The Properties of Nuclear Brominated Styrenes I—The Synthesis and Polymerization of Dibromostyrene and Tribromostyrene

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Mixtures of 2,4- and 3,4-dibromostyrene have been prepared by two synthetic routes. The rate of polymerization observed in the absence of solvents and chain transfer agents showed a marked acceleration from very low conversion, and insoluble polymer was obtained. The acceleration in rate of the bulk polymerization has been attributed to a Trommsdorf effect, and the formation of insoluble polymer to crosslinking by chain transfer to monomer and polymer. The new monomer 2,4,5-tribromostyrene has also been prepared and characterized. The following order of rates of thermal polymerization has been established in solution:

2,4,5-tribromostyrene > 2,4- and 3,4-dibromostyrene ≫ styrene

An insoluble polymer was also obtained from the bulk thermal polymerization of 2,4,5-tribomostyrene.

INTEREST has recently been stimulated in the nuclear halogenated styrenes, because unsaturated polyester resins crosslinked with these monomers can have flame-retardant properties[1-3]. Dibromostyrene is of particular interest in this application[4]. Although the nuclear chlorinated styrenes have been known for many years, very much less work has been done on the nuclear brominated styrenes. The preparation of o-, m- and p-bromostyrenes[5-7] and 2,5- and 3,4-dibromostyrenes[8] has been reported. Koton[8] has prepared the dibromostyrenes by acetylation of the appropriate dibromobenzene followed by reduction of the carbonyl group and dehydration, e.g.
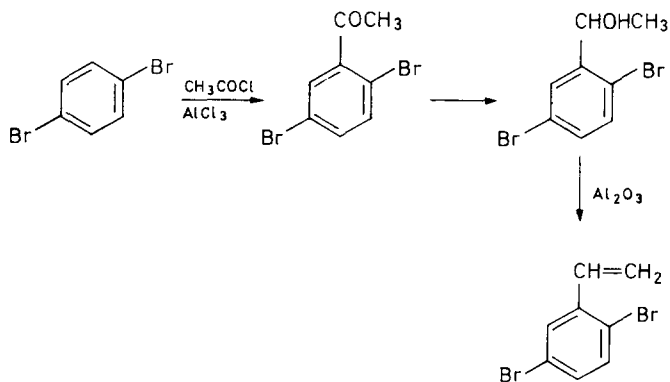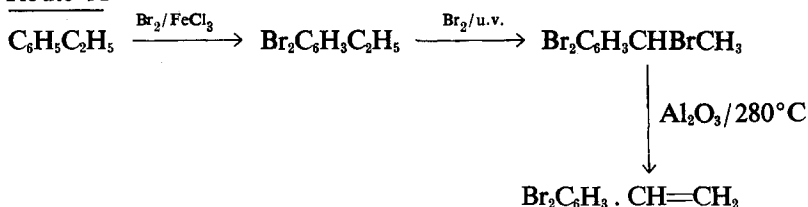

However, recent work by Olah[9] has shown that the dibromobenzenes can isomerize in the presence of aluminium chloride, and it follows that the structure of the dibromostyrene prepared by Koton must be rather uncertain.

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In this work we report the synthesis and characterization of mixtures of 2,4- and 3,4-dibromostyrene by two routes. The novel monomer 2,4,5-tribromostyrene has also been prepared. The rates of polymerization of these monomers have been briefly investigated.

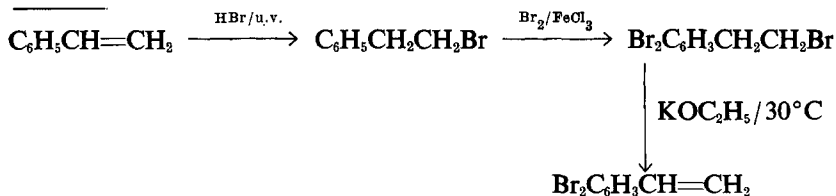<div align="center">EXPERIMENTAL</div>

(1) *Synthesis of dibromostyrene*

The synthesis of dibromostyrene from ethylbenzene (Route A) has already been described elsewhere[1]. The only modification to the published method was the use of activated alumina in either pellet or granular form to catalyse the dehydrobromination.

Route A

$$C_6H_5C_2H_5 \xrightarrow{Br_2/FeCl_3} Br_2C_6H_3C_2H_5 \xrightarrow{Br_2/u.v.} Br_2C_6H_3CHBrCH_3$$

$$\downarrow Al_2O_3/280°C$$

$$Br_2C_6H_3 . CH{=}CH_2$$

The dibromostyrene obtained by this route contained traces of ethylbenzene, 0·1 per cent ethyl dibromobenzene, 0·7 per cent 1-bromoethyldibromobenzene and 3 per cent p-bromostyrene. The very rapid thermal polymerization of this monomer at temperatures of 60° to 80°C, even in the presence of inhibitors, effectively prevented any further purification of the dibromostyrene by vacuum distillation. Inhibitors normally used for styrene were found to be very much less effective in suppressing the polymerization of dibromostyrene. However, it was found possible to inhibit polymerization for about six weeks at room temperature with a mixture of 100 p.p.m. t-butyl catechol and 100 p.p.m. picric acid.

Dibromostyrene was also prepared from styrene by Route B.

Route B

$$C_6H_5CH{=}CH_2 \xrightarrow{HBr/u.v.} C_6H_5CH_2CH_2Br \xrightarrow{Br_2/FeCl_3} Br_2C_6H_3CH_2CH_2Br$$

$$\downarrow KOC_2H_5/30°C$$

$$Br_2C_6H_3CH{=}CH_2$$

2-Bromoethylbenzene was prepared as described in the literature[10]. Bromine (336 g, 2·1 mole) was added dropwise with stirring to 2-bromoethylbenzene (185 g, 1 mole) and anhydrous ferric chloride (2·4 g) over a period of four and a half hours. The reaction mixture was maintained at 0°C throughout the bromination and for a further two hours. The product was washed with water, aqueous sodium bisulphate, and finally water. After drying over anhydrous calcium sulphate, an 87 per cent yield of

product was obtained which analysed satisfactorily for 2-bromoethyl-dibromobenzene (*Table 1*). A solution of potassium ethoxide was prepared by dissolving potassium (70 g, 2 g atom) in one litre of ethanol.

Table 1. Analytical data for the monomers and intermediates

No.	Compound	Formula
1	Dibromostyrene (Route A)	$Br_2C_6H_3CH=CH_2$
2	Dibromostyrene (Route B)	$Br_2C_6H_3CH=CH_2$
3	Tribromostyrene (Route B)	$Br_3C_6H_2CH=CH_2$
4	1-Bromoethyldibromobenzene	$Br_2C_6H_3CHBrCH_3$
5	2-Bromoethyldibromobenzene	$Br_2C_6H_3CH_2CH_2Br$
6	2-Bromoethyltribromobenzene	$Br_3C_6H_2CH_2CH_2Br$

No.	Found, % by wt				Required			
	C	H	Br	Hydrolysable Br	C	H	Br	Hydrolysable Br
1	37·3	2·9	61·2	0·35	36·7	2·3	60·9	0
2	36·9	2·5	59·5	0·16	36·7	2·3	60·9	0
3	28·9	1·9	70·4	0·15	28·2	1·4	70·4	0
4				22·9				23·6
5			69·5	22·8			69·9	23·6
6			73·8	18·8			75·8	18·9

This solution was maintained at 30°C, and the 2-bromoethyldibromobenzene (206 g, 0·6 mole) was added dropwise over 20 minutes. The reaction mixture was stirred for a further three hours at 30°C, poured into water (1000 ml), and extracted three times with methylene chloride. The combined methylene chloride extracts were washed with water and dried over anhydrous calcium sulphate. The methylene chloride was distilled off under reduced pressure to leave dibromostyrene (156, g) (*Table 1*).

The dibromostyrenes prepared by the two routes have different isomer ratios and consequently rather different properties (*Table 2*). The isomeric

Table 2. Properties of dibromostyrene

Source	Isomer ratio by GLC*	d^4_{30} g/ml	n^D_{25}	B.pt
Route A	3·0:1	1·810	1·6266	80°C/0·5 mm
Route B	1·0:1	1·758	1·6326	—

*Separation was carried out with a column of 'Daltolac 10' on Chromosorb-W support.

constitution of the dibromostyrenes was established by the oxidation of the saturated side chains of the intermediates to give the known dibromo-benzoic acids.

$Br_2C_6H_3C_2H_5$ ⎯⎯⎯⎯⎯⎯⎯⎯⎯⎯

$Br_2C_6H_3CH_2CH_2Br$ ⎯⎯⎯⎯⎯⎯⎯⎯ $\xrightarrow{HNO_3/120°C}$ $Br_2C_6H_3COOH$
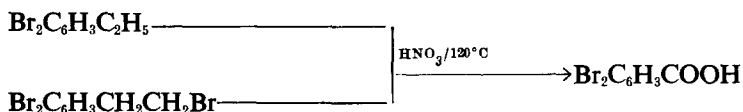
A near quantitative oxidation (90 to 95 per cent) was obtained using a 35 per cent nitric acid–acetic acid mixture at 120°C for 14 or 15 hours. The 2,4-, 2,5- and 3,4-dibromobenzoic acids were isolated by precipitation, and identified by melting points and comparison of the infra-red spectra with the authentic acids[11,12]. Some difficulty was experienced in separating the small amounts of 2,5-dibromobenzoic acid from the 2,4-isomer. The approximate composition of the dibromostyrenes found in this way is given in *Table 3*.
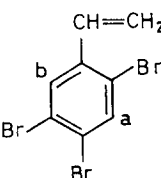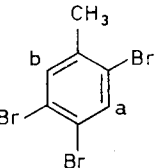
Table 3. Isomeric constitution of the dibromostyrenes determined by oxidation of the intermediates

Source	Isomer ratio of the dibromo-styrenes by GLC	Dibromobenzoic acids isolated, wt %		
		2,4-	2,5-	3,4-
Route A	3·0 : 1	70	∼5	25
Route B	1·0 : 1	45–55	0–10	45–55

(2) Synthesis of 2,4,5-tribromostyrene

Tribromostyrene was prepared by Route B by using the stoichiometric amount of bromine in the nuclear bromination stage. The monomer was recrystallized from methylene chloride, m.pt 64·5° to 65·5°C. The analytical data are included in *Table 1*. The substitution pattern was established by comparison of the ^{1}H n.m.r. spectrum with that of 2,4,5-tribromo-toluene prepared as described in the literature[13] (*Table 4*).

Table 4. ^{1}H n.m.r Spectrum of tribromostyrene and 2,4,5-tribromotoluene

Compound	τ value	Multiplicity	Relative intensities	Assignment
CH=CH₂ structure	2·23	Singlet	1	Nuclear proton (a)
	2·31	Singlet	1	Nuclear proton (b)
	2·88, 3·07, 3·17, 3·32	AB₂	1	Vinyl group CH
	4·19, 4·47, 4·50, 4·68	A₂B	2	Vinyl group CH₂
CH₃ structure	2·29	Singlet	1	Nuclear proton (a)
	2·58	Singlet	1	Nuclear proton (b)

(3) Polymerization studies

The rates of the bulk polymerization of the two types of dibromostyrene were followed at 30°C in calibrated dilatometers sealed under vacuum. For

this purpose freshly prepared samples of polymer-free monomer were introduced into the dilatometers and then outgassed several times under vacuum (10^{-2} mm Hg.). After sealing under vacuum the dilatometers were placed in a thermostat bath at $30° \pm 0.05°C$, and the volume contractions were measured with a cathetometer. The percentage conversion was calculated from the density of the monomer (*Table 2*) and the density of the polymer (2·16 g/ml). This corresponds to 19·4 per cent contraction at 30°C for 100 per cent conversion to polymer.

The rate of polymerization of 2,4,5-tribromostyrene in benzene solution at 30°C was followed by withdrawing samples, precipitating the polymer in methanol and weighing.

RESULTS AND DISCUSSION

The two synthetic routes utilized in this work both provide dibromostyrene in good yield. The principal difference is the ease of dehydrobromination of the intermediates. Thus, the 1-bromoethyldibromobenzene must be dehydrobrominated at high temperatures ($> 200°C$), while 2-bromoethyldibromobenzene can be readily dehydrobrominated by bases at ambient temperature. In consequence, a monomer with a much lower side chain bromine content can be obtained by Route B (*Table 1*). The results of the oxidation of the intermediates show that the dibromostyrenes produced by the two routes differed in the 2,4-/3,4-dibromostyrene ratio. 2,5-Dibromostyrene was only a minor component in each case (*Table 3*). It might be argued that in Route A some nuclear isomerization might take place under the conditions employed in dehydrobromination, and consequently the isomer ratio of the intermediate and the monomer would not
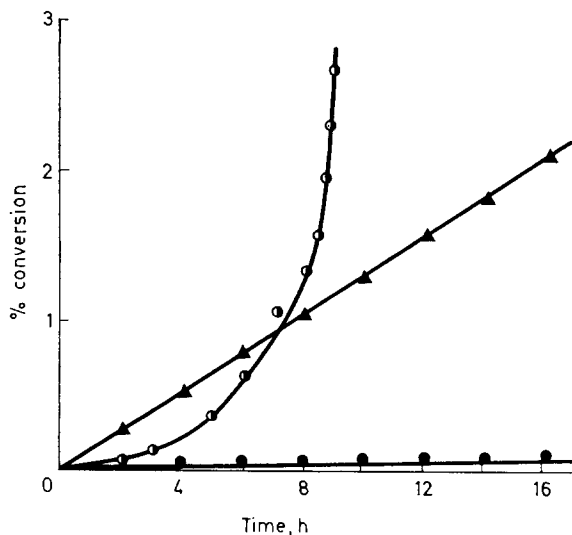

Figure 1—Polymerization of the dibromostyrenes at 30°C.
● Styrene. ◐ DBS route 'B'. ▲ DBS route 'A'

be the same. However, analysis of the isomer ratio by gas liquid chromatography showed that the ratio was identical in 1-bromoethyl dibromobenzene and the dibromostyrene. Thus, the oxidation of the side chains of the intermediate bromoethyldibromobenzenes can be regarded as a satisfactory method of characterizing the monomers. Direct oxidation of the dibromostyrenes was not possible, because polymerization occurred at the temperatures employed.
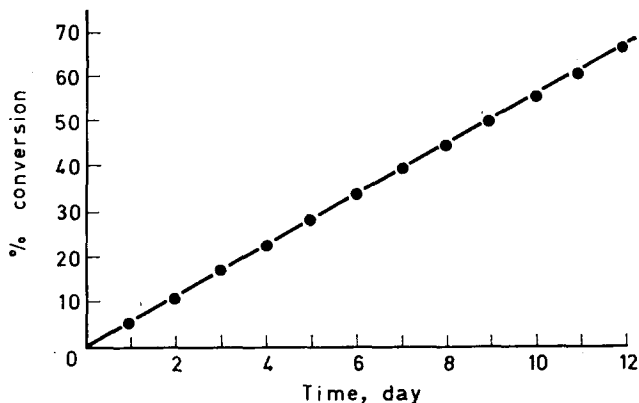

Figure 2—Polymerization of route 'A' DBS at 30°C

An investigation of the rates of bulk polymerization at 30°C of the Route A and Route B dibromostyrenes revealed major differences in behaviour (*Figure 1*). The Route B monomer had a shorter induction period and showed an accelerating rate of polymerization from two per cent conversion. This monomer polymerized to an insoluble gel. The Route A dibromostyrene showed a longer induction period, and a constant rate of polymerization up to 65 per cent conversion (*Figure 2*). The Route A monomer polymerized to a soluble low molecular weight polymer (*Table 5*).

Table 5. Intrinsic viscosities of the polybromostyrenes

Monomer	Polymerization conditions	Intrinsic viscosity of polymer, dl/g	Ref.
Styrene	Bulk at 60°C	4·0*	14
p-Bromostyrene	Bulk at 60°C	0·4*	14
2,5-Dibromostyrene	Benzene at 100°C	0·26	8
3,4-Dibromostyrene	Benzene at 100°C	0·12	8
Route 'A' dibromostyrene	Bulk at 30°C	0·08†	This work
Route 'B' dibromostyrene	Bulk at 30°C	Insoluble	This work
Route 'B' dibromostyrene	Benzene at 30°C	Soluble	This work
2,4,5-Tribromostyrene	Bulk at 100°C	Insoluble	This work
	Benzene at 30°C	0·05†	This work

*Measured in benzene at 20°C.
†Measured in benzene at 30°C.

This latter result accounts for the absence of a Trommsdorf[15] effect in the polymerization of the Route A monomer, and suggests that this monomer contained a chain transfer agent not present in the Route B monomer. The Route A monomer contained 1-bromoethyldibromobenzene, which would be expected to be a very active transfer agent, because of the possibility of forming a resonance-stabilized benzyl radical[16]. In agreement with this theory, the introduction of 1-bromoethyldibromobenzene into Route B monomer prevented the formation of insoluble polymer. The 2-bromoethyldibromobenzene present in the Route B monomer must be a much less active chain transfer agent than 1-bromoethyldibromobenzene, and this conclusion is supported by the low chain transfer constant of 1-bromobutane compared with that of p-xylylene dibromide[17]. Thus the chain transfer theory provides a convincing explanation for the differences in kinetic behaviour of the two monomers. It would be difficult to explain the differences in terms of the known relatively small change in isomeric composition of the dibromostyrenes.

It follows from the preceding arguments that the kinetic behaviour of the Route B monomer must be more representative of dibromostyrene than the Route A monomer. Hence, the unusual features of the bulk polymerization of 2,4- and 3,4-dibromostyrenes which require explanation are: (i) the acceleration in rate from two per cent conversion; and (ii) the formation of insoluble polymer. The acceleration in rate can be attributed to a Trommsdorf effect brought about by the high viscosity of the branched and crosslinked polymers. It therefore remains to explain how the crosslinking takes place. It is well established that halobenzenes participate in chain transfer in the polymerization of styrene[18,19] and other monomers[20]. Chain transfer to dibromostyrene and to polymer by attack on the aromatic ring could lead to crosslinking. Possible transfer mechanisms are bromine (1) and hydrogen abstraction (2) and homolytic substitution (3). This latter mechanism has been proposed by Ham and Ringwald[21] to account for the formation of insoluble polymer from vinyl benzoate. These types of transfer to monomer lead to a polymer chain with a pendant vinyl group. Participation of the vinyl group in polymerization results in branching and crosslinking. The analogous chain transfer reactions to polymer also lead to crosslinking. However, Mayo[18] has shown that polystyrene prepared in bromobenzene does not contain any bromine and has proposed the chain transfer mechanism (4). Clearly if chain transfer to dibromostyrene occurs by mechanism (4) crosslinking will not result. This type of transfer probably occurs in the bulk polymerization of p-bromostyrene, since soluble low molecular weight polymers have been obtained (Table 5). 2,4,5-Tribromostyrene resembles dibromostyrene in that the bulk polymerization gave crosslinked polymer. In the presence of solvent, the polymerizations of dibromostyrene and tribromostyrene gave soluble low molecular weight polymers. Presumably the dilution of the system suppressed the crosslinking due to transfer with polymer. The introduction of the chain transfer agent 1-bromoethyldibromobenzene into the bulk polymerization of dibromostyrene reduced the molecular weight

of the polymer (and hence the number of crosslinks per molecule) sufficiently to give a soluble polymer. Koton *et al.*[8] found no signs of a Trommsdorf effect in bulk polymerization of dibromostyrene, and soluble polymers were obtained. This parallels the behaviour of the Route A
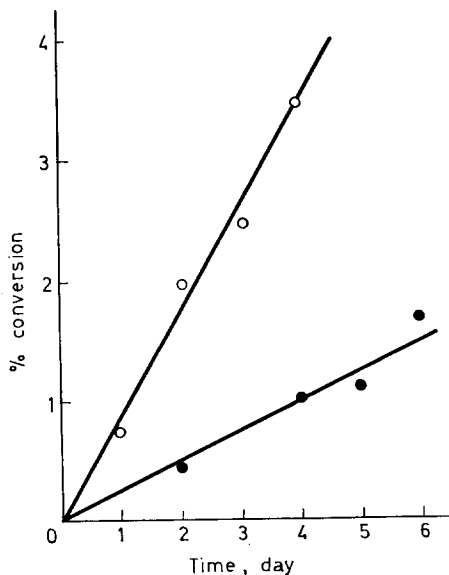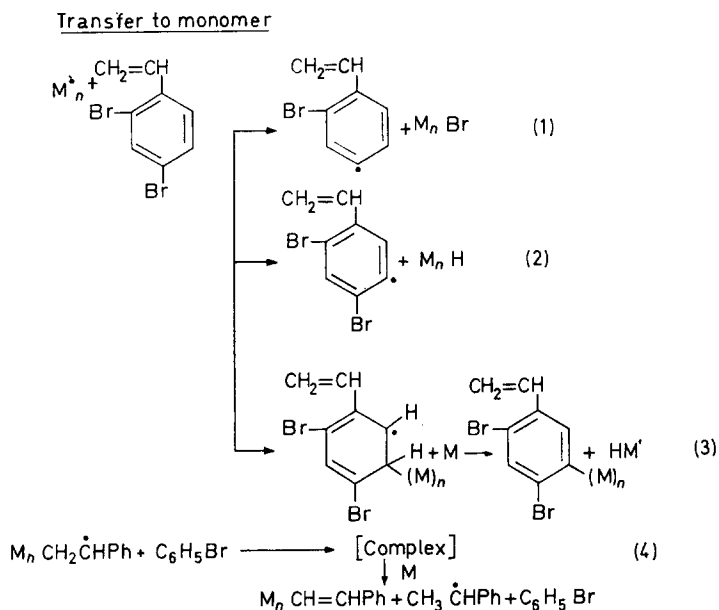
Transfer to monomer

$$M_n CH_2\dot{C}HPh + C_6H_5Br \longrightarrow [Complex] \quad (4)$$
$$\downarrow M$$
$$M_n CH=CHPh + CH_3 \dot{C}HPh + C_6H_5 Br$$

Figure 3—Polymerization of DBS and TBS in benzene at 30°C.
○ IM tribromosytrene. ● IM dibromostyrene

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monomer in this work. It is possible that Koton's monomers contained some 1-hydroxyethyldibromobenzene, which could act as a chain transfer agent in the same way as 1-bromoethyldibromobenzene.

The rates of polymerization in solution of dibromostyrene and 2,4,5-tribromostyrene are compared in *Figure 3*. It is apparent that the introduction of the bromine atoms activates the vinyl group towards polymerization giving the following order of rates of polymerization: 2,4,5-tribromostyrene > 2,4- and 3,4-dibromostyrene ≫ styrene. Koton[22] has observed the same order of polymerization rates for the analogous chlorostyrenes.

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