

Hydroxyl-Terminated Cotelomers of Butadiene and Bromostyrene

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Synopsis

The synthesis of hydroxyl-terminated cotelomers of 1,3-butadiene and bromostyrene was studied. Hydrogen peroxide was used in solution copolymerization to obtain cotelomers of average molecular weights of 1000–4000. The higher the hydrogen peroxide concentration, the broader the molecular weight distribution. The molecular weight is apparently unaffected by the hydrogen peroxide concentration within the limits studied. The concentration of bromostyrene in the products is correlated with its concentration in the monomers. Microstructure of the cotelomers is analyzed. Vinyl content is about 25% of the butadiene content. A correlation of the glass transition temperatures of the cotelomers with those of pure polybromostyrene and polybutadiene is discussed.

INTRODUCTION

The use of telechelic polymers (i.e., low molecular weight prepolymers containing reactive functional groups) has been growing in recent years. Hydroxyl, carboxyl, and amine are among the functional groups introduced to prepare prepolymers,^{1,2} which serve as propellant binders, as crosslinking agents, and as chain extenders in various polyurethane and epoxy systems. Hydroxyl-terminated telomers of the diene type have been prepared by anionic³ and free-radical^{4–8} polymerization. Hydrogen-peroxide-initiated polymerization of butadiene was studied in organic solvents^{4–8} and with ferrous ions catalysis.⁹ Hydrogen peroxide has been used by Brosse et al.^{5–7} in the polymerization of isoprene, butadiene, vinyl acetate, and methyl methacrylate. The effect of the reaction medium, such as mixtures of methanol and benzene, on the conversion to low molecular weight polymers was also studied.^{5–7} High molecular weight copolymers of butadiene and halogenated styrenes were prepared to impart superior rubberlike properties to those of styrene copolymers.¹⁰ Bromine-containing prepolymers have been also introduced to epoxy systems to impart flame retardancy and to decrease water absorption of the matrix.¹¹

It is the object of the present work to study the synthesis of low molecular weight hydroxyl-terminated cotelomers of butadiene and bromostyrene using hydrogen peroxide as the initiator and to evaluate their properties.

EXPERIMENTAL

Materials

1,3-Butadiene was obtained from Fluka (puriss). Bromostyrene was obtained from Makhteshim Chemical Works (bp 55°C/2.5 mm). Toluene, hy-

drogen peroxide (30%), tetrahydrofuran, and chloroform were analytical grade (Frutarom) and sodium dodecyl sulfate was BDH.

Procedure

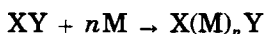
Copolymerization was carried out in thick wall sealed glass ampoules. An ampoule fitted with a stopcock containing the reaction components, except butadiene, was cooled in liquid nitrogen. Butadiene was condensed into the ampoule. Excess butadiene was cautiously boiled off and the ampoule was cooled again and sealed. It was then placed in a holder inside an oven fitted with a rotating arm. At the end of the reaction the ampoule was cooled again and opened. The content of the ampoule was poured into a fortyfold excess of methanol, dissolved in toluene, and reprecipitated in methanol. Volatiles were removed by pumping out at 0.2 mm and ambient temperature to a constant weight. The products were tacky, yellowish, clear viscous fluids.

Analytical

Bromine content was determined by the Schoniger method.¹² The hydroxyl number was measured according to Pinazzi et al.⁵ Molecular weight was determined by vapor phase osmometry with a Hitachi-Perkin-Elmer 115 Molecular Weight instrument, using chloroform as the solvent at 30°C. Gel permeation chromatography was carried out on an Aerograph 8500 Varian instrument fitted with a UV detector. Styragel columns (Waters Assoc.) were used with flowing rate of 1 mL/min. of degassed tetrahydrofuran. Retention times were calculated as polystyrene equivalents. Proton nuclear magnetic resonance spectroscopy was carried out on a Varian FT NMR 80A Spectrometer, using deuterated chloroform as the solvent with TMS as reference. Infrared spectroscopy was carried out on a Nicolet MX 1 FTIR spectrophotometer. The copolymers were pressed between two NaCl pellets. Differential scanning calorimetry was performed on a Mettler DSC 30 system at 20°C/min under nitrogen flow. Thermogravimetric Analysis was carried out on a Perkin-Elmer TGS 1 at 8°C/min in still air.

RESULTS AND DISCUSSION

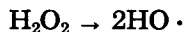
Telomerization is the polymerization of a monomer in the presence of a chain transfer agent to yield low molecular weight products¹³:



where XY is a telogen and M is the monomer. Accordingly, cotelomerization is a reaction in which two monomers and one telogen react to produce a cotelomer.

Hydrogen-peroxide-initiated cotelomerization of 1,3-butadiene and bromostyrene may lead to a variety of products. These may vary in molecular weight and the ratio between bromostyrene and butadiene in the cotelomer. The molecular weight of the polymer will depend on the ratio of the reacting

monomers and the concentration of hydrogen peroxide. Hydrogen peroxide decomposes by heat to two OH radicals:



and serves both as the initiator and the telogen in these reactions. It was assumed that, by carefully choosing the ratio of the monomers in the reaction mixture and the use of a two-phase polymerization with excess hydrogen peroxide in the aqueous phase, it would be possible to obtain hydroxyl-terminated low molecular weight cotelomers and to control their molecular weights and the ratio of the monomers in the product:

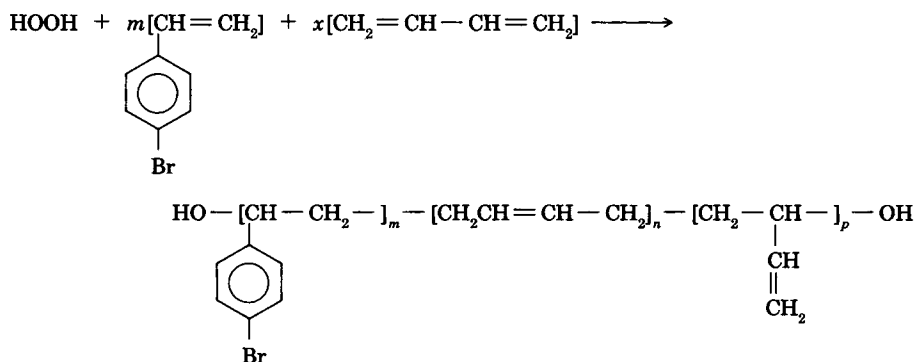


Table I summarizes the results of the cotelomerization of 1,3-butadiene and bromostyrene in toluene. The products were all low molecular weight cotelomers with molecular weights ranging from about 1000 to 4000. Figure 1 shows conversion as a function of time of a cotelomer produced from monomer feed containing 20 mol % bromostyrene and 80 mol % butadiene. It is evident that the conversion is much higher than that reported for the polymerization of butadienes.⁵ Samples left in the oven without rotating had a very low conversion after 24 h. In our system, hydrogen peroxide is probably dissolved to saturation in the organic medium with the aqueous phase serving as a reservoir of hydrogen peroxide. It seems that varying its concentration from 24 mol % of total monomers to 53 mol % does not affect the molecular weight and the bromine content of the cotelomers. However, such concentrations are appropriate for generating low molecular weight cotelomers as the excess hydrogen peroxide increases the velocity of the termination step. The number of hydroxyl groups in the cotelomer molecule were determined according to Pinazzi.⁵ The hydroxyl numbers range from 1.5 to 2.7 without any apparent trend as a function of the monomer ratio in the feed or of the present reaction conditions. Theoretically, the hydroxyl number should be 2, but termination other than by hydroxyl radicals may lead to hydroxyl numbers smaller than 2 and branching and hydroxylation of double bonds may lead to hydroxyl numbers greater than 2.

TABLE I
Butadiene-Bromostyrene Cotelomers^a

Expt no.	Butadiene (mol %)	Bromostyrene (mol %)	Hydrogen peroxide ^b	Bromine content ^c			\bar{M}_n^d	T_g (°C)
				Feed	NMR	Expt		
110	89.8	10.2	24.4	12.1	12.2	10.9	2750	—
112	81.8	18.2	25.5	18.8	16.8	17.2	3580	-47
113	81.5	18.5	31.9	19.0	19.1	18.0	1680	-45
114	80.1	19.9	42.0	20.0	19.6	19.2	2330	-34
115	81.1	18.9	44.6	19.2	20.0	19.2	4240	-53
116	81.2	18.8	52.6	19.2	19.6	18.8	2400	-48
117	90.1	9.9	35.6	11.9	12.1	11.3	1100	-54
118	86.7	13.3	37.3	15.0	15.2	11.2	1440	-49
120	72.5	27.5	37.5	24.6	19.0	20.1	1120	-45
121	61.6	38.4	38.1	29.6	28.0	25.9	1700	-25
122	100.0		42.3					-65
123		100.0	42.3	43.7				129
124		100.0		43.7				-5
125 ^e	85.9	14.1	37.8	15.6				-11
126 ^e	80.9	19.1	37.5	19.4				-10

^a Total monomers: 0.07–0.10 mol; toluene 10 mL; emulsifier 0.15 g; reaction temperature 98°C; reaction time 24 h.

^b Mol % of total monomers.

^c Wt %.

^d VPO by Hitachi-Perkin-Elmer 115 in chloroform at 30°C.

^e Bulk polymerization.

The reactivity of a monomer can be calculated from the Alfrey-Price equation¹⁴:

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

where r_1 is the reactivity of monomer 1 and Q and e are the Alfrey-Price values. According to Q and e values for butadiene and bromostyrene $r_1 =$

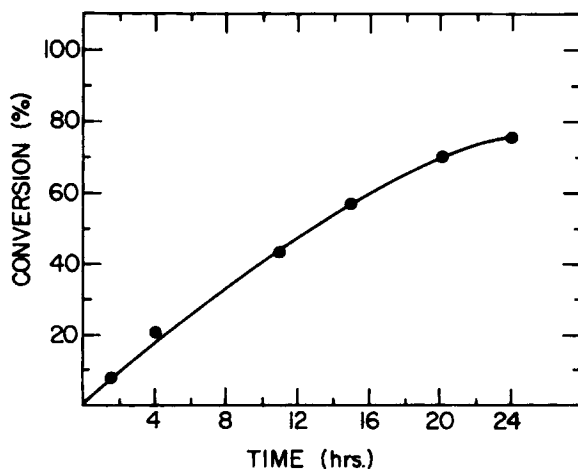


Fig. 1. Conversion as a function of time in a system containing 80 mol % butadiene and 20 mol % bromostyrene.

1.068 and $r_2 = 0.550$, respectively. Recently, Q and e values were recalculated by Greenley.¹⁵ These values yield $r_1 = 1.431$ and $r_2 = 0.677$. The ratio of butadiene to bromostyrene in the cotelomer can be calculated as a function of their ratio in the feed mixture¹⁴:

$$\frac{a}{b} = \frac{r_1 x + 1}{r_2(1/x) + 1}$$

where a/b is the ratio of the monomers in the copolymer, $x = A/B$ is the ratio of the unreacted monomers, and r_1 and r_2 are the reactivities of the monomers. Figure 2 shows the correlation between the content of bromostyrene in the cotelomer and in the feed. The experimental results agree well with the calculations using Greenley's values for Q and e .

At high bromine concentrations, a small amount of a solid crosslinked polymer is formed. This polymer, with about the same bromine content as the cotelomer, may be easily separated from the reaction mixture.

The molecular weight distribution of the cotelomers can be calculated from gel permeation chromatography using polystyrene equivalents as approximation. A factor of 4 has been assumed for the butadiene-bromostyrene cotelomers. Results in Table II show that low molecular weight cotelomers with a broad molecular weight distribution are obtained. The rather high concentration of hydrogen peroxide is needed to obtain this range of average molecular weights, but it is apparent that the higher the concentration of hydrogen peroxide, the broader the molecular weight distribution of the cotelomers. Varying the content of bromostyrene in the monomers apparently does not affect the molecular weight and its distribution. The broad range of molecular weights is therefore attributed to the free radical cotelomerization as indicated by French¹ and Idage et al.⁸ This range of molecular weights is in agreement with that of hydroxyl-terminated polybutadienes polymerized with hydrogen peroxide,⁵ which had molecular weights ranging from 1500 to 11000.

The fraction of the bromostyrene in the cotelomer, and the content of 1,4- and 1,2-butadiene were calculated from proton NMR spectroscopy. A representative spectrum of a cotelomer is shown in Figure 3. The absorption

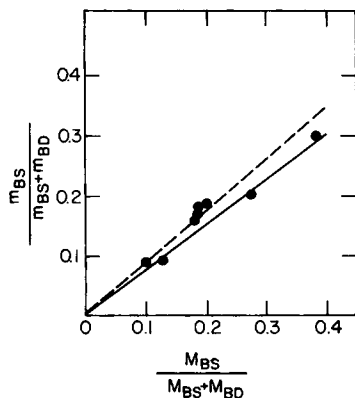


Fig. 2. Fraction of bromostyrene in the cotelomer as a function of bromostyrene in the feed: (—) according to Greenley,¹⁵; (---) according to Ham.¹⁴

TABLE II
Molecular Weights by Gel Permeation Chromatography

Expt no.	\bar{M}_n^a	\bar{M}_w^a	MWD ^b	\bar{M}_n^c	HP ^d	Bromine ^e
110	2920	7770	2.66	2750	24.4	10.9
112	2650	9440	3.56	3580	25.5	17.2
113	1890	8880	4.7	1680	31.9	18.0
114	1970	9060	4.60	2330	42.0	19.2
115	2160	9300	4.31	4240	44.6	19.2
116	1940	14870	7.66	2400	52.6	18.8
117	2060	4970	2.41	1100	35.6	11.3
120	1580	4970	3.15	1120	37.5	20.1
121	2440	7260	2.98	1700	38.1	25.9

^a Polystyrene equivalents, $Q = 4$.

^b Molecular weight distribution.

^c VPO by Hitachi-Perkin-Elmer 115 in chloroform at 30°C.

^d Hydrogen peroxide mol %.

^e Wt %.

at $\delta = 6.9-7.3$ (A) is due to aromatic hydrogens of the bromostyrene. Since the absorption of the solvent (CHCl_3) masks part of this absorption, only the high-field half of the aromatic absorption (at $\delta = 6.9$, A/2) was used for the calculations. The absorption at $\delta = 5.4$ (B) is due to tertiary hydrogens of double bond in both 1,2 and 1,4 structures and at $\delta = 5.0$ (C), due to methylene hydrogens of double bond of the 1,2 structure.^{4,16,17} The percentage of the 1,4 content is thus given by

$$\frac{B - 0.5C}{B + 0.5C} \times 100$$

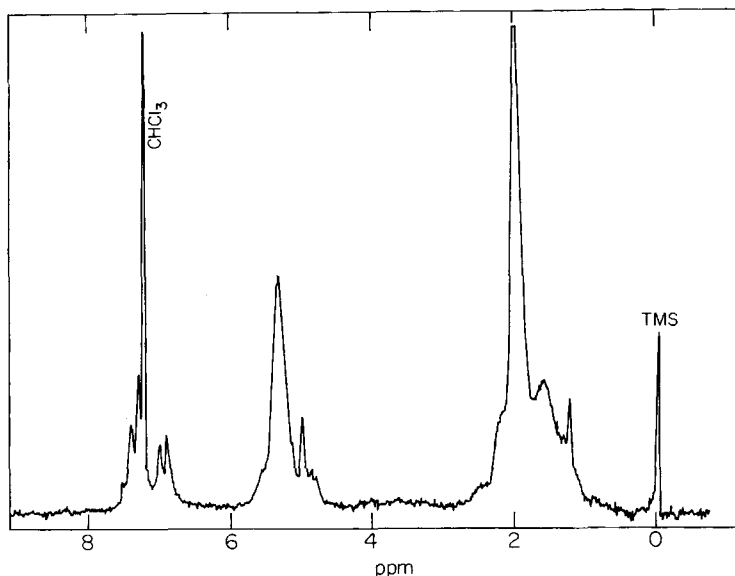


Fig. 3. NMR spectrum of a copolymer containing 80 mol % butadiene and 20 mol % bromostyrene.

The ratio of bromostyrene to butadiene is calculated by the ratio of the absorption at $\delta = 6.9$ to those of $\delta = 5.4$ and $\delta = 5.0$. The ratios between m , n , and p are calculated as follows: Let $m = 1$; then

$$p = \frac{2C}{A} \quad \text{and} \quad n = \frac{2B - 0.5pA}{A}$$

Table III presents the microstructure analysis of the various butadiene-bromostyrene cotelomers. It is apparent from the table that the content of the vinyl structure is similar to that found in polybutadienes of low molecular weights (experiment 122). Pinazzi⁵ also reported that the dominant structure in such polymers is the 1,4 structure which comprises about 80% of this polymer. The results also indicate that the higher the content of bromostyrene in the cotelomer, the higher the vinyl content of the butadiene part. This may be due to the increased polarity in the environment, induced by the bromostyrene component which enhances the 1,2 mechanism. The effect of the concentration of hydrogen peroxide is also evident: The higher the hydrogen peroxide concentration, the higher the vinyl content. However, the 1,4 structure is still the dominant one.

Analysis of infrared spectra according to Silas et al.¹⁸ may be misleading since the spectra are complex due to the overlap of absorptions by bromostyrene and those of butadiene and since extinction coefficients of the cotelomers are unknown. A qualitative analysis of subtracting the absorption of bromostyrene relative to its absorption by 1600 cm^{-1} shows that the *cis* structure comprises about 30% of the 1,4 structure and that the 1,2 structure is about 33% of the total butadiene content. This is somewhat higher than the content found by NMR analysis (about 25%) and is probably due to differences in extinction coefficients.

It was already noted that the cotelomers are viscous fluids. Their glass transition temperatures (T_g) are higher than that of polybutadiene (-76°C)

TABLE III
Microstructure of Butadiene Bromostyrene Cotelomers^a

Expt no.	BS ^b	BD 1,4 ^b	BD 1,2 ^b	Vinyl content ^c	Bromine ^d
110	10.3	69.2	20.5	22.9	12.2
112	15.6	65.7	18.7	22.2	16.8
113	18.6	61.5	19.9	24.4	19.1
114	19.3	61.3	19.4	24.0	19.6
115	20.0	57.1	22.9	28.6	20.0
116	19.4	56.8	23.8	29.5	19.6
117	10.1	66.7	23.2	25.8	12.1
118	13.6	62.6	23.8	27.5	15.2
120	27.8	50.0	22.2	30.7	19.0
121	34.8	42.9	22.3	34.2	28.1
122		76.2	23.8	23.8	

^a All data in this table are based on NMR microstructure analysis. BS = bromostyrene; BD = butadiene.

^b Mol %.

^c Mol % of total butadiene.

^d Wt %.

and lower than that of polybromostyrene (144°C).^{19,20} The fact that only one glass transition temperature was recorded for each cotelomer indicates that no blocks are formed, and one can assume a random distribution. The glass transition temperature can thus be correlated with the weight fraction of the bromostyrene, W_2 , according to

$$\frac{1}{T_g} = \frac{1}{W_1 + BW_2} \left[\frac{W_1}{T_{g1}} + \frac{BW_2}{T_{g2}} \right]$$

where W_1 is the weight fraction of butadiene and T_{g1} and T_{g2} are the glass transition temperatures of the pure low molecular weight polybutadiene and polybromostyrene respectively. For random copolymers $B = 1$, hence,

$$\frac{1}{T_g} - \frac{W_1}{T_{g1}} = \frac{W_2}{T_{g2}}$$

Figure 4 shows a plot of $1/T_g - W_1/T_{g1}$ as a function of W_2 . The dashed line represents high molecular weight random copolymers. It is apparent from the figure that glass transition temperatures of low molecular weight cotelomers fit this correlation. However, these T_g values are much lower from those predicted for high molecular weight copolymers.

Inspecting Figure 4, T_g for low molecular weight polybromostyrene is predicted to be about -7°C . We found that bromostyrene polymerized in the presence of a chain transfer agent yielding a low molecular weight oligomer with $M_n = 730$ had a $T_g = -5^\circ\text{C}$. T_g values of copolymers synthesized in the bulk (experiments 125, 126) are in agreement with the correlation for high molecular weight copolymers.

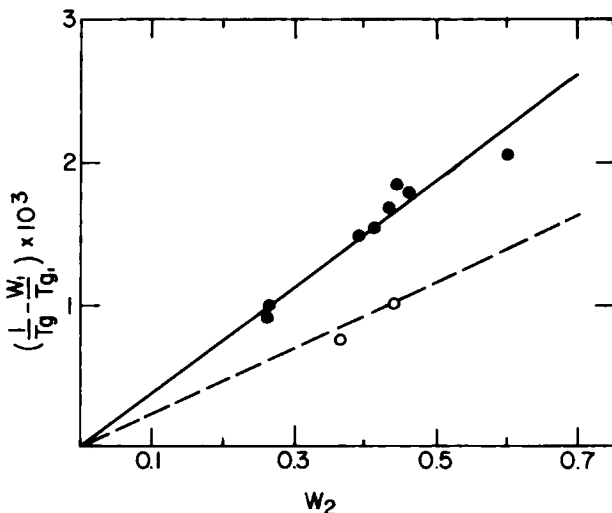


Fig. 4. $1/T_g - W_1/T_{g1}$ as a function of bromostyrene fraction: (—) low molecular weight; (---) high molecular weight copolymer.

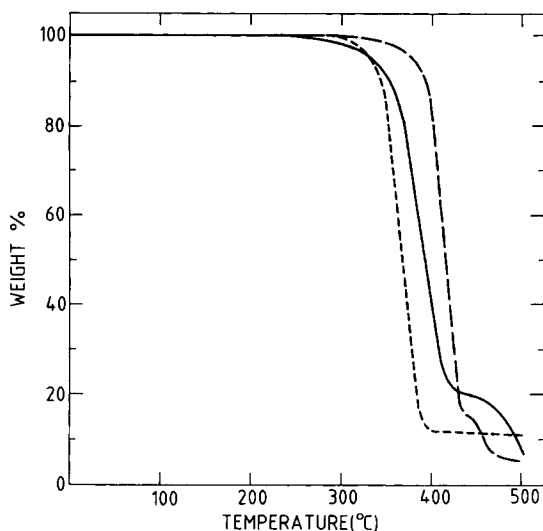


Fig. 5. Thermogravimetric analysis of cotelomers in still air. Rate: 8°C/min. (---) hydroxyl-terminated butadiene-bromostyrene; (—) polybromostyrene; (· · ·) polybutadiene.

The cotelomers exhibit high stability to heat. No heat event has been observed in the DSC experiments up to 200°C and their thermogravimetric analysis shows no weight loss up to about 250°C and a major degradation which occurs only at about 375°C. A TGA of a cotelomer containing 26% bromine (w/w) is shown in Figure 5. The thermograms of polybutadiene and bromostyrene, which were polymerized under the same conditions, are also shown. The degradation of polybromostyrene and polybutadiene are similar to those reported.²⁰⁻²² It is interesting to note that the cotelomer degrades at a higher temperature than polybromostyrene and its char residue remains high up to about 460°C (about 19%).

These cotelomers of butadiene and bromostyrene may be used as flame-retardant reactive additives in polymeric systems. Their flame retardancy and compatibility with polymeric systems such as urethane and epoxy resins are being studied.

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