Cyclopolymerization.   V.   Copolymerization of Acrylic and Methacrylic Anhydrides with Vinyl Monomers

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Synopsis

The copolymerizations of acrylic (AA) and methacrylic (MAA) anhydrides (M_1) with styrene (St) and methacrylonitrile (MAN) have been examined; similarly that of acrylic anhydride with allyl chloride.   In these systems the reactivity ratio of an open unit radical (r_1) is equal to that of a cyclized radical (r_3), and the usual Alfrey-Price equation is valid.   By using a graphical method the ratios of the cross propagation rate constant to the cyclization rate constant (k_{12}/k_c) have been also evaluated.   The following values for r_1, r_2, and k_{12}/k_c respectively have been found, M_1 being the anhydride: for the system AA (M_1)–St, 0.1, 0.17, and 4; for the system AA–MAN, 0.9, 0.04, and 0.14; for the system AA–allyl chloride, 11.5, 0.01, and 0.   For the same systems with MAA, the values of r_1, r_2, and k_{12}/k_c were 0.26, 0.12, and 0.2 with St, and 1.6, 0.27, and about zero with MAN.   These data indicate also that the cyclization reaction is always more pronounced for methacrylic anhydride than for the acrylic anhydride.

I. INTRODUCTION

The copolymerization of divinyl monomers undergoing cyclization with another monomer has been considered by several authors from the point of view of the solubility of the copolymers; in this sense the copolymerizations of diallyl ether with maleic anhydride[1] and of diallyldimethylammonium chloride with acrylonitrile and acrylamide[2] have been described.

Marvel and Vest studied the copolymerization of α,α'-dimethylene-pimelic dinitrile and dimethyl ester with acrylonitrile and methyl acrylate and showed also the influence of the monomer ratio on the solubility, and consequently on the degree of branching and crosslinking of the copolymers.[3]   Similarly, Milford pointed out the influence of the monomer concentration on the solubility of various copolymers of substituted heptadienes.[4]

More recently Matsoyan and co-workers have especially studied the copolymerization of several divinyl acetals with each other or with foreign vinyl monomers; they obtained soluble and fusible divinylbutyral–styrene copolymers.[5]

A quantitative study has been published by one of us[6] on the case of the copolymerization of vinyl cinnamate, and a more elaborate kinetic analysis of the phenomena has been proposed, assuming an addition of vinyl cinna-

mate essentially through the vinyl group, and consequently one type of growing radical M_1^*.

In the present paper the same kinetic scheme has been applied to the study of the copolymerization of acrylic and methacrylic anhydrides on the basis of their symmetrical structures.

Hwa and Miller[7] have already examined the copolymerization of methacrylic anhydride with vinyl monomers and considered the kinetic requirements for producing a soluble copolymer. They assumed that the rate of cyclization is very much greater than the rate of bimolecular propagation with a new anhydride or comonomer molecule. On this basis they obtained a copolymer composition equation similar to the common Alfrey-Price equation, in which the reactivity ratios measure the competition between a methacrylic group and the comonomer for the cyclized radical and for the chain radical ending in the comonomer. Moreover they showed that soluble copolymers were more likely to form: (*1*) the less reactive the comonomer (e.g., with benzyl vinyl sulfone, 2-chloroethyl vinyl ether, and allyl urea, allyl chloroacetate soluble products are obtained, while with styrene and methyl and hexyl methacrylate the copolymers are always insoluble); (*2*) the greater the dilution (the cyclization rate being unimolecular is independent of the concentration); (*3*) the lower the conversion; (*4*) the greater the difference in moles of the two components in the charge.

It must be pointed out that no determination of unsaturation was reported by these authors. Moreover with highly reactive monomers, such as methacrylates, styrene, and ethyl acrylate, the conversions were too high to permit an evaluation of copolymerization parameters. One major difference between their results[7] and ours[8] consists in their claim that pure methacrylic anhydride cyclopolymerizes without gelation; the validity of their solubility criterion, however, may be contested, because on heating at 130–150°C. intramolecular cyclic anhydride formation may proceed easily between neighboring side chains.

Nevertheless, as far as possible, a comparison between the results will be established and discussed in the present paper.

II. COPOLYMER COMPOSITION EQUATIONS

As shown previously by Roovers and Smets,[6] the copolymerization of a diene monomer undergoing cyclization involves at least six bimolecular propagation steps besides the monomolecular cyclization reaction. Assuming steady-state conditions, the copolymer composition equation becomes:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left\{ \frac{r_1[M_1] + [M_2] + K'_c}{r_2[M_2] + [M_1] + K'_c \left(\frac{r_2[M_2] + [M_1]}{r_3[M_1] + [M_2]} \right)} \right\} \tag{1}$$

where $[M_1]$, $[M_2]$, r_1, and r_2 have the usual significance, while $r_3 = k_{31}/k_{32}$ is the reactivity ratio of the cyclized radical towards the monomers M_1 and

M_2, and $K_c = k_c/k_{11}$, and $K'_c = k_c/k_{12}$ are the ratios of the monomolecular cyclization rate constant k_c to that of monomer and comonomer addition to an open unit.

Equation (1) relates the copolymer composition to the absolute monomer concentration; it becomes equal to the usual Alfrey-Price equation, when the cyclization constants K_c and K'_c are very high, or when r_1 is equal to r_3.

Similarly the ratio of polymerized diene monomer (M_1) to the amount of cyclized units in the copolymer (m) can be expressed by

$$\frac{d[M_1]}{d[m]} = 1 + \frac{[M_1]}{K_c} + \frac{[M_2]}{K'_c} \qquad (2)$$

this equation relates the copolymer composition and the degree of cyclization to the cyclization parameters K_c and K'_c.

When the degree of cyclization of the diene is independent of the presence of the second monomer ($k_{12} \rightarrow 0$) these equations give on simplification:

$$\frac{d[M_1]}{d[M_2]} = \left\{ \frac{[M_1]}{[M_2]} \left(\frac{r_3[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right) \right\} \left(1 + \frac{[M_1]}{K_c} \right) \qquad (3)$$

$$\frac{d[M_1]}{d[m]} = 1 + \frac{[M]_1}{K_c} \qquad (4)$$

III. RESULTS

Copolymerization with Styrene and Methacrylonitrile

The cyclocopolymerization of acrylic and methacrylic anhydrides with styrene and methacrylonitrile have been examined and compared to each other. Both comonomers are unreactive toward the anhydride function; moreover the copolymers are soluble in cyclohexanone and their composition can be easily determined by chemical analysis.
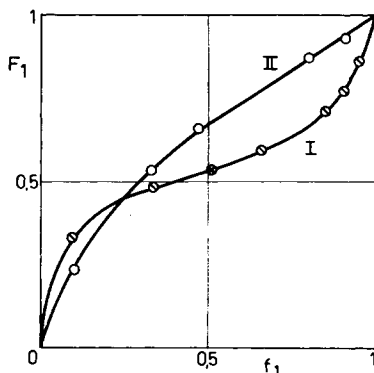

Fig. 1. Copolymerization of methacrylic anhydride with (I) styrene and (II) with methacrylonitrile.

As can be seen from Tables I and II, at the same monomer ratio, the copolymer composition is independent of the overall monomer concentration in both cases, i.e. $r_3 = r_1$; consequently the usual Alfrey-Price equation can be used instead of the more elaborate one. The reactivity ratios r_1 and r_2 were evaluated by the method of Fineman and Ross[8] (Figs. 1 and 2).
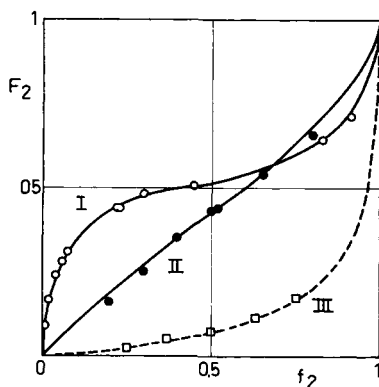

Fig. 2. Copolymerization of acrylic anhydride with (*I*) styrene, (*II*) with methacrylonitrile, and (*III*) with allyl chloride.
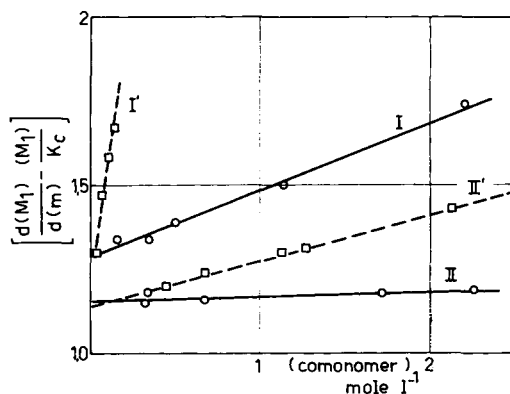

Fig. 3. Copolymerization of methacrylic anhydride (—) and acrylic anhydride (- -) with (*I*) styrene and (*II*) with methacrylonitrile. Determination of $K_c' = k_c/k_{12}$.

The different K'_c values were determined graphically by plotting $\{(d[M_1]/d[m]) - ([M_1]/K_c)\}$ versus the comonomer concentration (M_2) in agreement with the eq. (2). The values of K_c for acrylic and methacrylic anhydrides used in this equation have been determined and are equal respectively to 6 and 45 per C=C bond.[9] Some of the data summarized in Tables I and II are represented in Figure 3. F_2 and f_2 represent the mole fractions of monomer M_2 in the copolymer and the unreacted monomer mixture, respectively.

TABLE I
Copolymerization of Methacrylic Anhydride (M_1)[a]

Comonomer (M_2)	$[M_1]$, mole/l.	$[M_2]$, mole/l.	$[M_1]$ $+[M_2]$, mole/l.	f_2	F_2	F_1 Unsat. units	Cyclized units	$\dfrac{d[M_1]}{d[m]}$ $-\dfrac{[M_1]}{K_c}$
Styrene	1.271	1.271	2.542	0.5	0.484			
	1.656	1.656	3.312	0.5	0.473			
	2.21	2.21	4.421	0.5	0.47	0.25	0.28	1.74
	3.167	0.163	3.33	0.049	0.14	0.28	0.58	1.34
	3.052	0.345	3.397	0.101	0.22	0.25	0.52	1.34
	2.979	0.502	3.481	0.145	0.29	0.25	0.47	1.39
	2.253	1.144	3.397	0.335	0.41	0.22	0.37	1.50
	1.156	2.244	3.40	0.66	0.52			
	0.34	3.06	3.40	0.9	0.67			
Methacrylonitrile	3.618	0.905	4.523	0.2	0.13			
	2.703	0.676	3.379	0.2	0.13	0.22	0.65	1.16
	1.348	0.337	1.685	0.2	0.13			
	3.071	0.318	3.389	0.094	0.07	0.22	0.71	1.15
	1.356	0.329	1.685	0.195	0.13	0.22	0.65	1.18
	1.497	1.725	3.222	0.53	0.34	0.16	0.50	1.18
	1.127	2.276	3.403	0.67	0.47	0.12	0.41	1.19
	0.34	3.06	3.40	0.9	0.76			

[a] Temperature 36.6°C.; [AIBN] $= 0.02$ mole/l.

The plot corresponding to eq. (4) is represented by Figure 4; the slope indicates a K_c value of six, while the intercept at the ordinates is equal to 1.1 instead of one. These results agree remarkably with the data from homopolymerization experiments previously described.[9]
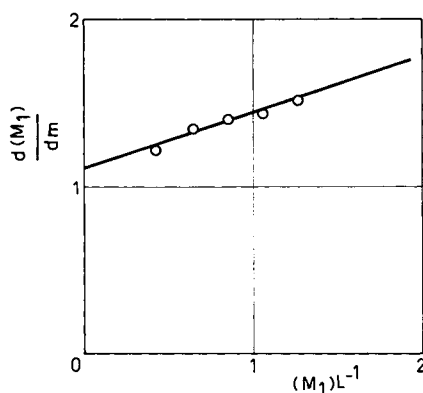

Fig. 4. Copolymerization of acrylic anhydride with allyl chloride. Determination of K_c.

Copolymerization with Allyl Chloride

The low reactivity value of allyl chloride with respect to acrylic derivatives[10−14] makes the system allyl chloride–acrylic anhydride more simple

TABLE II
Copolymerization of Acrylic Anhydride (M₁)ᵃ

Copolymerization of Acrylic Anhydride (M_1)[a]

Comonomer (M_2)	[M_1], mole/l.	[M_2], mole/l.	[M_1] +[M_2], mole/l.	f_2	F_2	F_1 Unsat. units	F_1 Cyclized units	$\dfrac{d[M_1]}{d[m]} = \dfrac{[M_1]}{K_c}$
Styrene	5.152	1.515	6.66	0.227	0.44			
	3.24	0.95	4.19	0.227	0.44			
	1.94	0.57	2.51	0.227	0.44			
	1.275	1.042	2.137	0.449	0.505			
	1.275	0.554	1.829	0.302	0.48			
	1.275	0.361	1.639	0.219	0.44			
	1.717	0.145	1.862	0.077	0.31	0.38	0.31	1.67
	1.717	0.11	1.827	0.06	0.28	0.39	0.33	1.58
	1.717	0.076	1.793	0.042	0.24	0.39	0.37	1.47
	1.717	0.041	1.758	0.023	0.17	0.39	0.44	1.3
	1.717	0.019	1.737	0.011	0.094			
	0.385	1.77	2.055	0.83	0.64			
	0.112	1.170	1.282	0.913	0.71			
Methacrylo-nitrile	1.449	0.944	2.393	0.4	0.35			
	2.863	1.861	4.724	0.4	0.36			
	2.931	1.90	4.831	0.4	0.35			
	1.81	0.45	2.26	0.2	0.16	0.38	0.46	1.20
	1.58	0.68	2.26	0.3	0.25	0.33	0.42	1.24
	1.13	1.13	2.26	0.5	0.43	0.23	0.34	1.3
	0.45	1.81	2.26	0.8	0.656			
	1.175	1.269	2.444	0.52	0.44	0.23	0.33	1.31
	1.178	2.13	3.318	0.65	0.54	0.21	0.25	1.43

ᵃ Temperature 35°C.; [AIBN] = 0.02 mole/l.

than those with styrene and methacrylonitrile, and it may be expected that equations (3) and (4) will be valid in this particular case. Indeed as can be seen from Table III, allyl chloride is only poorly incorporated in the copolymers, and exerts practically no influence upon the degree of cyclization of acrylic anhydride polymers (about 65%); the addition of allyl chloride proceeds only with the cyclized radical. The copolymer composition diagram is given in Figure 2, curve III.

TABLE III
Copolymerization of Acrylic Anhydride with Allyl Chloride (M₂)ᵃ

[M_1], mole/l.	[M_2], mole/l.	f_2	F_2	F_1 Unsat. units	F_1 Cyclized units	$\dfrac{d[M_1]}{d[m]}$
1.277	0.425	0.25	0.027	0.329	0.644	1.51
1.064	0.638	0.37	0.053	0.292	0.655	1.44
0.851	0.851	0.50	0.076	0.279	0.645	1.40
0.638	1.064	0.63	0.117	0.230	0.653	1.35
0.425	1.277	0.75	0.175	0.151	0.674	1.22

ᵃ Temperature = 35°C.; [AIBN] = 0.02 mole/l.; [M₁] + [M₂] = 1.702 mole/l.

TABLE IV
Copolymerization Data of Acrylic and Methacrylic Derivatives

M_1	Styrene			Methacrylonitrile			Allyl chloride			
	$r_1 = r_3$	r_2	k_{12}/k_c	$r_1 = r_3$	r_2	k_{12}/k_c	r_3	r_2	k_{12}/k_c	k_{11}/k_c
Acrylic anhydride	0.1	0.17	4	0.9	0.4	0.14	11.5	0.01	0	0.17
Acrylic acid	0.25	0.15[a]					—			—
Acrylonitrile	0.07	0.37[b]		0.32	2.68[c]					
2-Hydroxyethyl acrylate							8.85	0.016[a]		0.22
Methacrylic anhydride	0.26	0.12	0.2	1.6	0.27	Very low				
Methacrylic acid	0.7	0.15[a]		1.63	0.59[c]					
Methacrylonitrile	0.16	0.3[f]								

[a] Data of Chapin et al.[15]
[b] Data of Thompson and Raines.[16]
[c] Data of Okamura and Yamashita.[17]
[d] Data of Ioshi and Kapur.[18]
[e] Data of Cameron et al.[19]
[f] Data of Lewis et al.[20]

IV. DISCUSSION

The copolymerization ratios and cyclization constants for both anhydrides are summarized in the Table IV, together with some values for other acrylic and methacrylic derivatives given in the literature.

For both anhydrides the copolymer composition was independent of the overall monomer concentration, i.e., r_1 is equal to r_3. The same result was recently found for divinyl acetals[21] and seems to be a general rule for symmetric dienes.

TABLE V

Monomer polarities	e
Methyl methacrylate	+0.4
Methyl acrylate	+0.6
Methacrylonitrile	+1
Methacrylic anhydride	+1.1
Acrylonitrile	+1.2
Acrylic anhydride	+1.2
Acrylic acid	+1.3

From their r_1r_2 values toward styrene the polarities e of acrylic and methacrylic derivatives can be ranged in order in the series, shown in Table V, e for styrene being equal to -0.8.

Acrylic derivatives are thus always more positive than their methacrylic homologs, and the same statement can be made from the r_1r_2 values towards methacrylonitrile, differences of polarity Δe of 0.9 and 1.0 being found for methacrylic and acrylic anhydride, respectively. The polarity values, however, in this system are shifted to much higher values, when compared to styrene.

Cross propagation reactions are enhanced by a great difference of polarity between the monomers; for methacrylic anhydride $1/r_1r_2$ is equal to 32 with respect to styrene while only 2.3 with methacrylonitrile. Moreover, the intramolecular cyclization reaction is strongly dominant in the presence of methacrylonitrile. On the other hand, as could be expected from the homopolymerization data, the cyclization tendency is most pronounced for methacrylic anhydride due to the presence of the α-methyl groups.

V. EXPERIMENTAL

The monomers were commercially available products. Before use they were freshly distilled under reduced nitrogen atmosphere.

The copolymerizations were carried out in high vacuum sealed tubes in cyclohexanone solution at 35°C. in the case of acrylic anhydride and at 36.6°C. for methacrylic anhydride. The degree of conversion never exceeds 10%. The copolymers of acrylic anhydride with methacrylonitrile and allyl chloride were precipitated by pouring the solution in dry hexane; acrylic anhydride–styrene copolymers and methacrylic anhydride copoly-

mers were precipitated in dry diethyl ether. The copolymers were filtered off, washed and dried in vacuum at room temperature to constant weight.

The methacrylonitrile content was determined by the Kjeldahl method, that of allyl chloride with the method of Schöniger and Volhardt, that of styrene by elemental C/H/O determinations (A. Bernhardt, Mikroanalytisches Laboratorium, Mülheim, Germany).

The unsaturation of the copolymers was determined by the bromometric method of Polgar and Jungnickel as for the homopolymers.[22] The copolymers were dissolved in 0.1N sodium hydroxide; thereafter the solution was neutralized at pH 6 and treated with bromine. The excess of bromine was determined iodometrically. The applicability of this method to copolymers as well as its reliability have been determined. Acrylic acid–styrene and acrylic acid–methacrylonitrile copolymers are inert toward bromine in the same experimental conditions.

VI. CONCLUSIONS

The intramolecular cyclization reaction of acrylic and methacrylic anhydrides is dependent on the presence of foreign monomers, especially when the polarities of the double bonds differ considerably. The tendency for cyclization is always most pronounced for methacrylic anhydride. The reactivity ratios of open and cyclized unit radicals are identical ($r_1 = r_3$); consequently the normal Alfrey-Price copolymerization equation is valid for these symmetrical dienes.

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Résumé

On a étudié la copolymérisation des anhydrides (M_i) acrylique (AA) et méthacrylique (MAA) avec le styrène (St) et le méthacrylonitrile (MAN), de même qu'avec le chlorure d'allyle dans le cas de l'anhydride méthacrylique. Le rapport de réactivité d'un radical correspondant à un diène (r_1) ouvert est égal à celui d'un radical cyclisé (r_3), de sorte que l'équation habituelle d'Alfrey-Price reste valide. Sur la base d'une méthode graphique, on a pu évaluer également les rapports de la constante de vitesse de propagation croisée à celle de cyclisation intramoléculaire (k_{12}/k_c). Les valeurs suivantes de r_1, r_2 et (k_{12}/k_c) ont été trouvées, M_1 désignant l'anhydride: pour la paire AA–St, 0.1, 0.17, et 4; pour la paire AA–MAN, 0.9, 0.04, et 0.14; pour la paire AA–chlorure d'allyle, 11.5, 0.01, et 0. Pour le système MAA–St on a trouvé 0.26, 0.12, et 0.2; et pour le système MAA–MAN, 1.6, 0.27, et environ zéro. De ces résultats il résulte également que la cyclisation est toujours beaucoup plus prononcée avec l'anhydride méthacrylique qu'avec l'anhydride acrylique.

Zusammenfassung

Die Copolymerisation von Acrylsäure-(AA)- und Methacrylsäure-(MMA)- anhydrid (M_1) mit Styrol (St) und Methacrylnitril (MAN) wurde untersucht, und ebenso diejenige von Acrylsäureanhydrid mit Allylchlorid. Bei diesen Systemen ist das Reaktivitätsverhältnis eines Radikals des offenen Bausteins (r_1) gleich demjenigen eines cyklisierten Radikals (r_3) und die übliche Alfrey-Price-Gleichung erweist sich als gültig. Mit Hilfe einer graphischen Methode wurde auch das Verhältnis der Geschwindigkeitskonstanten für das gekreuzte Wachstum zu der Geschwindigkeitskonstanten der Cyklisierung (k_{12}/k_c) ermittelt. Folgende Werte wurden für r_1, r_2 bzw. k_{12}/k_c, mit Anhydrid = M_1 gefunden: für das System AA(M_1)-St 0,1, 0,17 und 4; für das System AA-MAN 0,9, 0,4 und 0,14; für AA-Allylchlorid 11,5, 0,01 und 0. Für MAA waren sie gleich 0,26, 0,12 und 0,2 mit Styrol und 1,6, 0,27 und etwa 0 mit MAN. Diese Ergebnisse zeigen auch, dass die Cyclisierungsreaktion bei Methacrylsäureanhydrid immer stärker ausgeprägt ist als bei Acrylsäureanhydrid.