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Studies on the Polymerization of Methacrylic Esters

Part III. Copolymerization of *n*-Butyl Methacrylate and Isobutyl Methacrylate with Vinyl Acetate and Acrylonitrile

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SUMMARY:

Copolymerizations of *n*-butyl methacrylate and isobutyl methacrylate with acrylonitrile and vinyl acetate as comonomers have been studied and the reactivity ratios of the monomers in copolymer reactions computed.

ZUSAMMENFASSUNG:

Die Copolymerisation von *n*-Butylmethacrylat und Isobutylmethacrylat mit Acrylnitril und Vinylacetat wurde untersucht und die Copolymerisationsparameter berechnet.

Studies on the copolymerization of different monomers are of considerable importance inasmuch as they lead to suitable modification of the properties of the resulting product. The reactivities of different monomers may also be compared through studies of this kind. From a theoretical point of view, it is the reactivity ratios rather than the kinetic investigations which have received the greater attention. The formation of true, random or alternate copolymers depends on the nature of the monomer pairs and their reactivities, and the activities of the free radicals that are formed in solution. In the present paper, copolymerizations of *n*-butyl methacrylate and isobutyl methacrylate with acrylonitrile and vinyl acetate as comonomers are reported.

Theoretical

The copolymer composition equation¹⁾ (given below) gives the relation between the rate of disappearance of two monomers $d[M_1]/d[M_2]$ in a copolymerization reaction and their reactivity ratios,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (1)$$

¹⁾ T. ALFREY and G. GOLDFINGER, J. chem. Physics **12** (1944) 205.

Where $[M_1]$ and $[M_2]$ represent the concentrations of the two monomers M_1 and M_2 and r_1 and r_2 are the reactivity ratios of the two monomers respectively.

When the conversion to polymer is low, (say upto about 10%) $d[M_1]/d[M_2]$ can be taken to be the same as the ratio of the two monomers in the copolymer, m_1/m_2 .

So we can rewrite Eq. (1) as

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (2)$$

or

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{m_2}{m_1} \left(1 + \frac{[M_1]}{[M_2]} r_1 \right) - 1 \right] \quad (3)$$

Thus any one experiment determines one straight line in the plot of r_1 against r_2 . The point of intersection of the lines resulting from different experiments gives the values of r_1 and r_2 . In practice, however, all lines do not pass through the same point, but will define an area which is characteristic of the errors involved in the determination of the reactivity ratios. Generally, the centroid of the triangle with the least area is taken to represent r_1 and r_2 values for the system.

When conversion is high the integrated form of Eq. (3) may be used.

Experimental

Purified monomers, *n*-butyl methacrylate, isobutyl methacrylate, vinyl acetate and acrylonitrile were fractionally distilled before use. The copolymerizations of *n*-butyl methacrylate and isobutyl methacrylate with vinyl acetate and acrylonitrile were carried out by mixing the methacrylic ester with the other comonomer in various proportions using benzoyl peroxide (0.1% by weight of monomer mixture) as initiator. The polymerizations were carried out in sealed pyrex glass tubes at 59.8°C. and were generally stopped at low conversions. Acetone-dimethylformamide mixture was used as solvent for the copolymers containing acrylonitrile and pure acetone for the other copolymers. Aqueous methanol was used as precipitant. In all the cases the copolymers were reprecipitated several times, and dried under vacuum at 40°C.

In the case of copolymers containing acrylonitrile, the copolymer composition was determined by estimating the amount of nitrogen in a known weight of the copolymer by the micro-combustion (DUMAS) method. For the copolymers of methacrylic esters and vinyl acetate microcombustion analysis of carbon and hydrogen was followed.

Results

1. Copolymerization of *n*-butyl methacrylate and isobutyl methacrylate with acrylonitrile

Since the conversions were reasonably low the Eq. (3) was used to calculate the reactivity ratios. The plot of r_1 against r_2 was made for both the systems. The centroid of the triangles obtained was taken in each

case. For the system *n*-butyl methacrylate – acrylonitrile the values of r_1 and r_2 are found to be 1.08 and 0.31 respectively. In the case of isobutyl methacrylate and acrylonitrile r_1 and r_2 are obtained as 1.04 and 0.21 respectively.

Table I. Composition of the monomer feed and the copolymer formed

		$\left. \begin{array}{l} n\text{-Butyl methacrylate} \\ \text{Isobutyl methacrylate} \end{array} \right\} \text{ monomer } M_1$			$\left. \begin{array}{l} \text{Acrylonitrile} \end{array} \right\} \text{ monomer } M_2$	
Monomer M_1	Expt. No.	Composition of monomer feed		Per- centage con- version	Composition of copolymer	
		$[M_1]$ (moles $\cdot 10^2$)	$[M_2]$ (moles $\cdot 10^2$)		m_1 (moles $\cdot 10^2$)	m_2 (moles $\cdot 10^2$)
<i>n</i> -Butyl methacrylate	1	1.056	5.024	3.232	0.0534	0.1109
	2	1.584	3.768	3.612	0.0753	0.0876
	3	2.113	2.512	4.013	0.0961	0.0704
	4	2.640	1.256	7.984	0.2174	0.0826
Isobutyl methacrylate	1	1.035	5.024	5.957	0.1040	0.1858
	2	1.552	3.768	7.000	0.1475	0.1597
	3	2.070	2.512	6.354	0.1533	0.1014
	4	2.588	1.256	8.750	0.2355	0.0857

2. Copolymerization of *n*-butyl methacrylate and isobutyl methacrylate with vinyl acetate

Table II. Composition of the monomer feed and the copolymer formed

		$\left. \begin{array}{l} n\text{-Butyl methacrylate} \\ \text{Isobutyl methacrylate} \end{array} \right\} \text{ monomer } M_1$			$\left. \begin{array}{l} \text{Vinyl acetate} \end{array} \right\} \text{ monomer } M_2$	
Monomer M_1	Expt. No.	Composition of monomer feed		Per- centage con- version	Composition of copolymer	
		$[M_1]$ (moles $\cdot 10^2$)	$[M_2]$ (moles $\cdot 10^2$)		m_1 (moles $\cdot 10^2$)	m_2 (moles $\cdot 10^2$)
<i>n</i> -Butyl methacrylate	1	1.056	3.580	6.633	0.6618	0.0701
	2	1.584	2.685	7.071	0.6798	0.0402
	3	2.113	1.790	7.927	0.6923	0.0196
Isobutyl methacrylate	1	1.164	3.357	7.141	0.6738	0.0502
	2	1.552	2.685	9.486	0.6803	0.0394
	3	2.070	1.790	11.74	0.6923	0.1965

As in the previous case here also Eq. (3) was made use of for calculating the reactivity ratios. For the system *n*-butyl methacrylate – vinyl acetate r_1 and r_2 are obtained as 28.8 and 0.023 respectively. In the isobutyl methacrylate-vinyl acetate system, we get r_1 and r_2 as 29.8 and 0.025 respectively.

Discussion

For the system *n*-butyl methacrylate-acrylonitrile the reactivity ratios are 1.08 and 0.31 respectively as already mentioned. The product of the reactivity ratios, $r_1 \cdot r_2$ is 0.3348. The values of r_1 and r_2 for the system isobutyl methacrylate – acrylonitrile are 1.04 and 0.21 respectively. The value of $r_1 \cdot r_2$ for this system is 0.2184. These results compare satisfactorily with that reported for the copolymerization of the system methyl methacrylate-acrylonitrile²⁾ where r_1 and r_2 are 1.35 and 0.18 respectively and the product $r_1 \cdot r_2$ is 0.243.

In the copolymerization of *n*-butyl methacrylate with vinyl acetate the reactivity ratios obtained are 28.8 and 0.023 respectively. The product $r_1 \cdot r_2$ for this system is 0.6624. Whereas for the system isobutyl methacrylate – vinyl acetate the values of r_1 and r_2 are 29.8 and 0.025 respectively and $r_1 \cdot r_2$ is 0.7450. The values of r_1 and r_2 reported for the system methyl methacrylate – vinyl acetate³⁾ are 20 and 0.015 respectively. The product $r_1 \cdot r_2$ in this case is 0.300. Our results are in satisfactory agreement with the values reported for the system methyl methacrylate – vinyl acetate.

This study reveals that the methacrylic ester chain prefers to add its own monomer as compared with acrylonitrile and vinyl acetate. It is also evident from the results that the tendency of the methacrylic esters to add their own monomers in preference to the second monomer is more pronounced in the copolymerization with vinyl acetate than in the copolymerization with acrylonitrile.

For the systems reported in this paper the product $r_1 \cdot r_2$ is less than unity, which indicates that for these systems the alternation tendency predominates over the occurrence of sequence of like units, thus tending to give true copolymers. The value of r_1 in all the cases studied is greater than one, though the deviation from unity in the system methacrylic

²⁾ F. M. LEWIS, F. R. MAYO, and W. F. HULSE, J. Amer. chem. Soc. **67** (1945) 1701.

³⁾ F. R. MAYO, C. WALLING, F. M. LEWIS, and W. F. HULSE, J. Amer. chem. Soc. **70** (1948) 1523.

ester-acrylonitrile is not much. This shows that in the copolymers formed the respective methacrylic ester will be in greater proportion than in the monomer feed.

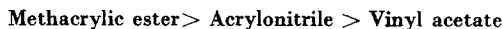
The relative reactivity of the monomer with *n*-butyl methacrylate radical may be expressed as follows (taking the reactivity of *n*-butyl methacrylate monomer to its own radical as equal to one).

<i>n</i> -Butyl methacrylate	= 1
Acrylonitrile	= 1/1.08 = 0.9260
Vinyl acetate	= 1/28.8 = 0.0347

Similarly for isobutyl methacrylate we have

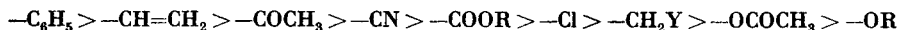
Isobutyl methacrylate	= 1
Acrylonitrile	= 1/1.04 = 0.9616
Vinyl acetate	= 1/29.8 = 0.0336

Hence towards methacrylic ester free radical it is found that the relative reactivities are in the order

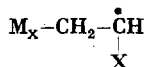


Thus we find that towards methacrylic ester free radicals acrylonitrile monomer is more reactive than vinyl acetate monomer. This can be explained qualitatively in terms of the structures of the two monomers. Acrylonitrile is a conjugated monomer and hence should be more reactive than vinyl acetate which is unconjugated.

MAYO and WALLING⁴⁾ have shown that the effect of substituents in increasing the reactivity of monomers towards radicals are in the order



and this order is in agreement with increasing stabilization of the product radical



due to resonance. Hence we may expect the acrylonitrile monomer to be more reactive than vinyl acetate monomer towards methacrylic ester free radicals.

⁴⁾ F. R. MAYO and C. WALLING, Chem. Reviews **46** (1950) 191.