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Calculation of Reactivity Ratios and Sequence Distributions in Copolymers from Monomers ^{13}C -NMR Data

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ABSTRACT

A screening procedure has been developed to predict the average sequence distribution in vinyl copolymers from monomer ^{13}C -NMR data. The ^{13}C -NMR absorption frequencies of the carbon atoms of the polymerizable double bond are used to calculate the Alfrey-Price Q and e values as previously described by Borchardt and Dalrymple. These, in turn, are used to calculate the monomer reactivity ratios. Reactivity ratios for 54 copolymerizations were calculated by this procedure and compared to literature values. The copolymer sequence distribution may then be determined by means of a computer program written by Harwood. The sequence distribution in copolymers of methacrylic acid and dimethylaminoethyl methacrylate, acrylonitrile and methyl methacrylate, 1,1-dichloroethylene and methacrylonitrile, ethyl acrylate and n-butyl methacrylate, and acrylamide and sodium 2-acrylamido-2-methylpropane sulfonate were calculated from reactivity ratios

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derived from ^{13}C -NMR data and compared to literature values. This procedure may be used to calculate the reactivity ratios from ^{13}C -NMR spectra of monomers for which no Q and e values are known. By this method the average sequence distribution of such monomers in copolymers may be predicted, significantly reducing the number of copolymers to be synthesized and tested for use in various applications.

INTRODUCTION

Research in progress in our laboratories is aimed at relating copolymer microstructure to observed performance in various applications. While the Q and e values and reactivity ratios of many interesting monomers are not known, we required a screening procedure for the prediction of monomer sequence distribution to reduce the number of vinyl copolymers to be synthesized and evaluated. A screening procedure utilizing only the ^{13}C -NMR absorption frequencies of the carbon atoms of the polymerizable carbon-carbon double bond, C_α and C_β , has been developed. The method involves calculation of the Alfrey-Price Q and e values from the ^{13}C -NMR spectra of the vinyl comonomers by previously developed equations and a multiple correlation analysis procedure [1]. The general form of these equations is given in

$$\begin{aligned}
 Q =, e = & a\alpha + b\beta + c(\alpha - \beta) + d(\alpha/\beta) + f(\alpha - \beta)^3 + g(\alpha/\beta)^{1/2} \\
 & + h(\alpha^2 - \beta^2) + i\alpha^2 + j\beta^2 + k\alpha\beta + 1/\alpha + m/\beta + n\alpha^{1/2} + o\beta^{1/2} \\
 & + p(\alpha^2 + \beta^2)^{1/2} + r/(\alpha^2 - \beta^2)^3 + s(\alpha - \beta)^4 + t(\alpha - \beta)^2 + u(\beta/\alpha) \\
 & + v(\alpha - \beta)^3 + w(\alpha - \beta)^{10} + \text{intercept}
 \end{aligned} \quad (1)$$

where α and β represent the ^{13}C -NMR absorption frequencies of the respective olefinic carbon atoms of vinyl monomers. The reactivity ratios for a pair of monomers may then be calculated by using the following semiempirical [2] equations [3, 4]:

$$r_1 = \frac{Q_1}{Q_2} \exp [-e_1(e_1 - e_2)] \quad (2)$$

$$r_2 = \frac{Q_2}{Q_1} \exp [-e_2(e_2 - e_1)] \quad (3)$$

The copolymer microstructure may then be determined by use of a program developed by Harwood [5]. The input data consist of the monomer reactivity ratios, the molecular weights of the monomers, and the total monomer conversion. Copolymer composition and diad, triad, tetrad, and pentad distributions are calculated as well as the percent conversion of each monomer.

Before applying this procedure to calculate the reactivity ratios of monomers for which no Q and e values are known, the accuracy of this technique must be determined. Reactivity ratios derived from monomer ^{13}C -NMR spectra were first compared to those recently recalculated by Greenley [6]. Then sequence distributions for a series of copolymers were calculated by use of Harwood's program with the reactivity ratios derived from monomer ^{13}C -NMR data. The results so calculated were then compared to reported sequence distributions obtained from copolymer NMR data. The determination of copolymer microstructure from the ^{13}C -NMR spectra of the copolymer has been recently reviewed by Koenig [7].

EXPERIMENTAL SECTION

Nearly all the chemical shift values of the olefinic carbon atoms on which the Q and e value calculations have been made were taken from the literature [1]. The multiple correlation analysis program was described in Ref. 1. Harwood has described the program used to calculate copolymer sequence distributions [5]. This program was modified to a FORTRAN V format for the present research. Calculations were made using an interfaced IBM 370-3333/370-3081 computer system.

RESULTS AND DISCUSSION

Calculation of Reactivity Ratios

The reactivity ratios of a series of comonomers were calculated by Eqs. (2) and (3). The Q and e values were calculated by using Eq. (1) with the ^{13}C -NMR chemical shifts of the olefinic atoms of the comonomers. The coefficients of the terms of Eq. (1) used for each class of monomer are given in Ref. 1. The reactivity ratios so calculated are listed in Table 1. The literature values given in this table were recalculated by Greenley [6, 8] using the Kelen-Tüdös equations [9, 10]. The agreement between the calculated and the literature values for methyl methacrylate copolymerizations was fairly good. Reasonably good agreement between the calculated and the literature values of the reactivity ratios for styrene copolymer-

TABLE I. Comparison of r_1 and r_2 Values Calculated from ^{13}C -NMR Data and Literature Values

M_2	M_1	Literature [6]		Calculated	
		r_2	r_1	r_2	r_1
Methacrylic acid	Methyl methacrylate	1.355 ± 0.521^a	0.767 ± 0.548^a	1.08	0.88
Benzyl methacrylate	Methyl methacrylate	1.116	0.809	1.15	0.93
Butyl methacrylate	Methyl methacrylate	2.114	0.523	1.07	0.92
2-Hydroxyethyl methacrylate	Methyl methacrylate	0.842 ± 0.213^b	0.614 ± 0.211^b	1.57	0.32
2-Hydroxypropyl methacrylate	Methyl methacrylate	1.055	0.403	1.03	0.92
i-Butyl methacrylate	Methyl methacrylate	1.882	0.621	1.14	0.76
Methacrylic acid	Styrene	0.551 ± 0.053^b	0.170 ± 0.046^b	0.41	0.32
Benzyl methacrylate	Styrene	0.547 ± 0.113^b	0.462 ± 0.002^b	0.60	0.44
Butyl methacrylate	Styrene	1.413 ± 1.103^b	0.256 ± 0.306^b	0.61	0.51
2-Hydroxyethyl methacrylate	Styrene	0.697 ± 0.159^b	0.387 ± 0.055^b	2.09	0.77
Methyl methacrylate	Styrene	0.48	0.58	0.48	0.47
Acrylic acid	Styrene	0.128 ± 0.031^a	0.655 ± 0.337^a	0.12	0.51
Benzyl acrylate	Styrene	0.221 ± 0.025^b	0.542 ± 0.030^b	0.08	0.32
Butyl acrylate	Styrene	0.124 ± 0.230^b	0.836 ± 0.397	0.08	0.80
2-Cyanoacrylic acid, methyl ester	Styrene	0.61	0.05	1.05	0.05
Ethyl acrylate	Styrene	0.138	0.698	0.18	0.88

CALCULATION OF REACTIVITY RATIOS

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2-Ethylhexyl acrylate	Styrene	0.312	0.956	0.24	1.16
Methyl acrylate	Styrene	0.20	0.74	0.21	1.69
p-Bromostyrene	Styrene	1.046 ± 0.059^b	0.692 ± 0.018^b	1.44	0.69
p-Methylstyrene	Styrene	0.993	0.890	1.24	0.79
<i>o</i> -Methylstyrene	Styrene	0.250 ± 0.202^b	1.087 ± 0.125^b	0.97	1.21
m-Nitrostyrene	Styrene	0.500	0.280	1.81	0.20
Ethyl vinyl ether	Styrene	-0.114	115.8	0.0004	20.38
n-Butyl vinyl ether	Styrene	-0.075	21.38	0.01	11.58
i-Butyl vinyl ether	Styrene	-0.143 ± 0.097^b	0.844 ± 0.144^b	0.003	0.77
Vinyl acetate	Acrylic acid	0.023	9.285	0.05	19.62
Vinyl acetate	Methyl acrylate	0.217 ± 0.184^b	4.480 ± 1.902	0.01	7.58
Vinyl acetate	Butyl acrylate	0.018	3.458	0.02	2.92
Vinyl acetate	Methyl methacrylate	0.501 ± 0.310^b	70.112 ± 67.388^b	0.01	17.82
Vinyl acetate	n-Butyl methacrylate	-0.001	30.84	0.01	22.79
Vinyl acetate	i-Butyl methacrylate	0.057	34.86	0.01	33.36
Chloroethylene	Vinyl acetate	1.772 ± 0.449^a	0.405 ± 0.292^a	0.86	1.71
1,1-Dichloroethylene	Vinyl acetate	4.116 ± 0.618^b	0.031 ± 0.000^b	10.78	0.20
Trichloroethylene	Vinyl acetate	8.558	0.378	5.64	0.81
Chloroethylene	Vinyl stearate	0.718	0.244	0.48	3.61
1,1-Dichloroethylene	Vinyl stearate	3.924	0.074	6.31	0.40

(continued)

TABLE 1 (continued)

M ₂	M ₁	Literature [6]		Calculated	
		r ₂	r ₁	r ₂	r ₁
Acrylic acid	1,1-Dichloroethylene	1.247	0.437	0.83	0.66
Butyl acrylate	1,1-Dichloroethylene	0.873	0.935	0.56	0.87
Ethyl acrylate	1,1-Dichloroethylene	0.720	0.578	1.10	0.85
Methyl acrylate	1,1-Dichloroethylene	0.949	0.897	1.18	0.64
Benzyl acrylate	Acrylonitrile	0.725	0.277	1.56	0.63
Butyl acrylate	Acrylonitrile	0.920 ± 0.131 ^b	1.180 ± 0.498 ^b	0.95	0.91
2-Cyanoacrylic acid, methyl ester	Acrylonitrile	1.762	0.122	6.61	0.07
2-Cyanoacrylic acid, ethyl ester	Acrylonitrile	0.68	0.01	13.62	0.07
Ethyl acrylate	Acrylonitrile	0.81	1.16	1.15	0.87
2-Hydroxyethyl methacrylate	Butyl acrylate	4.764	0.086	3.18	0.06
2-Hydroxyethyl methacrylate	Ethyl acrylate	11.22	0.190	3.02	0.12
2-Hydroxyethyl methacrylate	Methyl acrylate	8.696	-0.005	2.25	0.15
Hydroxypropyl methacrylate	Butyl acrylate	5.360	0.173	2.57	0.24
Hydroxypropyl methacrylate	Ethyl acrylate	13.32	0.274	2.23	0.39
Hydroxypropyl methacrylate	Methyl acrylate	7.369	0.015	1.69	0.49

^a Average value ± standard deviation of six or more values.

^b Average value ± average deviation of less than six values.

izations with methacrylates and some acrylates was observed. The r_1 values for styrene copolymerization with ethyl acrylate, 2-ethylhexyl acrylate, and methyl methacrylate derived from ^{13}C -NMR data were significantly greater than the literature values. The difference in the calculated and literature values of the reactivity ratios for a series of styrene-substituted styrene copolymerizations did not appear large in view of the variation in the literature values of the reactivity ratios for styrene-*p*-bromostyrene copolymerization and for styrene- α -methylstyrene copolymerization.

The large difference in reactivity between styrene and a series of alkyl vinyl ethers could account for the differences between literature values of the reactivity ratios and values derived from monomer ^{13}C -NMR data. However, there was good agreement between calculated and literature values of the reactivity ratios for a series of vinyl acetate copolymerizations with acrylates and methacrylates despite substantial differences in the reactivity of the comonomers.

Agreement between calculated and literature values of the reactivity ratios for copolymerizations of chlorinated ethylenes varied with the identity of the comonomer. The same was true for a series of acrylonitrile copolymerizations. Some of the variation between calculated and literature values of the reactivity ratios for copolymerizations of a series of hydroxyalkyl methacrylates and hydroxyalkyl acrylates may have been due to the possible role of the hydroxyalkyl group as a chain transfer agent or as a branching site in the copolymer chain. This potential behavior is reflected to at least some degree in the literature values of the reactivity ratios, based as they are on measurements of unreacted comonomer concentrations. However, the ^{13}C -NMR experiment does not take into account this potential reactivity of the hydroxyalkyl groups.

For best results, the conditions under which the ^{13}C -NMR spectra of the comonomers are determined, i.e., solvent, pH, temperature, concentration, pressure, etc., should be the same as those of the copolymerization reaction. Because the Q and e values were calculated by use of ^{13}C -NMR spectral data taken from the literature [1], it has not been possible to achieve this in this initial study. However, despite variations in the test conditions between the ^{13}C -NMR analyses and the copolymerizations, fairly good agreement between the reactivity ratios derived from monomer ^{13}C -NMR spectra and reported ratios [6] was obtained. The agreement between calculated and literature values of the reactivity ratios reported in Table 1 was generally considered good, particularly in view of the careful and tedious experiments required to obtain reasonably accurate kinetic data and the assumptions and approximations inherent in the different methods of determining the reactivity ratios from kinetic data [1, 11-13].

The reactivity ratios for the copolymerization of methacrylic acid and dimethylaminoethyl methacrylate in different solvents, at different pH values, and with different initiator systems have been determined by various workers [14-16] and are reported in Table 2. The ^{13}C -NMR

TABLE 2. Reactivity Ratios of Methacrylic Acid (A) and Dimethylaminoethyl Methacrylate (B)

r_A	r_B	Polymerization conditions	Reference
1.43	0.66	CH ₃ OH (A), CDCl ₃ (B) ^a	This work
0.52 ^b	1.28 ^{b,c}	CH ₃ OH/H ₂ O, K ₂ S ₂ O ₈	14
0.98	0.90 ^c	pH = 1.2, K ₂ S ₂ O ₈	14
0.08	0.65 ^c	pH = 7.2, K ₂ S ₂ O ₈	14
0.42 ^d	1.02 ^d	CH ₃ OH/H ₂ O	15
0.45	0.98	CH ₃ OH/H ₂ O	15
0.67	3.0	CH ₃ OH, AIBN n-C ₄ H ₉ SH	16

^a¹³C-NMR solvent for each comonomer. No copolymerization experiment was performed.

^bRecalculated by Merle and Merle [15] using the Kelen-Tüdös method.

^cMonomer B was diethylaminoethyl methacrylate.

^dRecalculated by Merle and Merle [15] using Chujo's method [17]

experiments were performed in two different solvents, methanol and deuteriochloroform. Thus, the conditions of the NMR experiment were significantly different from the copolymerization reaction conditions. The differences in the calculated and literature Q and e values for methacrylic acid and dimethylaminoethyl methacrylate were greater than for most of the monomers included in the earlier study [1]. The differences between the calculated and literature values of the reactivity ratios are reported in Table 2. These experiments illustrate the importance of conducting the NMR experiment under the same conditions as are to be used in the copolymerization. This is especially true for such monomers as methacrylic acid, whose reactivity is particularly sensitive to solvent and pH [18, 19]. The differences in the values of the reactivity ratios determined at pH 1.2 and 7.2 (see Table 2) have been attributed to the formation of a complex between ionized methacrylic acid and protonated dimethylaminoethyl methacrylate [15].

There are several reported determinations of the monomer reactivity ratios reported in the literature for acrylonitrile-methyl methacrylate copolymerization. These are summarized in Table 3. The calculated reactivity ratio for acrylonitrile is fairly consistent with

TABLE 3. Reactivity Ratios of Acrylonitrile (A) and Methyl Methacrylate (B)

r_A	r_B	Polymerization conditions ^a	Reference
0.23	2.33	CDCl_3 (NMR solvent)	This work
0.25	1.20	$\text{CH}_3\text{C}_6\text{H}_5$, DMF, 60°C, AIBN ^b	20
0.25	1.17	$\text{CH}_3\text{C}_6\text{H}_5$, DMF, 60°C, AIBN ^c	21, 22
0.29	1.53	DMSO, 54°C, AIBN	22
0.22	1.15	THF, 60°C, AIBN ^d	23
0.32	1.11	DMF, 60°C, AIBN ^d	23
0.31	1.15	50°C	24
0.10	1.35	40°C	25
0.15	1.22	80°C	25
0.16	1.19	100°C	25
0.15	1.20	No solvent, 60°C, benzoyl peroxide	26
0.15	1.65	H_2O , $\text{K}_2\text{S}_2\text{O}_8$, Na bisulfite, 20°C	27

^a AIBN = azobis(isobutyronitrile), DMF = dimethylformamide, DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

^b Reactivity ratios were calculated using the Mayo-Lewis procedure.

^c Reactivity ratios were calculated using the Fineman-Ross method.

^d Reactivity ratios were calculated using the Mortimer-Tidwell procedure.

a number of reported values, particularly those from the more recent literature. However, the methyl methacrylate reactivity ratio calculated from monomer ^{13}C -NMR data was considerably greater than the previously reported values. The deviations of ^{13}C -NMR spectra-derived Q and e values for methacrylates from the literature values were generally greater than those for other classes of monomers [1].

Considerable effort has been devoted to relating copolymer properties with copolymer composition and microstructure for a series of sodium poly(acrylamide-co-2-acrylamido-2-methylpropane sulfonate) copolymers [28-30]. Monomer reactivity ratios were cal-

TABLE 4. Reactivity Ratios for Copolymerization of Acrylamide (A) and Sodium 2-Acrylamido-2-methylpropanesulfonate (B)

Method of calculation	r_A	r_B
Calculation from ^{13}C -NMR data	0.55	1.48
Fineman-Ross ^a	0.98 ± 0.09	0.49 ± 0.02
Kelen-Tüdös ^a	1.00 ± 0.08	0.52 ± 0.07
Mayo-Lewis ^a	1.02 ± 0.01	0.50 ± 0.01

^a Taken from Ref. 30.

culated by using the Fineman-Ross [31], Kelen-Tüdös [9, 10], and Mayo-Lewis [32] methods (see Table 4). The Q and e values of sodium 2-acrylamido-2-methylpropane sulfonate were calculated from the ^{13}C -NMR chemical shifts of the olefinic carbon atoms and the following equations [1]:

$$Q = 13.66 - 1.74/(\alpha - \beta) - 1.08 \times 10^3/\beta - 0.0256 (\alpha^2 - \beta^2)^{1/2} + 3.26 \times 10^{-5} (\alpha - \beta) \quad (4)$$

$$e = -21.66 + 0.21\beta - 4.82 (\alpha/\beta) - 3.89/(\alpha - \beta)^{10} \quad (5)$$

where α and β represent the ^{13}C -NMR chemical shifts of the alpha- and beta-olefinic carbon atoms on the polymerizable carbon-carbon double bond of the monomer, respectively. The reactivity ratios were then calculated by Eqs. (2) and (3) and are given in Table 4. The reactivity ratios derived from ^{13}C -NMR data appeared to differ significantly from those reported by McCormick and Chen [30]. The difference may be due at least in part to pH differences in the copolymerization and NMR experiments.

Poly(Methacrylic Acid-co-Dimethylaminoethyl Methacrylate) Sequence Distribution

A comparison of sequence distributions of methacrylic acid-dimethylaminoethyl methacrylate copolymers determined from polymer ^{13}C -NMR analysis with those derived from monomer ^{13}C -NMR analysis is given in Table 5. Only the two copolymers Merle and Merle obtained by free-radical copolymerization [15] are included in the present study. (The other polyampholytes discussed by Merle and Merle were obtained by acidic or basic hydrolysis of poly(dimethylaminoethyl methacrylate).) Since Merle and Merle did not specify monomer con-

version in their synthetic studies (see Ref. 15 and references therein), monomer conversion was assumed to be 99.5% when monomer reactivity ratios and Harwood's program were used to calculate the comonomer sequence distribution. The same feed ratios used by the French workers were specified in Harwood's program. Inspection of Table 5 indicated fairly good agreement of the calculated diad and triad distributions with those reported by Merle and Merle. The A-centered and B-centered triad data reported by Merle and Merle [15] were each normalized to unity to provide a basis for comparison with the triad distributions calculated in the present study. A somewhat greater block tendency may be noted in the diad and triad distributions calculated with Harwood's program. However, overall agreement with the literature data was fairly good.

Poly(Acrylonitrile-co-Methyl Methacrylate) Sequence Distribution

Chujo, Ubara, and Nishioka determined the triad distributions resulting from copolymerization of acrylonitrile (A) and methyl methacrylate (B) at four temperatures [17]. Their data, summarized in Table 6, were determined at less than 2.5% conversion. Only the methyl methacrylate-centered triad distributions, based on the NMR absorption peaks of the methoxyl protons of the copolymers, were reported. By use of Eqs. (2) and (3) and the Q and e values calculated with Eq. (1) with the coefficients detailed in Ref. 1, the following reactivity ratios were calculated: $r_A = 0.23$ and $r_B = 2.33$. These values were then used with Harwood's program to calculate triad distributions assuming a monomer conversion of 2% and the same monomer feed ratios as employed by Chujo et al. The results are summarized in Table 6 for the methyl methacrylate-centered triads.

This copolymerization was also studied by Suggate [33], and the results are summarized in Table 7. Studies were performed with tetrahydrofuran and dimethylformamide as the 60°C polymerization solvents. The copolymer composition and methyl methacrylate-centered triad distributions were determined from copolymer $^1\text{H-NMR}$ data. Similar trends were observed for the results summarized in Tables 6 and 7. Calculations from monomer $^{13}\text{C-NMR}$ data predicted higher levels of methyl methacrylate in the copolymers than were actually obtained. Similarly, the calculated block tendency (F_{BBB} value) was significantly greater than that determined from $^1\text{H-NMR}$ analysis of the acrylonitrile-methyl methacrylate copolymers. This difference would appear to be due in part to the high calculated reactivity of methyl methacrylate in this copolymerization.

The existence of penultimate effects in acrylonitrile-methyl methacrylate copolymerization has been indicated by infrared and NMR copolymer studies and gas chromatographic analysis of residual monomer concentrations [20, 21, 23, 34, 35]. The omission of penultimate effects in the calculation of the sequence distributions may be a signi-

TABLE 5. Sequence Distribution in Copolymers of Methacrylic Acid (A) and Dimethylaminoethyl Methacrylate (B)

Feed ratio mol% A		Diad fractions								
		Reported ^a			Determined from ^c					
					Literature r_A, r_B			Calculated r_A, r_B ^d		
F_{AA}	F_{AB}	F_{BB}	F_{AA}	F_{AB}	F_{BB}	F_{AA}	F_{AB}	F_{BB}		
0.40	0.14	0.52	0.34	0.117	0.559	0.323	0.158	0.479	0.362	
0.60	0.34	0.57	0.14	0.322	0.549	0.128	0.358	0.481	0.161	

Feed ratio mol% A		A-Centered triad fractions								
		Reported ^b			Determined from ^c					
					Literature r_A, r_B			Calculated r_A, r_B ^d		
F_{AAA}	F_{AAB}	F_{BAB}	F_{AAA}	F_{AAB}	F_{BAB}	F_{AAA}	F_{AAB}	F_{BAB}		
0.40	0.06	0.35	0.59	0.094	0.404	0.502	0.162	0.471	0.367	
0.60	0.33	0.45	0.22	0.310	0.460	0.229	0.362	0.472	0.165	

Feed ratio mol% A		B-Centered triad fractions								
		Reported ^b			Determined from ^c					
					Literature r_A, r_B			Calculated r_A, r_B ^d		
F_{ABA}	F_{BBA}	F_{BAB}	F_{ABA}	F_{BBA}	F_{BAB}	F_{ABA}	F_{BBA}	F_{BBB}		
0.40	0.20	0.48	0.32	0.219	0.489	0.291	0.161	0.473	0.366	
0.60	0.38	0.55	0.08	0.470	0.423	0.106	0.361	0.475	0.164	

^aTaken from Ref. 15.^bTaken from Ref. 15 and normalized to unity.^cThese values were calculated using Harwood's program and the indicated reactivity ratios.^dCalculated using Eqs. (2) and (3) and Q and e values derived from monomer ¹³C-NMR data [1].

TABLE 6. Sequence Distribution in Copolymers of Acrylonitrile (A) and Methyl Methacrylate (B)

Polymerization temperature, °C	Feed ratio M_A/M_B	Literature triad fraction ^a			Calculated triad fraction ^b		
		F _{ABA}	F _{ABB}	F _{BBB}	F _{ABA}	F _{ABB}	F _{BBB}
40	1.26 ^c	0.236	0.506	0.258	0.125	0.457	0.418
60	1.26	0.241	0.501	0.258	0.125	0.457	0.418
80	1.02	0.214	0.497	0.289	0.125	0.425	0.481
100	1.26	0.260	0.503	0.243	0.125	0.457	0.418

^aData taken from Ref. 17. Monomer conversion was less than 2.5%.

^bMonomer conversion was assumed to be 2.0%.

^cThis value was misprinted in Ref. 8 as 12.6.

TABLE 7. Comparison of Literature [33] and Calculated Sequence Distributions in the Copolymerization of Acrylonitrile (A) and Methyl Methacrylate (B)

Polymer designation	Feed ratio $M_A:M_B$	Conversion wt%	% B in polymer		Literature triad fractions						Calculated triad fractions								
			Observed	Calculated	F_{BBA}^+			F_{BBA}^+			F_{BBA}^+			F_{BBA}^+					
					F_{BBB}	F_{ABB}	F_{ABA}	F_{BBB}	F_{ABB}	F_{ABA}	F_{BBB}	F_{ABB}	F_{ABA}	F_{BBB}	F_{ABB}	F_{ABA}			
T1	5:95	8.01	-	97.8	0.91	0.09	-	0.96	0.04	-	0.96	0.04	-	0.96	0.04	-	0.96	0.04	-
T2	10:90	7.74	92.8	95.4	0.82	0.18	0.01	0.86	0.13	0.01	0.86	0.13	0.01	0.86	0.13	0.01	0.86	0.13	0.01
T3	15:85	7.49	87.7	93.0	0.74	0.25	0.01	0.86	0.13	0.01	0.86	0.13	0.01	0.86	0.13	0.01	0.86	0.13	0.01
T4	20:80	7.00	84.3	90.5	0.65	0.32	0.03	0.81	0.18	0.03	0.81	0.18	0.03	0.81	0.18	0.03	0.81	0.18	0.03
T5	25:75	6.91	79.1	87.9	-	-	-	0.76	0.22	-	0.76	0.22	-	0.76	0.22	-	0.76	0.22	-
T6	30:70	6.87	78.0	85.1	-	-	-	0.71	0.27	-	0.71	0.27	-	0.71	0.27	-	0.71	0.27	-
T7	40:60	6.29	69.8	79.2	0.39	0.50	0.11	0.60	0.35	0.11	0.60	0.35	0.11	0.60	0.35	0.11	0.60	0.35	0.11
T8	50:50	5.78	65.1	72.6	0.29	0.53	0.18	0.48	0.42	0.18	0.48	0.42	0.18	0.48	0.42	0.18	0.48	0.42	0.18

T9	60:40	5.34	57.1	65.0	0.19	0.53	0.27	0.36	0.48	0.16
T10	70:30	4.72	49.2	56.0	-	-	-	0.24	0.50	0.26
T11	75:25	4.42	45.6	50.7	0.09	0.45	0.45	0.18	0.49	0.32
T12	85:15	3.78	34.0	37.4	-	-	-	0.08	0.41	0.51
D1	10:90	11.05	-	95.4	0.83	0.17	-	0.91	0.09	0.00
D2	15:85	11.18	86.4	92.9	0.73	0.25	0.02	0.86	0.13	0.01
D3	20:80	10.45	81.0	90.4	0.65	0.32	0.03	0.81	0.18	0.01
D5	30:70	10.6	76.5	85.0	0.49	0.43	0.08	0.71	0.27	0.03
D6	40:60	9.66	69.1	79.0	0.40	0.48	0.12	0.59	0.35	0.05
D7	50:50	5.20	62.4	72.6	0.27	0.53	0.20	0.48	0.42	0.09
D10	85:15	10.55	28.7	36.3	0.04	0.32	0.66	0.07	0.40	0.53

ficant factor in the variation between the literature and calculated triad distributions. Use of Harwood's program with monomer conversion between 1.0 and 2.5% did not substantially alter the calculated triad distributions detailed in Table 6.

Poly(1,1-Dichloroethylene-co-Methacrylonitrile) Sequence Distributions

The sequence distribution in copolymers of 1,1-dichloroethylene and methacrylonitrile was calculated by Harwood's program, and the results for triad distributions are summarized in Table 8. As might be expected, the agreement between the triad distributions calculated from the reactivity ratios experimentally determined by Suggate [33] (by the Kelen-Tüdös method [9, 10]) and the reactivity ratios determined from monomer ^{13}C -NMR data was quite good. Suggate determined the amount of 1,1-dichloroethylene present in the copolymer by polymer ^1H -NMR analysis [33]. This value and the values calculated with the Harwood program and both the literature reactivity ratios and the reactivity ratios derived from monomer ^{13}C -NMR spectral data were generally within experimental error for these copolymers. The differences in these values were somewhat greater for copolymers containing more than 50% 1,1-dichloroethylene.

Sodium Poly(Acrylamide-co-2-Acrylamido-2-Methylpropanesulfonate) Sequence Distribution

The computer program developed by Harwood [5] was then used to calculate the monomer sequence distribution in a series of sodium poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonate)s. Acrylamide content of the copolymers varied from 34.3 to 90.5 mol%. Input data were the reactivity ratios derived from monomer ^{13}C -NMR data, molecular weights of the comonomers, feed ratios, and the degree of conversion. Calculated diad distributions are summarized in Table 10 and are compared to reported diad distributions [28-30] and diad distributions determined from reactivity ratios calculated by the Mayo-Lewis procedure [30, 34]. The diad distributions reported by McCormick and Chen [28-30] were determined by the methods of Natta [38] and Igarashi [39]. Comparison of the diad distributions calculated by these three procedures indicated fairly close agreement. This may have been due in part to the fairly high degree of conversion in the actual copolymerization experiments. These same conversion values were used in the computer calculations. The main difference in the diad distributions calculated with Harwood's program appeared to be a somewhat greater tendency toward blockiness (A-A and B-B diad unit content) obtained with the reactivity ratios derived from monomer ^{13}C -NMR data.

The ^{13}C -NMR absorption frequencies of the olefinic carbon atoms of 2-acrylamido-2-methylpropanesulfonic acid did not vary greatly with solution pH. When the pH was increased from 0.5 to greater than 10, little change in the chemical shifts of the olefinic carbon atoms of this monomer was noted. However, in analogy with reported reactivity ratio determinations for copolymerizations of acrylamide with acrylic acid and methacrylic acid [18, 19], one would predict the composition and sequence distribution of poly(acrylamide-co-2-acrylamido-2-methylpropane sulfonic acid) to be dependent on polymerization reaction pH. For copolymerizations involving ionizing monomers, the accuracy of estimation of reactivity ratios and sequence distribution may vary with solution pH.

CONCLUSIONS

Generally the reactivity ratios calculated from comonomer ^{13}C -NMR chemical shifts of the olefinic carbon atoms of vinyl monomers were in reasonably good agreement with literature values. By using Harwood's program [5] for sequence distribution calculations, the copolymer microstructure may be calculated from these reactivity ratios and thus indirectly from the ^{13}C -NMR absorption frequencies of the olefinic carbon atoms of the vinyl monomers. These calculated sequence distributions are in fairly good agreement with those determined from copolymer ^{13}C -NMR analysis or calculated using other methods.

Modeling the copolymerization reaction conditions in the NMR experiment is helpful but not necessarily a panacea. The procedure is primarily intended for straightforward free-radical copolymerizations that can be described by a simple kinetic scheme. Ionic copolymerizations, reversible copolymerizations, heterogeneous copolymerizations, monomer-growing polymer chain complex formation, polymerization of a comonomer charge-transfer complex, chain transfer, branching, and steric effects on monomer and growing polymer chain reactivity would not be reflected in the comonomer ^{13}C -NMR spectra and thus cannot be taken into consideration.

The calculated reactivity ratios and sequence distributions for aqueous copolymerization of methacrylic acid and dimethylaminoethyl methacrylate and of acrylamide and sodium 2-acrylamido-2-methylpropane-sulfonate illustrate that reasonable estimates of the reactivity ratios and sequence distributions may be made even when physical effects (pH and resulting monomer ionization and hydration) associated with solvent variations were present.

While this method of estimating the reactivity ratios and sequence distributions does not yield precise results and certainly is not a substitute for experimental determination of these quantities, it may be used to predict reactivity ratios of monomers for which no Q and e values are known. The procedure is a very useful screening tool to

TABLE 8. Sequence Distribution in Copolymers of 1,1-Dichloroethylene (A) and Methacrylonitrile (B)

Mol% in monomer feed	Mol% A in copolymer, calculated		
	By NMR	Literature	This work
20.0	10 ± 1, 10.5 ± 1	9.2	11.4
30.0	14.5 ± 1	14.8	17.8
40.0	21 ± 2, 22 ± 1	21.3	24.8
50	27 ± 2	28.9	32.5
60	36 ± 2, 39 ± 1	37.9	41.3
70	48 ± 2	48.8	51.4
75	52 ± 2	55.1	57.1
80	60 ± 2	62.1	63.5
85	70 ± 3	69.9	70.7
90	79 ± 1	78.7	78.9
93	84 ± 1	84.5	84.4
94	88 ± 1, 87.6 ± 0.5	86.5	86.4
95	92 ± 1	88.6	88.4
96	94 ± 1, 92.8 ± 0.5	90.8	90.6
97	-	93.0	92.8
10	4.5 ± 1	4.3	5.5

Mol% in monomer feed	Triad distributions from literature reactivity ratios				Triad distributions from calculated reactivity ratios				
	F _{AAA}	F _{AAB}	F _{BAB}	F _{BBA}	F _{AAA}	F _{AAB}	F _{BAB}	F _{BBA}	
20.0	0.008	0.167	0.825	0.008	0.160	0.833	0.014	0.207	0.779
30.0	0.022	0.252	0.726	0.020	0.243	0.737	0.034	0.302	0.663
40.0	0.045	0.335	0.619	0.042	0.325	0.633	0.069	0.387	0.544
50	0.084	0.411	0.505	0.077	0.410	0.521	0.121	0.454	0.425
60	0.144	0.471	0.385	0.134	0.464	0.401	0.198	0.494	0.308
70	0.238	0.500	0.262	0.225	0.499	0.276	0.198	0.494	0.308
75	0.303	0.495	0.202	0.289	0.497	0.214	0.380	0.473	0.147
80	0.385	0.471	0.144	0.370	0.477	0.154	0.466	0.434	0.101
85	0.488	0.421	0.091	0.473	0.430	0.098	0.567	0.372	0.061
90	0.619	0.335	0.046	0.605	0.346	0.049	0.687	0.283	0.029
93	0.714	0.262	0.024	0.703	0.271	0.026	0.770	0.215	0.015
94	0.749	0.233	0.018	0.738	0.242	0.020	0.800	0.189	0.011
95	0.786	0.202	0.013	0.776	0.210	0.014	0.830	0.161	0.007
96	0.824	0.167	0.008	0.816	0.174	0.009	0.862	0.133	0.005
97	0.865	0.130	0.005	0.859	0.136	0.005	0.895	0.102	0.003
10	0.002	0.082	0.916	0.002	0.078	0.920	0.003	0.105	0.892

^aLiterature data taken from Ref. 35.

TABLE 9. Sequence Distribution of Copolymers of Ethyl Acrylate (A) and n-Butyl Methacrylate (B)

Feed ratio, % A	Copolymer composition, % A		Conversion, % by weight
	By NMR	Calculated [36]	
26.2	14.3, 14.1	11.9	9.2
48.6	31.7, 31.4	26.6	10.1
58.7	43.4, 41.7, 37.7	35.1	8.7
68.0	49.5, 45.5	44.7	9.4
85.0	78.2, 82.1	68.6	11.5

Feed ratio, % A	Total distribution from literature reactivity ratios						Triad distribution from calculated reactivity ratio					
	F _{AAA}	F _{AAB}	F _{BAB}	F _{FABA}	F _{BBA}	F _{BBB}	F _{AAA}	F _{AAB}	F _{BAB}	F _{FABA}	F _{BBA}	F _{BBB}
26.2	0.013	0.202	0.785	0.014	0.211	0.774	0.016	0.223	0.761	0.018	0.235	0.747
48.6	0.066	0.382	0.552	0.072	0.393	0.535	0.080	0.405	0.515	0.088	0.417	0.494
58.7	0.117	0.450	0.433	0.126	0.458	0.416	0.138	0.467	0.395	0.150	0.475	0.375
68.0	0.193	0.492	0.315	0.206	0.496	0.298	0.221	0.498	0.280	0.238	0.500	0.262
85.0	0.466	0.433	0.101	0.483	0.424	0.093	0.502	0.413	0.085	0.522	0.401	0.077

TABLE 10. Sequence Distribution in Copolymers of Acrylamide (A) and Sodium 2-Acrylamido-2-Methylpropanesulfonate (B)

Polymer designation	mol%		Diad	Reported distribution	Percent conversion	Reported r_A, r_B [28-30]	Calculated distribution based on	
	Am	NaAMPS					r_A, r_B	Calculated r_A, r_B
AMPS 1-5			Am-Am	0.822	28.67	0.823	0.732	
	90.5	9.5	Am-NaAMPS	0.166		0.172	0.251	
			NaAMPS-NaAMPS	0.012		0.005	0.018	
AMPS 2-5			Am-Am	0.641	50.05	0.663	0.550	
	81.0	19.0	Am-NaAMPS	0.338		0.317	0.392	
			NaAMPS-NaAMPS	0.021		0.019	0.058	
AMPS 3-5			Am-Am	0.500	51.07	0.530	0.403	
	72.1	27.9	Am-NaAMPS	0.443		0.426	0.479	
			NaAMPS-NaAMPS	0.057		0.044	0.118	
AMPS 4-5			Am-Am	0.350	49.82	0.403	0.277	
	62.4	37.6	Am-NaAMPS	0.548		0.513	0.521	
			NaAMPS-NaAMPS	0.102		0.083	0.202	
AMPS 7-5			Am-Am	0.082	53.04	0.127	0.068	
	34.3	65.7	Am-NaAMPS	0.522		0.558	0.415	
			NaAMPS-NaAMPS	0.396		0.315	0.517	

design copolymers of a particular monomer having a desired sequence distribution. Since determination of monomer reactivity ratios normally requires tedious experimental measurement of copolymer composition for different monomer feed ratios, the time savings by using the method described here to estimate reactivity ratios and sequence distributions is substantial.

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