence of this depropagation. The NMR spectrum of the reaction mixture before polymerization in Figure 1a displays the signals due to *cis*-β-deuteriostyrene (δ 7.25 (5 H, m, aromatic protons), 6.70 (1 H, d, α proton), 5.13 (1 H, d, β proton)) and initiator AIBN (δ 1.75). The formation of *trans*-β-deuteriostyrene during the copolymerization was confirmed by the appearance of the doublet at 5.62 ppm due to the β proton of the trans isomer (Figure 1b). The broad peak due to copolymer (δ 2.45) was also observed. The formation of the trans isomer is attributed entirely to the depropagation of $\sim\!\sim SO_2CH_2CH(Ph)\cdot$ radicals for the following reason. The possibility of cis–trans isomerization of styrene monomer without involving the intermediate $\sim\!\sim SO_2CH_2CH(Ph)\cdot$ radical is excluded since the trans isomer was not observed in a blank test in which *cis*-β-deuteriostyrene and SO_2 were heated to 50 °C in the absence of polymerization initiator (AIBN).

The dependence of the ratio of trans/cis isomers on polymerization time at various temperatures is shown in Figure 2. The ratio was derived from the area ratios of the signals at 5.62 and 5.13 ppm, due to trans and cis isomer, respectively. The ratio of trans/cis increases rapidly initially, and after attaining unity it becomes constant, even when the polymerization time is prolonged. The result shows that the depropagation of growing styryl radicals produces a nearly equal amount of *cis*- and *trans*-β-deuteriostyrene. Both the rates of isomerization and polymerization increase with increasing temperature; however, the former increases more steadily than the latter. We have estimated that the ratio of $(R_{\mathrm{iso}}/R_{\mathrm{p}})_{65\,^{\circ}\mathrm{C}}/(R_{\mathrm{iso}}/R_{\mathrm{p}})_{50\,^{\circ}\mathrm{C}} \simeq 2$, where R_{iso} and R_{p} are the initial rate of isomerization and polymerization, respectively. It follows that the depropagation is associated with a rather higher activation energy. Consequently, at low temperature the depropagation can be neglected, but it must be considered in the copolymerization at room temperature and above. However, to evaluate the contribution of the depropagation in the copolymerization, a detailed study of the isomerization, such as the dependency of the isomerization rate on the feed composition and total monomer concentration, is necessary.

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