respectively, hold satisfactorily. Here the numerical formulas used were

$$\xi_i - \xi_j = \frac{y_i - y_j}{\left(\frac{d\xi}{dy}\right)_i^{-1} - \left(\frac{d\xi}{dy}\right)_j^{-1}} \ln \frac{\left(\frac{d\xi}{dy}\right)_i}{\left(\frac{d\xi}{dy}\right)_j} \quad (20)$$

and

$$\xi_i - \xi_j = \frac{2(y_i - y_j)}{\left(\frac{d\xi}{dy}\right)_i^{-1} - \left(\frac{d\xi}{dy}\right)_j^{-1}} \quad (21)$$

If y_0 and C are near the infinite-thickness values, intervals must be shortened as y_0 is approached. In the thickest finite range, bounds for $\bar{y}(\xi_0)$ are

$$y_u + \xi_0^{-1}[I_2(\xi_1) - y_u\xi_1] < \bar{y} < y_2 + \xi_0^{-1}[I_2(\xi_2) - y_2\xi_2] \quad (22)$$

where ξ_0, as before, is the scaled thickness number, y_u is the lower limit of y for infinite thickness, $\xi_1(y_1)$, in the infinite-case integration employing $[y_u, C(y_u)]$, is any particular ξ at which integration is stopped, y_2 and ξ_2 are the boundary y_0 and ξ_0 for the highest finite case available, and

$$I_2(\xi) \equiv \int_1^{y(\xi)} y \frac{d\xi}{dy} dy$$

The situation is depicted in Figure 5. The stated inequalities follow from the diagram, which is based on families of numerical concentration profiles, *cf.* Figures 2 and 3, since

$$\bar{y} = \frac{\int y d\xi}{\int d\xi}$$

and

$$I_2(\xi_1) + y_u(\xi_0 - \xi_1) < \int_1^{\xi_0} y d\xi < I_2(\xi_2) + y_2(\xi_0 - \xi_2) \quad (23)$$

Reactivity Ratio Determinations by Sequence Distribution Measurements

N. W. Johnston

Union Carbide Corporation, Research and Development, Bound Brook, New Jersey 08805.
Received April 2, 1970

ABSTRACT: A relationship was developed for finding copolymer reactivity ratios using only one copolymer rather than a series of copolymers as is done in conventional approaches. This approach relates the comonomer feed, the copolymer composition, and the copolymer sequence distribution to reactivity ratios. Experimental evidence is shown that accurate measurements of the copolymer sequence distribution and the single copolymer reactivity ratio technique can be used to predict reactivity ratios that agree well with literature values obtained by standard techniques.

There are several standard methods for finding copolymer reactivity ratios. Approaches such as the Fineman–Ross[1] or Mayo–Lewis[2] relationships require preparation of a series of copolymers from various monomer feed compositions. The reactivity ratios for the series are then found by a graphical technique.

In preparing new copolymers, or when working with difficult-to-obtain monomers, it would be advantageous to be able to find copolymer reactivity ratios without the time and monomer consuming preparation of many samples. The use of copolymer sequence distribution statistical relationships and the development of advanced polymer analytical techniques for measuring sequence distributions now make this possible for some copolymer systems. Accurate measurement of the sequence distribution of one copolymer combined with the monomer feed and the copolymer composition can be used to give a pair of reactivity ratios. These reactivity ratios may then be used to predict the comonomer feed necessary to prepare a desired copolymer composition with a minimum investment of time and monomer.

Experimental Section

Preparation of Copolymers. Vinyl chloride–amyl methacrylate (VCl–AMA), vinyl chloride–hexyl methacrylate (VCl–HxMA), and vinyl chloride–heptyl methacrylate (VCl–HpMA) copolymers were prepared in 2-butanone at 40° from freshly distilled monomers which contained 0.4 wt % *t*-butyl peroxypivalate as initiator. Conversions were kept low and polymers were isolated by pouring the polymerization mixtures into a large excess of methanol. The polymers were reprecipitated several times from 2-butanone solutions by addition of the solutions to methanol. The samples were dried *in vacuo* and copolymer compositions were determined by C, H, Cl analysis.

Preparation of vinyl chloride–methyl methacrylate[3] (VCl–MMA), vinyl chloride–butyl methacrylate[4] (VCl–BMA),

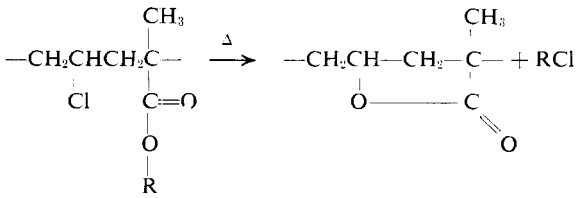
(1) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
(2) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
(3) N. W. Johnston and H. J. Harwood, *J. Polym. Sci., Part C*, **22**, 591 (1969).
(4) N. W. Johnston, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Sci.*, **10** (2), 608 (1969).

TABLE I
FEED-COPOLYMER COMPOSITION DATA

Copolymer	Mol % RMA Feed	Mol % RMA Copolymer	Convn, wt %	Source
VCl–MMA	19.9	75.9	1.6	Ref 3
VCl–BMA	2.0	26.1	1.0	This work
VCl–AMA	2.0	24.9	1.0	This work
VCl–HxMA	2.0	24.4	0.5	This work
VCl–HpMA	2.0	25.6	1.1	This work
BD–MMA	73.0	55.0	2.4	Ref 5
STY–MMA	80.0	72.8	7.0	Ref 6

butadiene–methyl methacrylate[5] (BD–MMA), and styrene–methyl methacrylate[6] (STY–MMA) copolymers was described in previous papers. Information on monomer feeds, copolymer compositions, and conversion for all copolymers studied is shown in Table I.

Sequence Distribution. Zutty and Welch[7] found that vinyl chloride–alkyl methacrylate copolymers will undergo an intramolecular intersequence cyclization reaction to form a lactone ring in the polymer backbone and liberate alkyl chloride.



Previous quantitative studies of these types of cyclizations in copolymers[3] and terpolymers[8] have shown the reaction to produce a statistically predictable extent of cyclization. Mass spectra and infrared data indicate the gas given off to be pure alkyl chloride.

Data on the cyclization of VCl–MMA copolymers were obtained from earlier work.[3] VCl–BMA, VCl–AMA, VCl–HxMA, and VCl–HpMA copolymers were cyclized at 200° for 2 hr *in vacuo* using the technique developed in the study of VCl–MMA systems.[3,8] The experimental extent of cyclization was determined through weight loss measurements. The moles of alkyl halide evolved were divided by the moles of alkyl methacrylate in the copolymer to yield the fraction of alkyl methacrylate (RMA) units cyclized

$$f_c(\text{RMA}) = \frac{\text{moles of alkyl halide}}{\text{moles of RMA}} \quad (1)$$

The fraction of uncyclized RMA is then

$$f_u(\text{RMA}) = 1.0 - f_c(\text{RMA}) \quad (2)$$

Sequence distribution measurements of BD–MMA copolymers[5] and STY–MMA copolymers[6] were available from previous papers.

Results and Discussion

Theoretical Considerations. Alfrey, Lewis, and Magel[9] derived eq 3 to calculate the fraction, $f_u(B)$, of B units in an AB copolymer which would not cyclize with A units, assuming A–B pairs cyclized at random. Here

$$f_u(B) = [\cosh (P_{AB}P_{BA})^{1/2} - (P_{BA/AB})^{1/2} \sinh (P_{AB}P_{BA})^{1/2}]^2 \quad (3)$$

P_{AB} and P_{BA} are the probabilities of an A unit being linked to a B or a B unit being linked to an A, respectively. Equation 3 may be rearranged[3] to eq 4 where R is the run number,[10] defined as the average number of uninterrupted monomer sequences which occur in a copolymer chain per 100 monomer units, and A and B are the copolymer composition in mole per cent.

$$f_u(B) = [\cosh (R^2/4AB)^{1/2} - (A/B)^{1/2} \sinh (R^2/4AB)^{1/2}]^2 \quad (4)$$

Values predicted with a computerized version[11] of eq 4 agree very well with experimental values found for several copolymer systems.[3,5] For convenience in the computation of R, eq 4 may be rearranged to the form

$$(R^2/4AB)^{1/2} = \ln \{[f_u(B)]^{1/2} \pm [f_u(B) - 1 + (A/B)]^{1/2}\} - \ln [1 - (A/B)^{1/2}] \quad (5)$$

Two values for the run number, R, may be obtained for each copolymer using eq 5, the experimental fraction of uncyclized B units, $f_u(B)$, and the copolymer molar composition, A and B.

Reactivity ratios may be calculated from run number values by relating probabilities based on run numbers to probabilities based on monomer feed compositions (AF and BF) and reactivity ratios[12] as is shown in eq 6.

$$P_{AB} = R/2A = (BF/AF)/(BF/AF + r_A) \quad (6)$$

Equation 6 may be solved for the reactivity ratio r_A, and r_B may be found in a similar manner.

As eq 5 gives two values for R, two sets of reactivity ratios can be predicted for each copolymer. In all systems thus far studied, one of these sets of reactivity ratios has contained negative values and could be disregarded. The other set, in cases where literature comparisons are available, compares well with reactivity ratios obtained by standard techniques. This is not surprising as it is reactivity ratios that determine the copolymer sequence distribution for any given monomer feed.

Reactivity Ratios. Using the feed–copolymer composition data in Table I and experimental sequence distribution values from cyclization reactions or nmr studies, several sets of reactivity ratios were predicted. These values predicted using a FORTRAN IV computer program based on eq 5 and 6 are compared with reactivity ratios available in the literature in Table II. In all cases, the comparisons are favorable.

As shown in Table II, the reactivity ratio of RMA in

(5) N. W. Johnston and H. J. Harwood, *Macromolecules*, **3**, 20 (1970).
(6) H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Part B*, **3**, 419 (1965).
(7) N. L. Zutty and F. J. Welch, *ibid., Part A*, 2289 (1963).
(8) N. W. Johnston and H. J. Harwood, *Macromolecules*, **2**, 221 (1969).
(9) T. Alfrey, C. Lewis, and B. Magel, *J. Amer. Chem. Soc.*, **71**, 3793 (1949).
(10) H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Part B*, **2**, 601 (1964).
(11) H. J. Harwood, N. W. Johnston, and H. Piotrowski, *ibid., Part C*, **25**, 23 (1968).
(12) E. Merz, T. Alfrey, and G. Goldfinger, *ibid.*, **1**, 75 (1946).

TABLE II
REACTIVITY RATIOS

Copolymer	Mol % RMA copolymer	Exptl f_u-(RMA)	Reactivity ratios—Calcd[a]	Reactivity ratios—Found
VCl–MMA	75.9	0.691	0.03/9.6	0.04/11.2[c]
VCl–BMA	26.1	0.090	0.05/13.7	0.05/13.5[d]
VCl–AMA	24.9	0.108	0.06/17.3	
VCl–HxMA	24.4	0.107	0.06/17.2	
VCl–HpMA	25.6	0.107	0.06/16.2	
BD–MMA	55.0	0.340	0.98/0.24	0.73/0.18[e]
STY–MMA	72.8	*b*	0.54/0.51	0.52/0.47[f]

[a] Predicted using eq 5 and 6 and experimental data. [b] *R* value from nmr data used.[6] [c] See ref 3. [d] G. V. Tkachenko, L. V. Stupen, L. P. Kofman, and L. A. Karachera, *Zh. Fiz. Khim.*, **32**, 2492 (1958). [e] See ref 5. [f] See ref 6.

TABLE III
COMPOSITION OR PENULTIMATE EFFECTS IN VCl–BMA

Mol % BMA—Feed	Mol % BMA—Copolymer	Convn, wt %	Exptl f_u-(RMA)	Reactivity ratios
2.0	26.1	1.0	0.090	0.053/13.7
6.0	50.1	1.5	0.357	0.057/14.3
16.5	72.8	6.5	0.672	0.069/13.4

TABLE IV
COMPOSITIONS PREDICTED USING EXPERIMENTAL REACTIVITY RATIOS

Copolymer	Exptl *rr*[a]	Mol % RMA feed	Convn, wt %	Mol % RMA copolymer Exptl	Mol % RMA copolymer Predicted[b]
VCl–AMA	0.06/17.3	10.0	0.6	65.0	65.2
VCl–HxMA	0.06/17.2	10.0	2.0	64.8	64.6
VCl–HpMA	0.06/16.2	10.0	1.8	64.0	63.8

[a] Predicted using eq 5 and 6. [b] Predicted using one-point *rr* values.

length of the alkyl group in styrene–alkyl acrylate copolymers.[14]

In some copolymer systems, changing monomer feed ratios or copolymer compositions can result in a shift in reactivity ratios due to penultimate type effects or simply due to the change in polarity of the polymerization medium with changing monomer feeds. The use of eq 5 and 6 and the one copolymer reactivity ratio system to give a reactivity ratio for each copolymer in a series of copolymers would seemingly be a good technique for measuring these effects.

A series of VCl–BMA copolymers was cyclized and a set of reactivity ratios predicted for each member of the series based on its extent of cyclization. Table III shows that each member of this series had similar reactivity ratios that agree fairly well with the literature values of 0.05/13.5 for VCl–BMA of Tkachenko, *et al.*[15] Although the VCl–BMA copolymer system did not exhibit a strong composition or penultimate effect and thus little reactivity ratio shift, the technique is still a plausible one and could be used to determine this type of reactivity ratio anomaly.

The reactivity ratios found in Table II for VCl–AMA, VCl–HxMA, and VCl–HpMA were used to predict copolymers produced from other monomer feed compositions. These predicted compositions are compared with experimentally found compositions in Table IV. The predicted and actual compositions agree well.

Discussion

The results shown in Tables II, III, and IV indicate the general validity of the approach outlined in the section on theoretical considerations. It appears that for some copolymer systems, reactivity ratios may be predicted from sequence distribution measurements. The lack of strong penultimate-type effects in VCl–BMA systems was pointed out and changes were noted in the reactivity ratios of VCl–RMA systems when the length of the R group was varied.

It should be pointed out, however, that these reactivity ratio predictions are quite sensitive. Care must be taken to obtain accurate compositions and sequence distribution measurements. Copolymers having appreciable monomer feed ratio drift at low conversions or nonuniform copolymers would have nonuniform sequence distributions and may give erroneous reactivity ratios.

TABLE V
REACTIVITY RATIO ERRORS

Copolymer	Exptl f_u(RMA)	Mol % RMA—Copolymer	Mol % RMA—Feed	Reactivity ratios[a]—r_A	Reactivity ratios[a]—r_B
VCl–BMA	0.090 ± 0.008	26.1	2.0	0.053 ± 0.002	13.71 ± 1.63
VCl–BMA	0.090	26.1 ± 2.0	2.0	0.053 ± 0.010	13.71 ± 0.85
VCl–BMA	0.090	26.1	2.0 ± 1.0	0.053 ± 0.028	13.71 ± 14.00
VCl–BMA	0.090 ± 0.002	26.1 ± 0.5	2.0 ± 0.04	0.053 ± 0.001	13.71 ± 0.81
BD–MMA	0.34 ± 0.06	55.0	73.0	0.981 ± 0.677	0.246 ± 0.121
BD–MMA	0.34	55.0 ± 2.0	73.0	0.981 ± 0.517	0.246 ± 0.037
BD–MMA	0.34	55.0	73.0 ± 1.0	0.981 ± 0.050	0.246 ± 0.012
BD–MMA	0.34 ± 0.007	55.0 ± 1.1	73.0 ± 1.5	0.981 ± 0.450	0.246 ± 0.015

[a] Reactivity ratio errors predicted by varying values in eq 5 and 6.

VCl–RMA copolymers increases as the length of the alkyl group increases and then remains fairly constant after reaching amyl methacrylate. An increase in alkyl acrylate reactivity ratios with increasing length of the alkyl group was noted by Tkachenko in VCl–alkyl acrylate copolymers.[13] Ratzsch and Stephan noted a decrease in alkyl acrylate reactivity ratios with increasing

(13) G. V. Tkachenko, *Zh. Fiz. Khim.*, **31**, 2676 (1957).

(14) M. Ratzsch and L. Stephan, *Plaste Kaut.*, **15**, 884 (1968).
(15) See Table II, footnote *d*.

Table V shows the effect on the error range of the predicted reactivity ratios of varying either the sequence distribution, the polymer composition, or the monomer feed while holding the other variables constant. Effects on predicted reactivity ratios of errors of ~9% in the sequence distribution, ~8% in the polymer composition, and ~50% in the monomer feed are shown for a VCl–BMA copolymer. Errors of ~18% in the sequence distribution, ~4% in the polymer composition, and ~1% in the monomer feed are shown for a BD–MMA copolymer. Large errors are not expected in any of the variables, but erroneous reactivity ratios may also arise from a cumulation of smaller errors. The effect on predicted reactivity ratios of an ~2% error in all variables is also shown in Table V for both the VCl–BMA and BD–MMA copolymers. It is doubtful that errors of this degree would occur in all variables simultaneously, but the error range found indicates the experimental care that must be taken in using this approach. Accurate measurement of variables will, however, give favorable reactivity ratio comparisons as shown in Table II.

Conclusions

Reactivity ratios may be predicted in copolymer systems susceptible to sequence distribution measurements by accurately knowing the monomer feed, the copolymer composition, and the copolymer sequence distribution. Reactivity ratios can be obtained with a minimum amount of polymer synthesis and may be used to predict desired copolymer compositions. The single-copolymer reactivity ratio technique could possibly be used to illustrate shifts in reactivity ratios attributed to penultimate effects or polymerization mixture polarity changes.

The single-copolymer reactivity ratio method may prove to be valuable in specific systems where accurate sequence distribution data can be obtained and the use of conventional methods for finding reactivity ratios is not practical.

Acknowledgments. The author would like to acknowledge helpful discussions with Professor H. James Harwood of the University of Akron and the technical assistance of J. E. Simborski of Union Carbide.

Structural Studies of Polyethers $[-(CH_2)_m O-]_n$. VIII. Polyoxacyclobutane Hydrate (Modification I)

Hideto Kakida,[1a] Daisuke Makino, Yozo Chatani, Masamichi Kobayashi, and Hiroyuki Tadokoro[1b]

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, Japan. *Received March 30, 1970*

ABSTRACT: The structure of crystal modification I of polyoxacyclobutane has been studied by the use of X-ray diffraction and infrared spectroscopic methods. The crystal lattice is monoclinic, $C2/m$-C_{2h}^3, a = 12.3 Å, b = 7.27 Å, c (fiber axis) = 4.80 Å, and β = 91°. Four molecular chains (four monomeric units) and four water molecules are contained in the unit cell, *i.e.*, the crystal is a hydrate. Two polymer chains with essentially planar zigzag structures are joined by a hydrogen-bonded chain of water molecules, resulting in a planar ribbonlike structure. This structure has been corroborated by the normal coordinate treatments carried out on H_2O and D_2O hydrates.

In a previous paper[2] we reported three modifications of polyoxacyclobutane (POCB). The structure determinations of modifications II and III have been described in detail. In this paper we report the structure determination of modification I, the crystal structure of which was found to be a hydrate.

As has been reported in the previous paper, modification II is obtained only as oriented samples and modification III is the most thermally stable form. Figure 1 shows the molecular models of the three modifications. The molecular conformation of modification II is $T_3GT_3\bar{G}$, and that of modification III is $(T_2G_2)_2$. Here G and $\bar{G}$ indicate the right- and left-handed *gauche* forms, respectively. The conformation of modification I is planar zigzag.

(1) (a) Research Laboratory, Mitsubishi Rayon Co. Ltd., Otake, Hiroshima, Japan; (b) to whom correspondence should be addressed.

(2) H. Tadokoro, Y. Takahashi, Y. Chatani, and H. Kakida, *Makromol. Chem.*, 109, 96 (1967).

Experimental Section

Samples. The sample of modification I was prepared by quenching a molten sample in ice water. The uniaxially oriented sample was obtained by stretching the sample in ice water, and the doubly oriented sample was made by rolling the uniaxially oriented sample at a low temperature (about 4°). The deuterated sample was made by steeping the original sample in heavy water for a few days.

Measurements. X-Ray diffraction measurements were made with Ni-filtered Cu Kα radiation. Fiber photographs were taken with cylindrical cameras with radii of 35 and 50 mm. In order to obtain the diffraction spots of higher angles, low-temperature measurements (*ca.* −100°) were also made, giving three times as many reflections as were obtained at room temperature. The intensities of the reflections obtained by the multiple film method were measured by visual comparison with a standard intensity scale.

Japan Spectroscopic Co. DS-402G and Hitachi FIS-1 grating infrared spectrophotometers were used for the infrared absorption measurements. The polarization measurements were made with AgCl and polyethylene polarizers.