# Radical Copolymerization of *m*-Bromostyrene with Liquid Sulfur Dioxide*[1]

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The simple olefins, such as ethylene, propylene, and butenes, readily form alternating copolymers with sulfur dioxide from a wide range of feed compositions by means of a radical initiator.

Styrene also reacts with sulfur dioxide by means of a radical initiator and forms a 2 : 1 copolymer (molar ratio of styrene unit to sulfur dioxide unit) from a wide range of feed compositions above room temperature.1),2) The fact that the resulting copolymers are not alternating but 2 : 1 copolymers suggests that the propagation reaction can not be elucidated by the ordinary mechanism of copolymerization.

Thus, Barb1) has given an interpretation involving reversible propagation steps and the inclusion of sulfur dioxide in the copolymer only by the reaction of a growing chain with a 1 : 1 styrene-sulfur dioxide complex, which can be shown to be present spectroscopically.

However, as an entirely equivalent scheme can be derived without invoking any complex participation,3) Barb's postulation appears to be uncertain.

Concerning this problem, we have investigated the copolymerization of various styrene derivatives with sulfur dioxide.4) We have found that *p*-isopropylstyrene4b) or *p*-methylstyrene,4a) whose substituent is an electron-donating group, forms a 2 : 1 copolymer like that in the case of styrene, but *p*-nitrostyrene,4c) with an electron-withdrawing group, does not form a 2 : 1 copolymer.

The results in the case of *p*-nitrostyrene are thus different from those in the case of styrene, but *p*-nitrostyrene reacts with sulfur dioxide heterogeneously, unlike as in the case of styrene; therefore, it is possible to consider that this abnormality in the *p*-nitrostyrene - sulfur dioxide system is due to its heterogeneity.

To elucidate this problem we have investigated the copolymerization of *m*-bromostyrene with sulfur dioxide, because *m*-bromostyrene, whose substituent, *m*-Br, was electron-withdrawing, as in the case of *p*-nitrostyrene, has reacted with sulfur dioxide homogeneously.

## Experimental

Styrene, $\alpha, \alpha'$-azobisisobutyronitrile (AIBN), and liquid sulfur dioxide were purified by a method similar to that described in a previous paper.4)

*m*-Bromostyrene was prepared from *m*-bromobenzaldehyde.5) Elementary analysis: Found: C, 52.78; H, 4.11; Br, 43.36%. Calcd for $C_8H_7Br$: C, 52.48; H, 3.82; Br, 43.68%.

Bp 76.5—78.0°C/11 mmHg; $n_D^{17}$, 1.5882. The *m*-bromostyrene thus obtained was distilled twice in a nitrogen atmosphere at a reduced pressure.

The *n*-hexane used in the measurement of the ultraviolet spectra was purified in the usual way.

The method of the copolymerization was similar to that described in a previous paper.2)

The compositions of the copolymers were determined from the results of elementary analyses of carbon. The ultraviolet spectra of a *m*-bromostyrene-liquid sulfur dioxide mixture were measured in *n*-hexane by using a pressure cell.

## Results and Discussion

**Copolymerization of *m*-Bromostyrene and Liquid Sulfur Dioxide.** The radical copolymerization of *m*-bromostyrene with sulfur dioxide was carried out at 50°C, using AIBN as an initiator, and was stopped at a low conversion (below 7%).

As is shown in Fig. 1, the sulfur dioxide contents (mol%) in the resulting copolymers vary with the feed composition but are all below that (about 33 mol%) in the case of styrene.

The *e* value (*Q*-*e* scheme) of styrene, *m*-bromostyrene, and *p*-nitrostyrene are $-0.8$, $-0.21$, and 0.39 respectively.6) The sulfur dioxide contents (mol%) of the copolymers obtained at 50°C from an equimolar feed composition in the case of styrene, *m*-bromostyrene, and *p*-nitrostyrene are 33, 24, and 8 respectively.

Therefore, it may be concluded that styrene derivatives, having an electron-withdrawing substituent and a larger *e* value than styrene, have no tendency toward constant copolymer compositions, and that the sulfur dioxide contents in the

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[*1] Polymerization in Liquid Sulfur Dioxide. Part XXVII.

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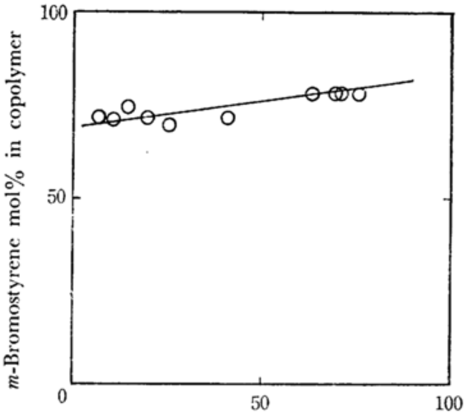

Fig. 1. Copolymer composition curve for *m*-bromostyrene - sulfur dioxide system.
Poly temp., 50°C; $[\mathrm{AIBN}]_0$, $3.0\times10^{-2}$—$3.0\times10^{-1}$(mol/*l*).

copolymers are lower than that in the case of styrene.

**Ultraviolet Spectra of the *m*-Bromostyrene-Liquid Sulfur Dioxide Mixture.** It is well known that sulfur dioxide forms a charge-transfer complex with some olefins, in which complex sulfur dioxide acts as an electron acceptor and olefin, as an electron donor.[7] In Fig. 2 the ultraviolet spectra of *m*-bromostyrene, sulfur dioxide, and *m*-bromostyrene - sulfur dioxide mixture are shown. It may be seen in Fig. 2 that a complex is formed in the *m*-bromostyrene - sulfur dioxide mixture, because there is a large shift in the absorption of the mixture in comparison with that of *m*-bromostyrene or sulfur dioxide only in the same concentration as in the mixture.

From the above results, in the *m*-bromostyrene - sulfur dioxide system a charge-transfer complex is formed as in the case of styrene; however, the compositions of the copolymers vary with the feed compositions, unlike the case of styrene.

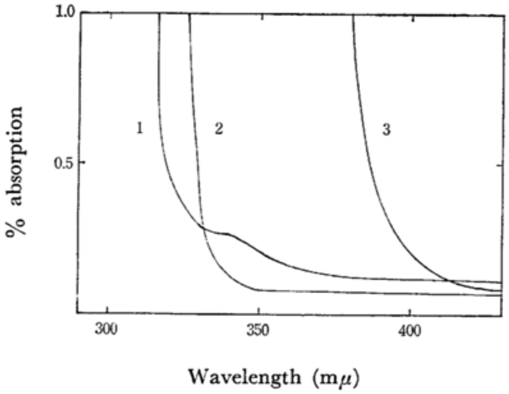

Fig. 2. Ultraviolet absorption for *m*-bromostyrene-sulfur dioxide system.
(1) *m*-Bromostyrene, 5.8 (mol/*l*)
(2) Sulfur dioxide, 5.6 (mol/*l*)
(3) *m*-Bromostyrene 5.8 (mol/*l*)) + sulfur dioxide(5.6(mol/*l*))
Solv., *n*-hexane; Cell depth, 0.4 mm; Room temperature.

As has previously been described, in the case of the *p*-nitrostyrene - sulfur dioxide system, the compositions of the copolymers vary with the feed compositions; the results of the ultraviolet spectra of the *p*-nitrostyrene - sulfur dioxide mixture suggest that no charge-transfer complex is formed.[4c]

Therefore, it may be concluded that, in the radical copolymerization of sulfur dioxide with styrene or its derivative (and perhaps also in that of sulfur dioxide with another olefin), the formation of a charge-transfer complex is not related to the constancy of the compositions of the copolymers when the feed compositions are varied.

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