The Properties of Nuclear Brominated Styrenes II—The Copolymerization of Dibromostyrene and 2,4,5-Tribromostyrene with Styrene

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The monomer reactivity ratios have been determined for the thermally initiated copolymerization of styrene with dibromostyrene and 2,4,5-tribromostyrene at 30°C. For the styrene (M_1)*–dibromostyrene system* $r_1=0{\cdot}22\pm0{\cdot}05$ *and* $r_2=1{\cdot}40\pm0{\cdot}15$*, and for the styrene–2,4,5-tribromostyrene system* $r_1=0{\cdot}05\pm0{\cdot}15$ *and* $r_2=0{\cdot}60\pm0{\cdot}35$*. The* r_1 *values establish the following order of monomer reactivities towards styryl radicals:*

2,4,5-tribromostyrene > dibromostyrene > styrene.

MONOMER reactivity ratios have been reported for the copolymerization of several nuclear halogenated styrenes with styrene. The nuclear halogenated styrenes which have been investigated include: *o*-, *m*- and *p*-chlorostyrenes[2-4]; 2,5-dichlorostyrene[5,6]; pentachlorostyrene[7]; *m*- and *p*-bromostyrene[2,3,8]; and *p*-iodostyrene[3,9]. We have recently synthesized dibromostyrene (largely the 2,4-isomer) and 2,4,5-tribromostyrene, and in this paper we describe the bulk copolymerization of these monomers with styrene.

EXPERIMENTAL

Materials

Dibromostyrene prepared as described previously[1] was used. The dibromostyrene had the following isomeric composition:

70 per cent 2,4-dibromostyrene
25 per cent 3,4-dibromostyrene
5 per cent 2,5-dibromostyrene.

In addition the monomer contained traces of ethyl benzene, ethyl dibromobenzene and 0·1 per cent 1-bromoethyldibromobenzene.

2,4,5-Tribromostyrene prepared as described previously[1] was recrystallized from methylene chloride (m.pt 64·5° to 65·5°C). The monomer was stored at – 10°C until required.

Styrene from Scott–Bader was freed from inhibitor by washing with aqueous alkali, dried over anhydrous calcium sulphate, and then fractionally distilled.

Benzene (B.D.H. AnalaR grade) was used without purification as the solvent for the copolymerization of 2,4,5-tribromostyrene with styrene.

Copolymerization procedure

Monomer mixtures with the required monomer feed compositions were placed in ampoules and outgassed under vacuum (10^{-2} mm Hg). The ampoules were then sealed off under vacuum and placed in a water thermostat bath at 30° ± 0·05 °C. At about 10 to 15 per cent conversion the ampoules were opened and the copolymers were precipitated in methanol.

The copolymer compositions were determined from the chemical analyses for carbon and bromine. The monomer reactivity ratio constants r_1 and r_2 were evaluated using the integrated equation of Lewis and Mayo[10]:

$$r_2 = \frac{\log \dfrac{M_2^0}{M_2} - \dfrac{1}{p} \log \left[\dfrac{(1 - pM_1/M_2)}{(1 - pM_1^0/M_2^0)} \right]}{\log \dfrac{M_1^0}{M_1} + \log \left[\dfrac{(1 - pM_1/M_2)}{(1 - pM_1^0/M_2^0)} \right]}$$

where $p = (1 - r_1)/(1 - r_2)$, M_1^0 and M_2^0 are the initial monomer concentrations, M_1 and M_2 are the monomer concentrations when the copolymerization is stopped.

The intrinsic viscosities of the copolymers were measured in toluene at 30 °C using an Ostwald dilution viscometer.

The rates of copolymerization were determined by the dilatometric procedure described in the previous paper[1].

RESULTS AND DISCUSSION

The dependence of copolymer composition on the monomer feed in the bulk thermal copolymerization of styrene and dibromostyrene is given in *Table 1*. The copolymer compositions calculated from carbon and from bromine analyses agreed to within ± 1·5 per cent. Average values were used in the computation of the reactivity ratios using the equation of Lewis and Mayo.

Table 1. Bulk thermal copolymerization of styrene and dibromostyrene at 30 °C

Monomer mole feed ratio styrene/DBS	*Analysis of the copolymer*			*Copolymer compn mole fraction*		*Intrinsic viscosity in toluene* $[\eta]$ *dl/g*
	C %	H %	Br %	*Styrene*	*DBS*	
4·12	58·8	4·8	37·2	0·604	0·396	0·235
1·07	45·8	3·5	50·6	0·345	0·655	0·150
0·244	43·1	3·4	55·9	0·190	0·810	0·140

Monomer reactivity ratios (styrene M_1) $r_1 = 0{\cdot}22 \pm 0{\cdot}05$, $r_2 = 1{\cdot}40 \pm 0{\cdot}15$.

The dependence of the copolymer composition on the monomer feed in the thermal copolymerization of styrene and 2,4,5-tribromostyrene in benzene is given in *Table 2*. Again good agreement was obtained between the copolymer compositions calculated from carbon and bromine analyses, although discolouration during the copolymerizations indicated that some bromine was liberated. The monomer reactivity ratios were calculated in the same way as for dibromostyrene.

Table 2. The thermal copolymerization of styrene and 2,4,5-tribromostyrene in benzene at 30°C

Monomer mole feed ratio styrene/TBS	*Analysis of the copolymer*			*Copolymer compn mole fraction*		*Intrinsic viscosity in toluene*
	C %	H %	Br %	*Styrene*	*DBS*	[η] *dl/g*
3·96	48·4	3·9	47·1	0·618	0·382	0·458
0·96	37·5	2·9	60·8	0·330	0·670	0·228
0·246	37·5	2·8	62·2	—	—	—

Monomer reactivity ratios (styrene M_1) $r_1 = 0{\cdot}05 \pm 0{\cdot}15$, $r_2 = 0{\cdot}60 \pm 0{\cdot}35$.

The reactivity ratios obtained for dibromostyrene and 2,4,5-tribromostyrene are compared with other reported values for the copolymerization of other halostyrenes with styrene in *Table 3.* Although the dibromostyrene used in this work contains some 3,4-isomer, this would not be expected to have a large effect on the reactivity ratios by analogy with the *o*-, *m*- and *p*-bromostyrenes which have very similar values. The r_1 values establish the following order of monomer reactivities towards styryl radicals:

$$2,4,5\text{-tri Br} > 2,4\text{-di Br} \approx 2,5\text{-di Cl} > o\text{-Cl}$$
$$m\text{-Cl} > p\text{-Br} \approx p\text{-Cl} > \text{penta Cl}$$

Thus increasing halogenation results in an increase in monomer reactivity, except in the case of pentachlorostyrene where steric hindrance to reaction becomes important. This reactivity sequence indicates that the monomer reactivity is increased by the electron withdrawing effect of the halogen substituents. Walling *et al.*[3] have drawn attention to this effect in a study of the copolymerization of *p*-substituted styrenes with styrene. Electron-

Table 3. Monomer reactivity ratio for the copolymerization of styrene (M_1) with nuclear halogenated styrenes (M_2)

Halostyrene M_2	r_1	r_2	*Temp.* °*C*	*Ref.*
o-Chloro-	0·56±0·03	1·60 ±0·07	60	2
m-Chloro-	0·64±0·05	1·09 ±0·23	60	3
p-Chloro-	0·74±0·03	1·032±0·030	60	4
2,5-Chloro-	0·27±0·04	2·00 ±0·20	70	6
Pentachloro	1·31±0·20	0·10 ±0·02	70	7
p-Bromo	0·71±0·02	1·05 ±0·05	60	8
Dibromo (largely 2,4-)	0·22±0·05	1·40 ±0·15	30	This work
2,4,5-Tribromo	0·05±0·15	0·60 ±0·35	30	This work

releasing groups such as *p*-methoxy deactivate the monomer, while electron-withdrawing groups such as *p*-chloro and *p*-nitro increase activity towards styryl radicals. It is apparent from our data that this effect operates in dibromostyrene and 2,4,5-tribromostyrene. However, further substitution of bromine might result in a deactivation for steric reasons.

Inspection of the r_2 values in *Table 3* shows the halostyrene monomers are in general at least as reactive as styrene with the halostyryl radical, with the exception of tribromostyrene and pentachlorostyrene. This effect can be understood in terms of steric hindrance, because this will be much more important in the homopolymerization of the halostyrene (k_{22}) than in the cross propagation reaction (k_{21}):

$$\mathrm{TBS}^{\bullet} + \mathrm{TBS} \xrightarrow{k_{22}} \mathrm{TBS}^{\bullet}$$

$$\mathrm{TBS}^{\bullet} + \mathrm{S} \xrightarrow{k_{21}} \mathrm{S}^{\bullet}$$

where TBS denotes 2,4,5-tribromostyrene, and S is styrene. It is clear that steric factors cannot have much influence on the k_{22} values for 2,5-dichlorostyrene, and the largely 2,4-dibromostyrene used in this work. However, in 2,4,5-tribromostyrene the steric factor is probably significant and $k_{21} > k_{22}$, although 2,4,5-tribromostyrene is a more reactive monomer than styrene towards styryl radicals.

The intrinsic viscosities of the copolymers recorded in *Tables 1* and *2* indicate that the molecular weight of the copolymers decreased as the halostyrene content in the monomer feed was increased. In dibromostyrene

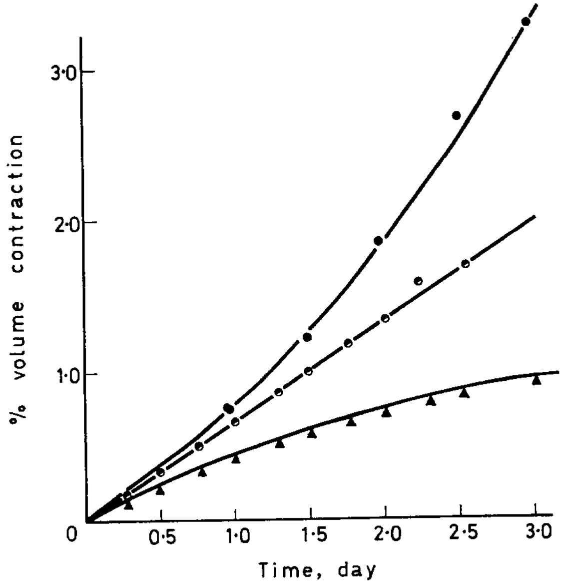

Figure 1—The copolymerization of DBS and styrene at 30°C
● DBS
⊖ 4:1 DBS/styrene
▲ 1:4 DBS/styrene

this can be partially attributed to chain transfer with the 1-bromoethyldibromobenzene impurity in the monomer. However, this explanation cannot be applied to 2,4,5-tribromostyrene which was obtained in a pure state, and chain transfer to 2,4,5-tribromostyrene monomer must be responsible for the drop in molecular weight. Evidence of chain transfer to monomer has been obtained in the previous study[1] of the homopolymerizations of dibromostyrene and 2,4,5-tribromostyrene.

The results of a dilatometric study of the thermal polymerization of dibromostyrene and the bulk copolymerization with styrene are plotted in *Figure 1*. Neglecting density differences the rates of contraction can be taken as the relative rates of polymerization and copolymerization. Thus *Figure 1* shows the rate of copolymerization decreased as the proportion of styrene in the monomer feed was increased. This is probably just the effect of dilution with the less reactive monomer. This has practical significance in that it has been found convenient to store dibromostyrene containing 25 per cent styrene to lengthen the shelf life of this very reactive monomer.

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