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Intersequence Cyclization in Methyl Methacrylate–Vinyl Chloride–Styrene Terpolymers

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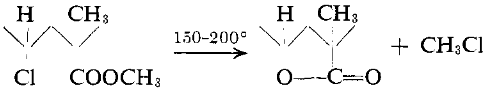
ABSTRACT: Quantitative studies on the extent of intersequence cyclization that occurs between vinyl chloride and methyl methacrylate units in methyl methacrylate–vinyl chloride–styrene terpolymers are described. The extents of cyclization obtained in these studies are in very good agreement with those calculated using statistical relationships developed previously. A method for determining one pair of monomer reactivity ratios from terpolymerization data and two known pairs of monomer reactivity ratios is described. Reactivity ratios determined for the styrene–vinyl chloride system by this approach are in good agreement with values obtained by the conventional copolymerization approach. The results obtained in this study provide evidence for the validity of using binary reactivity ratios in terpolymerization calculations.

The extent of cyclization that occurs between neighboring units in copolymers can provide information about the arrangement of monomer units in their chains. In a previous paper,[1] we reported that the yields of methyl halide obtained during the thermal decomposition[2] of vinyl halide–methyl methacrylate copolymers were in good accord with those expected,[3-9] assuming that the reaction occurred at random between adjacent pairs of vinyl halide–methyl methacrylate units. In addition, we developed statistical relationships[1,10] for predicting the extent of intersequence cyclization to be expected when *terpolymers* containing cyclizable substituents are cyclized.



In the present study, the extents of cyclization that occur between vinyl chloride and methyl methacrylate units in styrene–vinyl chloride–methyl methacrylate terpolymers were determined. The results obtained are in good agreement with theoretical predictions. In addition, a procedure for evaluating monomer reactivity ratios for one pair of monomers, given terpolymerization data and monomer reactivity ratios for the other monomer pairs, is described. Monomer reactivity ratios evaluated for the styrene–vinyl chloride system by this procedure are in good accord with those evaluated from copolymerization data.

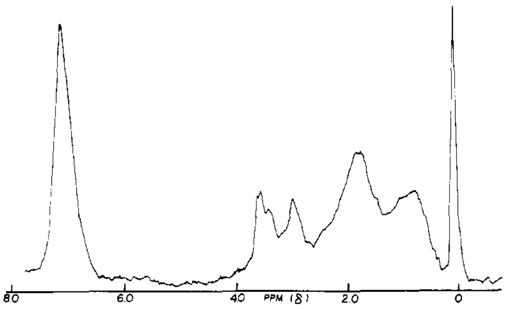


Figure 1. The nmr spectrum of a vinyl chloride–styrene–methyl methacrylate terpolymer (D-2).

Experimental Section

Preparation and Analysis of Terpolymers. Vinyl chloride–methyl methacrylate–styrene terpolymers were prepared in bulk at 68° from freshly distilled monomers in tumbled 4-oz bottles using 0.2 wt % azobisisobutyronitrile as an initiator. Conversions were kept below 4%. 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. Obtained as white powders, they were dried for 48 hr *in vacuo* in the absence of light, and were stored in amber bottles under nitrogen at 5°.

The compositions of the terpolymers were calculated from their chlorine contents and from the intensities of the aromatic proton magnetic resonance observed for the polymers in CCl_4 solution. Proton magnetic resonance spectra were obtained using an A-60 Varian 60-MHz nmr spectrometer at room temperature. Figure 1, the nmr spectrum of ter-

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Table I

Preparation of Methyl Methacrylate–Styrene–Vinyl Chloride Terpolymers

Sample	Monomer feed, mol %		Conv.,	Analysis		Polymer compn, mol %	
no.	VCl	MMA	wt %	% Cl	% aromatic[a]	VCl	MMA
D1	49.2	21.0	2.87	1.49	35.8	4	40
D2	82.6	8.7	1.07	6.46	29.5	17	40
D3	63.0	27.0	3.02	2.87	19.1	8	63
D4	56.2	24.1	2.78	2.12	27.9	6	51
D5	45.0	45.0	3.66	1.76	14.7	5	72
D6	58.3	35.7	3.42	2.67	12.8	7	73
D7	89.5	5.8	1.35	11.86	27.7	28	38

[a] Aromatic proton resonance area relative to that of all proton resonance observed.

Table II

Results of Intersequence Cyclizations in Low Conversion Methyl Methacrylate–Vinyl Chloride–Styrene Terpolymers

Sample	Terpolymer composn, mol %		F_c(MMA)	
no.	VCl	MMA	Exptl[a]	Calcd[b]
D1	4	40	0.070 ± 0.002	0.069
D2	17	40	0.269 ± 0.001	0.286
D3	8	63	0.120 ± 0.002	0.127
D4	6	51	0.092 ± 0.001	0.093
D5	5	72	0.066 ± 0.003	0.066
D6	7	73	0.105 ± 0.003	0.111
D7	28	38	0.448 ± 0.010	0.443

[a] Calculated from sample weight loss when sample was heated *in vacuo*. Values given are averages and average deviations obtained in two to four determinations. [b] Monomer reactivity ratio values used: VCl/MMA 0.044/11.20; MMA/styrene 0.52/0.47; VCl/styrene 0.04/17.88.

polymer D-2, shows an example of the spectra obtained. The resonance due to aromatic protons occurs at 6.7–7.0 ppm. If the aromatic proton resonance area is determined, relative to that of all proton resonance obtained, the percentage of aromatic proton resonance observed can be related to the terpolymer composition according to eq 1, where SWP and VWP are the weight percentages of styrene and vinyl chloride in the terpolymer. Since the latter quantity is easily calculated from the chlorine content of the polymer, eq 1 can be used to determine the styrene content of a terpolymer when its chlorine content and aromatic proton resonance area are known. Table I summarizes the results obtained in the preparations of the terpolymers and in their subsequent analyses.

$$\%\ \text{aromatic proton resonance} = \frac{500\left(\dfrac{\text{SWP}}{104.4}\right)}{8\left(\dfrac{\text{SWP}}{104.4}\right) + 8\left(\dfrac{100 - \text{SWP} - \text{VWP}}{100.1}\right) + 3\left(\dfrac{\text{VWP}}{62.5}\right)} \qquad (1)$$

Cyclization Studies. Samples (5- to 10-mg) of freshly dried terpolymers were introduced into previously tared 7 × 0.5 cm glass tubes and were weighed to the nearest 0.01 mg. Several such samples were introduced into a 17 × 1.6 cm glass tube which was then evacuated to 1 mm, sealed, and heated at 200° for 2 hr in a muffle furnace. During this time, the samples fused and formed thin films on the inner surfaces of the sample tubes. Such films lost methyl chloride rapidly, and there was little danger that any gases remained trapped in the samples. Several tests indicated that the heat treatment employed was sufficient to cause complete reaction, but not so vigorous that dehydrohalogenation occurred. Thus the infrared spectra of the gases formed during these reactions were identical with the infrared spectrum of methyl chloride; no hydrogen chloride was detected.

The sample tubes were then removed from the reactor and were stored briefly in a desiccator. They were then reweighed. The yields of methyl chloride formed in these reactions, expressed as the fractions of methyl methacrylate units cyclized, F_c(MMA), were calculated with the aid of eq 2 where W and W' are sample weights before and after cyclization, respectively, and where P is the weight percentage of methyl methacrylate in the sample. The results obtained in these studies are presented in Table II.

$$F_c(\text{MMA}) = \frac{(W - W')/50.5}{P/100.1} \qquad (2)$$

Results and Discussion

Prediction of Extent of Cyclization. A detailed discussion of the theoretical considerations involved in predicting by computer techniques the extent of intersequence cyclization to be expected for terpolymers was presented in our previous papers.[1,10] A simple approximate method for predicting the extent of cyclization to be expected from certain terpolymer cyclization reactions has also been developed.

This approximate method is very suitable for treating the cyclization of vinyl chloride (A)–methyl methacrylate (B)–styrene (C) terpolymers. The method is based on the assumption that A–B units in terpolymers may tend to be associated as pairs, or perhaps as ABA or BAB sequences, but not as larger sequences of alternating units. This will be particularly true when either the A or B monomer is relatively unreactive and when the C monomer is a very reactive monomer, such as styrene. In such a situation it is possible to predict the extent of cyclization from the propagation probabilities P_{AB} and P_{BA}. The probability P_{AB} can be evaluated as shown in eq 3 and the probability P_{BA} can be calculated *via* eq 4, where A_f, B_f, and C_f are molar monomer feed compositions and where r_{BA} and r_{BC} are binary monomer reactivity ratios.

$$P_{AB} = 1/[r_{AB}A_f/B_f + 1 + r_{AB}C_f/r_{AC}B_f] \qquad (3)$$

$$P_{BA} = 1/[1 + r_{BA}B_f/A_f + r_{BA}C_f/r_{BC}A_f] \qquad (4)$$

For the simplest case, where A and B units can cyclize with one another and are associated in pairs, the number of cyclizable units per 100 units of terpolymer is given by eq 5, where % A and % B are molar percentages of monomer units in the terpolymer.

$$\text{no. of cyclizable units per 100 units of terpolymer} = \%\,\mathrm{A}(P_{\mathrm{AB}}) + \%\,\mathrm{B}(P_{\mathrm{BA}}) \qquad (5)$$

However, if appreciable ABA and BAB triads are present in the terpolymer, each such triad will contain an unreacted AB or BA linkage after random cyclization. This is because the center unit of the triad may cyclize with the unit on the left or on the right but not with both, thus leaving an unreacted linkage after cyclization. The simple case, eq 5, must therefore be corrected by subtracting the number of these triads as shown in eq 6.

$$\text{no. of cyclizable units per 100 units of terpolymer} = \%\,\mathrm{A}(P_{\mathrm{AB}}) - \%\,\mathrm{A}(P_{\mathrm{AB}}P_{\mathrm{BA}}) + \%\,\mathrm{B}(P_{\mathrm{BA}}) - \%\,\mathrm{B}(P_{\mathrm{BA}}P_{\mathrm{AB}}) \qquad (6)$$

The fraction of cyclizable B units, $F_c(\mathrm{B})$, may then be obtained by dividing eq 6 by the molar percentage of B units in the polymer and by rearranging to obtain eq 7. Calculations based on eq 7 agree very well with those obtained using the computer approach previously discussed.[1,10]

$$F_c(\mathrm{B}) = P_{\mathrm{BA}}(1 - P_{\mathrm{AB}}) + P_{\mathrm{AB}}(1 - P_{\mathrm{BA}})\%\,\mathrm{A}/\%\,\mathrm{B} \qquad (7)$$

Monomer Reactivity Ratios. Reliable values of monomer reactivity ratios are required to predict the extent of intersequence cyclization to be expected in terpolymers. Reactivity ratios for the styrene–methyl methacrylate[11–14] copolymerization system seem to be well established, and vinyl chloride–methyl methacrylate reactivity ratios were evaluated in previous work,[15,16] but reactivity ratios reported for the styrene–vinyl chloride system are not at all consistent.[17–19] It was, therefore, important to redetermine these values in this work. Rather than take the conventional approach for such determinations, an effort was made to derive reactivity ratios for this system from the data presented in Table I. This approach was desirable not only because of convenience, but also because it is possible that more reliable reactivity ratios can sometimes be obtained from terpolymerization data than can be obtained from copolymerization results.[20] The general approach developed in this study for the evaluation of monomer reactivity ratios from terpolymerization results is based on eq 8, which relates the proportion of monomer units A, B, and C in terpolymer formed instantaneously from a given monomer mixture[21] (A_f, B_f, C_f). When this equation is used for the evaluation of monomer reactivity ratios from terpolymerization data, A, B, C, A_f, B_f, and C_f will generally be known. If r_{AB}, r_{BA}, r_{BC}, and r_{CB} are also known, then the equation involves only r_{AC} and r_{CA} as parameters and it can be used for their evaluation.

$$
\begin{aligned}
&A{:}B{:}C{::}\\
&A_f\left[\frac{A_f}{r_{\mathrm{CA}}r_{\mathrm{BA}}} + \frac{B_f}{r_{\mathrm{BA}}r_{\mathrm{CB}}} + \frac{C_f}{r_{\mathrm{CA}}r_{\mathrm{BC}}}\right]\left[A_f + \frac{B_f}{r_{\mathrm{AB}}} + \frac{C_f}{r_{\mathrm{AB}}}\right]:\\
&B_f\left[\frac{A_f}{r_{\mathrm{AB}}r_{\mathrm{CA}}} + \frac{B_f}{r_{\mathrm{AB}}r_{\mathrm{CB}}} + \frac{C_f}{r_{\mathrm{CB}}r_{\mathrm{AC}}}\right]\left[B_f + \frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right]:\\
&C_f\left[\frac{A_f}{r_{\mathrm{AC}}r_{\mathrm{BA}}} + \frac{B_f}{r_{\mathrm{BC}}r_{\mathrm{AB}}} + \frac{C_f}{r_{\mathrm{AC}}r_{\mathrm{BC}}}\right]\left[C_f + \frac{A_f}{r_{\mathrm{CA}}} + \frac{B_f}{r_{\mathrm{CB}}}\right] \qquad (8)
\end{aligned}
$$

If the upper proportion shown in eq 8 is rearranged, it can be set in the form of eq 9, where W, X, Y, and Z are complicated functions of A, B, A_f, B_f, C_f, r_{AB}, r_{BA}, r_{BC}, and r_{CB}. If values of the above quantities are known, then a set of W, X, Y, and Z values can be calculated for each terpolymerization experiment as shown in eq 9–13.

$$\frac{W}{r_{\mathrm{CA}}} + \frac{X}{r_{\mathrm{AC}}} + \frac{Y}{r_{\mathrm{AC}}r_{\mathrm{CA}}} + Z = 0 \qquad (9)$$

$$W = \frac{A_f^{\,2}}{B_f}\left[\frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right] + \frac{A_f}{r_{\mathrm{AB}}}\left[\frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right] - \frac{AA_f}{Br_{\mathrm{AB}}}\left[B_f + \frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right] \qquad (10)$$

$$X = \frac{C_fA_f}{r_{\mathrm{BA}}r_{\mathrm{CB}}} - \frac{AC_f}{Br_{\mathrm{CB}}}\left[B_f + \frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right] \qquad (11)$$

$$Y = \frac{C_fA_f}{B_f}\left[\frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right] \qquad (12)$$

$$Z = \frac{A_f^{\,2}}{r_{\mathrm{BA}}r_{\mathrm{CB}}} + \frac{A_fB_f}{r_{\mathrm{AB}}r_{\mathrm{BA}}r_{\mathrm{CB}}} + \frac{B_fA}{Br_{\mathrm{AB}}r_{\mathrm{CB}}}\left[B_f + \frac{A_f}{r_{\mathrm{BA}}} + \frac{C_f}{r_{\mathrm{BC}}}\right] \qquad (13)$$

If two equations having the form of eq 9 are combined, the second set of values being designated W', X', Y', and Z', then it is possible to derive eq 14.

$$\left[\frac{YZ'/Y' - Z}{X - YX'/Y'}\right] = \frac{1}{r_{\mathrm{CA}}}\left[\frac{W - YW'/Y'}{X - YX'/Y'}\right] + \frac{1}{r_{\mathrm{AC}}} \qquad (14)$$

A plot of the left-hand expression in eq 14 *vs.* the expression in brackets on the right side should, therefore, yield a straight line having $1/r_{\mathrm{CA}}$ as its slope and $1/r_{\mathrm{AC}}$ as its intercept. Equation 14 can thus be the basis of a graphical procedure for determining monomer reactivity ratios from terpolymerization data. The calculations involved in this approach are rather tedious and, therefore, a computer program[10] was written for analyzing the data. This program, given two sets of monomer reactivity ratios and a number of sets of monomer feed compositions and instantaneous

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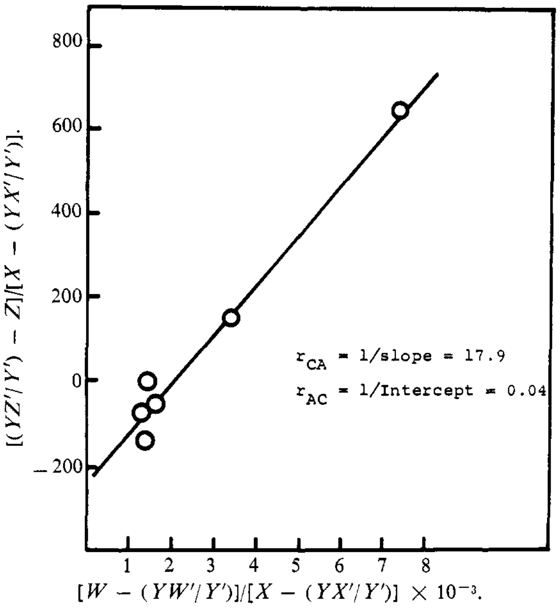

Figure 2. Terpolymer reactivity ratio plot for the methyl methacrylate–styrene–vinyl chloride terpolymerization system.

terpolymer compositions, evaluates the bracketed expressions in eq 14, using data obtained from pairs of terpolymerization experiments. r_{AC} and r_{CA} are then evaluated by a least-squares procedure from the calculated quantities.

In this study, reactivity ratios for the styrene–methyl methacrylate system[11,12] were taken to be 0.52 and 0.47, respectively, and those for the vinyl chloride–methyl methacrylate system[1,15,16] were taken to be 0.044 and 11.2, respectively. By using these values and the data in Table I, the monomer reactivity ratios for the styrene–vinyl chloride system at 68° (Figure 2) were determined to be 18 and 0.04, respectively. These values are to be compared with corresponding values of 17.0 ± 3 and 0.02 obtained by Doak[18] in studies on styrene–vinyl chloride copolymerizations.

Intersequence Cyclization Studies. The monomer reactivity ratios discussed above were then used to calculate the extent of cyclization to be expected for the various terpolymers. The calculations were done with the aid of an IBM 1620 computer programmed[10] for this purpose. The results of the calculations are compared with experimental results in Table II. The agreement obtained is very good, indicating the general validity of our statistical approach and the applicability of binary reactivity ratios to calculations concerning terpolymerization.

Conclusions

The extents of reaction obtained when intersequence cyclization are conducted in methyl methacrylate–vinyl chloride–styrene terpolymers are in excellent accord with those predicted from statistical considerations. Since the calculated values are based on binary monomer reactivity ratios and since reactivity ratios derived for the styrene–vinyl chloride system in the present study are in good agreement with those obtained from a study of styrene–vinyl chloride copolymerizations, we conclude that binary and ternary monomer reactivity ratios are identical for the terpolymerization system investigated in this study. There is thus no indication that penultimate effects are significant in these copolymerization and terpolymerization systems.

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