Intersequence Cyclization in Brominated Methyl Methacrylate–Butadiene Copolymers

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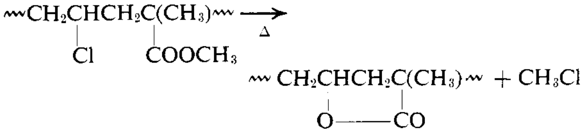
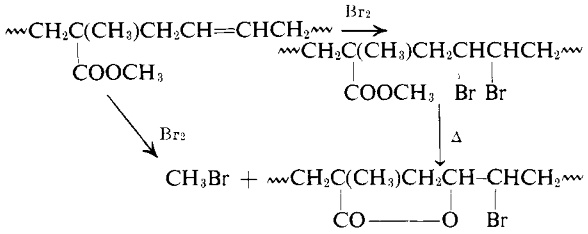
ABSTRACT: Bromination of butadiene–methyl methacrylate copolymers yields polymers containing lactone units, **1**, brominated butadiene units, and methyl methacrylate units. The lactone units are believed to result from an intersequence cyclization reaction involving methyl methacrylate units and bromonium ions derived from butadiene units adjacent to them. The fractions of methyl methacrylate units that were cyclized in this way were in good accord with statistical predictions, assuming that the reaction occurs randomly between adjacent pairs of butadiene and methyl methacrylate units. The reaction reported in this paper can, therefore, be used to obtain information about the distribution of monomer sequences in copolymers and terpolymers.

The extent of cyclization that occurs between neighboring monomer units in copolymers can provide information about the arrangement of monomer units in their chains. Previously we reported[1] that the extents of cyclization obtained during the thermal decomposition of vinyl halide–methyl methacrylate copolymers[2] were in good accord with those expected on the basis of statistical treatments of copolymer cyclization.[3–9] In addition, the extents of cyclization that occur between vinyl chloride and methyl methacrylate units in styrene–methyl methacrylate–vinyl chloride terpolymers[10] were found to agree with predictions based on a statistical treatment of terpolymer cyclization reactions.[11]



$$\sim\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_2\underset{\text{COOCH}_3}{\text{C}(\text{CH}_3)}\sim \xrightarrow{\Delta} \sim\text{CH}_2\underset{\text{O}}{\text{CH}}\text{CH}_2\underset{\text{CO}}{\text{C}(\text{CH}_3)}\sim + \text{CH}_3\text{Cl}$$

In an effort to extend the analytical utility of this cyclization process, a series of methyl methacrylate–butadiene copolymers was prepared and the copolymers were allowed to react with bromine. The brominated polymers were expected to undergo intersequence cyclization in the same manner as methyl methacrylate–vinyl halide copolymers.



$$\sim\text{CH}_2\underset{\text{COOCH}_3}{\text{C}(\text{CH}_3)}\text{CH}_2\text{CH}{=}\text{CHCH}_2\sim \xrightarrow{\text{Br}_2} \sim\text{CH}_2\underset{\text{COOCH}_3}{\text{C}(\text{CH}_3)}\text{CH}_2\underset{\text{Br}}{\text{CH}}\underset{\text{Br}}{\text{CH}}\text{CH}_2\sim$$

$$\xrightarrow{\Delta}\ \text{(or directly} \xrightarrow{\text{Br}_2}\text{)}\ \text{CH}_3\text{Br} + \sim\text{CH}_2\underset{\text{CO}}{\text{C}(\text{CH}_3)}\text{CH}_2\underset{\text{O}}{\text{CH}}\underset{\text{Br}}{\text{CH}}\text{CH}_2\sim$$

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We were surprised to note that *cyclization occurs during the bromination step* and that the extent of cyclization obtained is in good accord with that expected if cyclization is assumed to occur randomly between adjacent pairs of butadiene and methyl methacrylate units.

Experimental Section

Preparation of Copolymers. Butadiene–methyl methacrylate copolymers were prepared in bulk at 55° from freshly distilled monomer mixtures which contained 0.4 wt % azobisisobutyronitrile as initiator. Conversions were kept below 7.5%.

A bulk polymerization system was used for these preparations, primarily because it gave polymers of convenient molecular weight. Polymers prepared in emulsion systems were of very high molecular weight and it was difficult to prepare solutions of such polymers which were suitable for nmr studies.

The polymers were isolated by pouring the polymerization mixtures into a large excess of methanol. The polymers were reprecipitated several times from carbon tetrachloride solution by addition of the solutions to methanol. The samples were obtained as gums or white powders depending on their methyl methacrylate contents. The samples were dried for 48 hr *in vacuo* in the absence of light and were then stored in amber bottles *in vacuo* in the absence of light. Detailed information concerning the preparation of these polymers is given in Table I.

Bromination Studies. The copolymers were brominated by adding a dilute solution of bromine in chloroform to dilute (0.1 wt %) chloroform solutions of the copolymers. Reactions were carried out in the dark, at 0°, in a nitrogen atmosphere for 2 hr. Dilute solutions were used to prevent cross-linking and hydroquinone was added to the reaction mixtures to suppress free-radical formation. Under such reaction conditions, Pinazzi, *et al.*,[12] achieved 94% bromination of *cis*-1,4-polybutadiene. The reaction mixtures were then concentrated to easily handled amounts by use of a rotary solvent evaporator and the solutions were poured into methanol to precipitate the polymers. After reprecipitation from chloroform into methanol, the polymers were dried and stored *in vacuo* in the absence of light. The brominated polymers were all white solids and were completely soluble in chlorinated solvents. The brominated

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(3) P. J. Flory, *J. Amer. Chem. Soc.*, **61**, 1518 (1939).

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(7) F. T. Wall, *ibid.*, **64**, 269 (1942).

(8) I. Sakurada and I. Kawashima, *Chem. High Polym.* (Japan), **8**, 142 (1951); *Chem. Abstr.*, **47**, 344 (1953).

(9) T. Alfrey, Jr., C. Lewis, and B. Magel, *J. Amer. Chem. Soc.*, **71**, 3793 (1949).

(10) N. W. Johnston and H. J. Harwood, *Macromolecules*, **2**, 221 (1969).

(11) H. J. Harwood, N. W. Johnston, and H. Piotrowski, *J. Polym. Sci., Part C*, **25**, 23 (1968).

(12) C. Pinazzi, H. Gueniffey, and J. Buossas, *C. R. Acad. Sci., Paris*, **258**, 4982 (1964).

TABLE I

PREPARATION OF METHYL METHACRYLATE–BUTADIENE COPOLYMERS

Sample	MMA in monomer feed, mol %	Polymerization time, hr	Conversion, wt %	Anal. of copolymer, % C	Anal. of copolymer, % H	MMA in copolymer, mol % *a*	MMA in copolymer, mol % *b*
H-1	93	3	4.1	65.4	8.35	75	70
H-2	85	4	2.2	67.6	8.96	62	60
H-3	73	5	2.4	68.7	9.06	55	55
H-4	50	12	4.2	72.3	9.31	41	42
H-5	33	31	7.4	76.8	9.85	30	28

[a] Based on nmr analysis. [b] Based on elemental analysis.

TABLE II

ANALYSIS OF BROMINATED COPOLYMERS

Sample	% M	f_c (MMA)[a]	Calcd,[a] % C	H	Br	Found, % C	H	Br
H-1B	72.5	0.28	48.5	6.11	24.6	49.9	6.56	19.2
H-2B	61.0	0.50	44.7	5.46	32.9	43.9	5.97	27.2
H-3B	55.0	0.70	43.7	5.19	35.6	43.6	5.66	34.3
H-4B	41.5	0.88	36.8	4.35	48.7	36.3	4.59	46.6
H-5B	30.0	0.95	31.6	3.77	58.3	34.1	4.17	54.0

[a] Theoretical values based on predicted extent of cyclization.

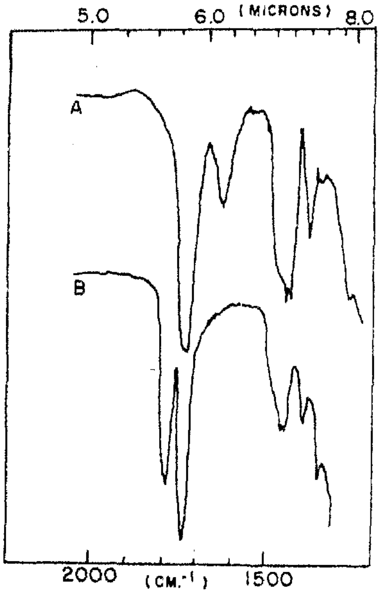

Figure 1. Infrared spectra of a methyl methacrylate–butadiene copolymer (A) and the same copolymer after bromination (B).

polymers were analyzed for carbon and bromine.[13] The results obtained are presented in Table II.

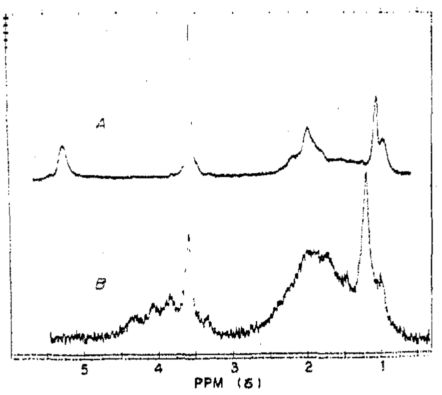

Figure 2. Nuclear magnetic resonance spectra of a 55/45 methyl methacrylate–butadiene copolymer (A) and the same copolymer after bromination (B).

Spectroscopic Studies. The infrared spectra of the parent and brominated copolymers, dispersed in Fluorolube mulls, were recorded by a Perkin-Elmer Model 21 recording infrared spectrophotometer. Figure 1 compares the spectra of H-1 (A) and brominated H-1 (B). Olefinic absorption at 1650 cm^{-1}, present in the spectrum of the parent copolymer, is not evident in the spectrum of the brominated copolymer. The spectrum of the brominated polymer contains a strong band at 1770 cm^{-1} which is not present in the spectrum of the parent polymer. This band is attributed to the stretching of carbonyl groups in γ-lactone structures[14] in the brominated polymers.

Nuclear magnetic resonance spectra of the butadiene–methyl methacrylate copolymers in CCl_4 solution were recorded at room temperature by a Varian HA-100 nmr spectrometer. Figure 2A shows the spectrum obtained for copolymer H-3. The fraction (F) of proton resonance assignable to methoxy proton resonance (3.6 ppm) in each spectrum provided a measure of copolymer composition, through use of eq 1, where *P* represents the molar percentage

$$P = 600F/(3 - 2F) \quad (1)$$

of methyl methacrylate in the copolymer. Table I lists the compositions determined for the various copolymers studied.

Nuclear magnetic resonance spectra of the brominated copolymers in deuteriochloroform were also recorded at room temperature using the 100-MHz spectrometer. The spectrum of brominated H-3 is shown in Figure 2B. No

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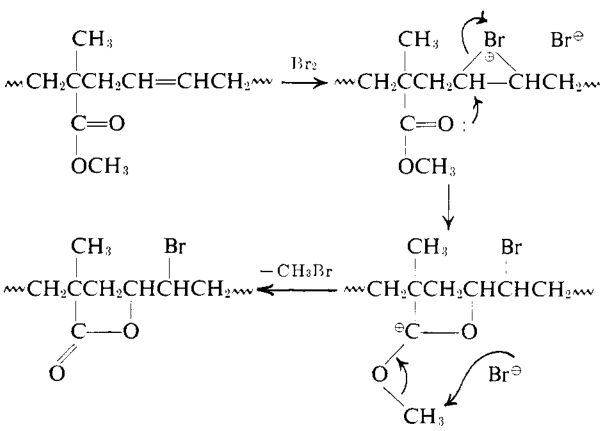
(13) Samples H-1B, H-2B, and H-3B were analyzed several months after preparation, whereas samples H-4B and H-5B were analyzed within 1 week after preparation. The samples were found to lose bromine, probably as HBr or CH_3Br, on storage. This may explain the slightly high carbon and low bromine contents of the brominated copolymers. It is also possible that bromination of butadiene units was incomplete.[12] This would have an influence on our nmr analysis only when diene units next to MMA units were not brominated. Apparently this did not occur to a significant extent.

(14) K. Nakanishi, "Infrared Absorption Spectroscopy," Nankodo Co., Ltd., Tokyo, Japan, 1962, p 44.

resonance due to olefinic protons (5.3 ppm) is present in this spectrum and resonance due to methoxy protons is less intense in the brominated sample than in the parent material. Furthermore, resonances in the brominated polymer spectrum are much broader than those in the spectrum of the parent copolymer, suggesting that the brominated polymer backbone is more rigid than that of the original copolymer.

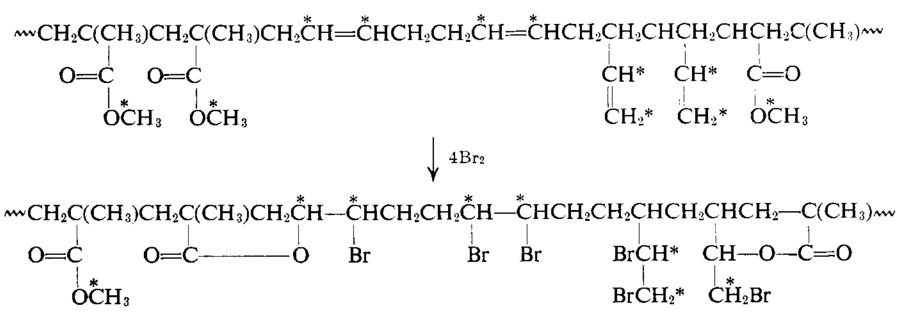
Results and Discussion

The infrared and nmr spectra of the brominated copolymers indicate that reaction of the copolymers with bromine was complete and that the resulting polymers contained γ-lactone units. Since the conditions for the bromination reaction were less severe than those required for the thermal cyclization of methyl methacrylate–vinyl bromide copolymers,[1] it does not seem reasonable to assume that the γ-lactone units resulted from a reaction between brominated diene and methyl methacrylate units. It seems more reasonable to believe that lactone formation occurs *during the bromination process*, according to the mechanism outlined.



A similar mechanism can be written to explain the formation of δ-lactone units from brominated 1,2-butadienyl units. The cyclization reaction encountered in this study is analogous to that reported by Tarbell and Bartlett to occur during the bromination of dimethylmaleic acid.[15] Boutsicarus and Hayes have recently reported a related cyclization process involving methacrylic acid–butadiene copolymers.[16]

SCHEME I



The extents of cyclization that occurred during bromination of the copolymers were calculated from the nmr spectra of the parent and brominated copolymers. It was assumed that only the reactions shown in Scheme I occurred during bromination. Those protons in Scheme I structures that would have chemical shifts (relative to TMS) greater than 3.0 ppm are marked by asterisks. It can be readily seen that all of the protons in the parent copolymers that have chemical shifts greater than 3.0 ppm also have chemical shifts greater than 3.0 ppm in the brominated copolymers. Similarly, all of the protons in the parent copolymers that have chemical shifts less than 3.0 ppm, also have chemical shifts less than 3.0 ppm in the brominated copolymers. If A and A' are defined to be the resonance areas observed for the parent and brominated copolymers, respectively, at low fields ($\delta > 3.0$ ppm), and if B and B' are defined to be the resonance areas observed for the parent and brominated copolymers at high fields ($\delta < 3.0$ ppm), then eq 2 and 3 can be written, where % M, % 1,4-B and % 1,2-B represent the molar percentages of methyl methacrylate, 1,4-butadiene, and 1,2-butadiene units, respectively, in the original copolymer and where f_c represents the fraction of methyl methacrylate units cyclized during the bromination reaction. Taking the 1,2-butadiene content of each copolymer to be 10% of the total butadiene content (% B), eq 2 and 3 can be simplified and combined to obtain eq 4, which can be used to calculate the extent of cyclization that occurs during bromination.

$$\frac{A}{B} = \frac{3\%\,M + 2\,(\%\,1{,}4\text{-B}) + 3(\%\,1{,}2\text{-B})}{5\%\,\mathrm{M} + 4(\%\,1{,}4\text{-B}) + 3(\%\,1{,}2\text{-B})} \tag{2}$$

$$\frac{A'}{B'} = \frac{3(1 - f_c)\%\,\mathrm{M} + 2(\%\,1{,}4\text{-B}) + 3(\%\,1{,}2\text{-B})}{5\%\,\mathrm{M} + 4(\%\,1{,}4\text{-B}) + 3(\%\,1{,}2\text{-B})} \tag{3}$$

$$f_c = (1 - A'B/B'A)(1 + 0.7\%\,\mathrm{B}/\%\,\mathrm{M}) \tag{4}$$

Table III lists the relative resonance areas determined from the spectra of the original and brominated copolymers, the methyl methacrylate contents of the original copolymers and the fractions of methyl methacrylate units that cyclized during bromination. Also included in Table III are theoretical values for the extents of cyclization expected, provided that methyl methacrylate and butadiene units cyclized at random, during bromination. The theoretical values were calculated using an IBM 1620 computer programmed to calculate f_c values for high-conversion copolymers.[11] The calculations are based on monomer reactivity ratios of 0.73 and 0.18 for butadiene and methyl methacrylate,

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(15) D. S. Tarbell and P. D. Bartlett, *J. Amer. Chem. Soc.* **59**, 407 (1937).

(16) S. P. Boutsicaris and R. A. Hayes, paper presented at the 1st Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 1968. See also German Patent 1,804,936 (June 19, 1969); *Chem. Abstr.*, **71**, 81901 (1969).

TABLE III
RESULTS OF INTERSEQUENCE CYCLIZATION IN METHYL METHACRYLATE–BUTADIENE COPOLYMERS

Sample	% M[a]	Relative resonance areas,[b] %				f_c (MMA)	
		A	B	A′	B′	Exptl	Theor[c]
H-1	72.5	36.1	63.9	29.3	70.7	0.33	0.28
H-2	61.0	35.5	64.5	26.4	73.6	0.50	0.50
H-3	55.0	34.6	65.4	23.2	76.8	0.66	0.70
H-4	41.5	35.1	64.9	23.4	76.6	0.86	0.88
H-5	30.0	33.3	66.7	24.9	75.1	0.91	0.95

[a] Average of compositions obtained through elemental and nmr analysis. [b] See text for definitions of *A*, *A′*, *B*, *B′*. [c] Based on monomer reactivity ratios of 0.73 and 0.18 for butadiene and methyl methacrylate, respectively.

respectively, these values being determined by the Fineman–Ross[17] and Mayo–Lewis[18] procedures from the compositions of the copolymers and the polymerization mixtures. These values are to be compared with corresponding values of 0.53 ± 0.05 and 0.06 ± 0.03 determined by Walling and Davison[19] for the copolymerization of butadiene with methyl methacrylate at 5°.

Experimentally determined f_c values (eq 3) are in good agreement with theoretical values, indicating that the spontaneous lactonization which occurs during the bromination of butadiene–methyl methacrylate copolymers obeys the statistical treatment of random intersequence cyclization reactions. It seems likely that the brominative cyclization reaction described in this paper will prove useful for characterizing the structures of other copolymers and terpolymers containing diene and acrylate or methacrylate units.

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Kinetics of Propagation of Living Poly-2-vinylpyridine

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ABSTRACT: Kinetics of homopropagation of living poly-2-vinylpyridine has been thoroughly investigated in THF and, less extensively, in other ethereal solvents. In addition we studied the conductance of the homopolymer solutions and of solutions of analogous polymers built from styrene units but terminated by single pyridine units. The results allowed us to determine the rates and the activation energies of the free $\sim$(2-VP)$^-$ ions and of $\sim$(2-VP)$^-$,Na$^+$ ion pairs, as well as the dissociation constants and heats of dissociation of the living polymers. Comparison of the systems $\sim$(2-VP)$^-$,Na$^+$ and sodium living polystyrene led to interesting conclusions about intra- and intermolecular solvation of ion pairs. In the latter case, solvent may separate an ion pair, thus increasing its dipole moment. The larger dipole moment makes the pairs more reactive and the separation facilitates its dissociation. The intramolecular solvation by partially immobile groups also increases its dipole moment by "stretching" the pair. This enhances its reactivity, but because the cation is bound to the solvating groups of the polymer its dissociation is hindered. The latter effect reduces somewhat the reactivity of the pair although such a retarding factor is less significant than the enhancing one arising from the increase of the dipole.

Kinetics of homopolymerization of 2-vinylpyridine was studied by Lee, *et al.*[1] Their work was limited to sodium salts in THF at 25°, and no attempt was made during that investigation to differentiate between free ions and ion pairs. We repeated now this study using a more versatile technique described elsewhere[2] and determined the propagation rate constants for the free ions and ion pairs over a wide temperature range (−60 to +25°). Moreover, a few kinetic experiments were performed in THP and dioxane in order to evaluate the effect of solvent on the rate of propagation. Also, in some preliminary runs Cs$^+$ salts were used instead of Na$^+$.

Experimental Section

Commercial 2-vinylpyridine was distilled at reduced pressure on a spinning band column and its purity ascertained by vpc analysis. The distilled monomer was dried by digesting it with CaH$_2$, the product distilled on a high-vacuum line into a bulb containing fresh CaH$_2$, and finally redistilled into ampoules equipped with break-seals in

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(1) C. L. Lee, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, **59**, 1192 (1963).

(2) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 796 (1967).