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Kinetic Investigations of the Copolymerization of Ethyl Acrylate and Acrylonitrile with Maleic Anhydride

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KINETIC INVESTIGATIONS OF THE COPOLYMERIZATION OF ETHYL ACRYLATE AND ACRYLONITRILE WITH MALEIC ANHYDRIDE

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ABSTRACT

The copolymerization of maleic anhydride with ethyl acrylate (I) in 1,2-dichloroethane and with acrylonitrile (II) in acetone at 50°C with AIBN as initiator was investigated. The ν_{Br} curves show no maximum. The ν_{Br} values and molecular weights decrease with the molar fraction x_{MAN} . The r values for both pairs of monomers were determined. For I, k_{St} , k_Z , and f were also ascertained and ν_{Br} curves calculated, and they are compared with the experimental results.

INTRODUCTION

The copolymerization of donor monomers, such as styrene, vinyl acetate, and different vinyl ethers, with maleic anhydride (MAN) has been reported extensively. By comparison, there is relatively little work dealing with mono-

mers that show positive e values with little or no EDA interaction with MAn. Among these are acrylic acid esters and acrylonitrile (AN). Many kinetic studies of the copolymerization of methyl methacrylate (MMA) and methyl acrylate (MA) have been reported [1-4]. In these, a maximum was found in the curve of ν_{B_1} for MMA/MAn. There are few experimental results concerning the monomer pairs investigated in this work. For AN/MAn, however, experimentally found r values have been reported [5].

According to the Q and e values of ethyl acrylate (EA) and AN, no alternating copolymers can be expected for copolymerization with MAn. The introduction of MAn into the copolymers and the dependence of ν_{B_1} on x_{MAn} are of special interest, particularly because the ν_{B_1} maximum observed by Blackley and Melville [1] for MMA/MAn has not, until now, been understood.

EXPERIMENTAL

Purification of Monomers and Solvents

Stabilizer was removed from EA and AN in the usual way by use of 5% aqueous sodium hydroxide. After drying over CaH_2 , these monomers were fractionated in vacuo under argon. In the case of EA, copper chips were added to inhibit polymerization. 1,2-Dichloroethane (DCE) was dried by refluxing over CaH_2 for 12 h and fractionated under argon. Acetone was dried by means of P_2O_5 .

Polymerization

The EA/MAn copolymerization was followed dilatometrically in 20-mL dilatometer ampules fitted with capillaries and ground joints. The AN/MAn copolymerization was followed gravimetrically by means of the ampule technique.

For the experiments with EA/MAn, MAn for four dilatometers was degassed in one ampule by repeated melting in vacuo and already degassed EA and DC were condensed in. AIBN initiator was added to the dilatometers as DCE solution (2 mL), and the solvent evaporated in vacuo. Then the monomer solution was added by means of an injection syringe. The dilatometers were degassed five more times and the polymerization performed at 50°C in a water bath. The ampules for the AN/MAn copolymerization were prepared analogously to avoid the effect of oxygen, which has been observed for the system styrene/MAn [6, 7]. The ampules were filled under argon and then

the contents were melted. All the polymerizations were performed at 50°C. The concentration of the monomers was always $[M_1 + M_2] = 3 \text{ mol/L}$.

The EA/MAN copolymers were precipitated and reprecipitated from DCE solutions at -10 to -20°C with mixtures of petroleum ether and ether (90:10). The AN/MAN copolymers were copolymerized in acetone and precipitated and reprecipitated with *n*-heptane.

RESULTS AND DISCUSSION

By contrast with literature data [1, 2], no curves with maxima were obtained for the dependence of the rate of the copolymerization, v_{BR} , upon the composition of the monomers (Fig. 1). The v_{BR} values decrease distinctly for EA/MAN and for AN/MAN with increasing MAN content in the monomer mixture.

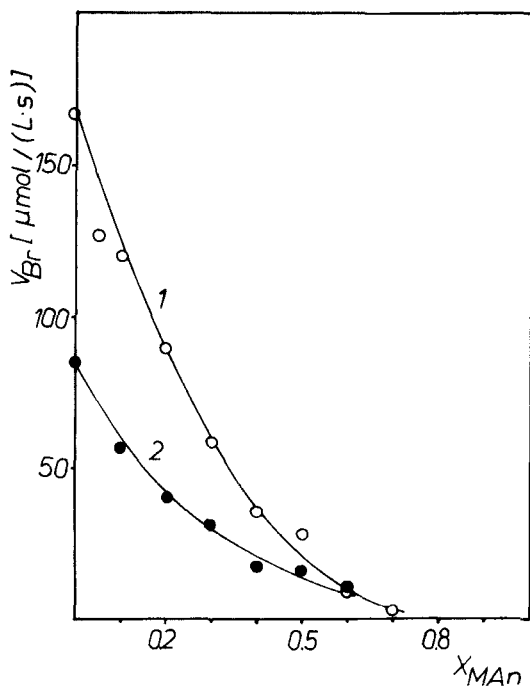


FIG. 1. Dependence of v_{BR} on x_{MAN} for the copolymerization of EA/MAN in DCE (1) and AN/MAN in acetone (2). (1): $[AIBN] = 1 \text{ mmol/L}$. (2): $[AIBN] = 5 \text{ mmol/L}$.

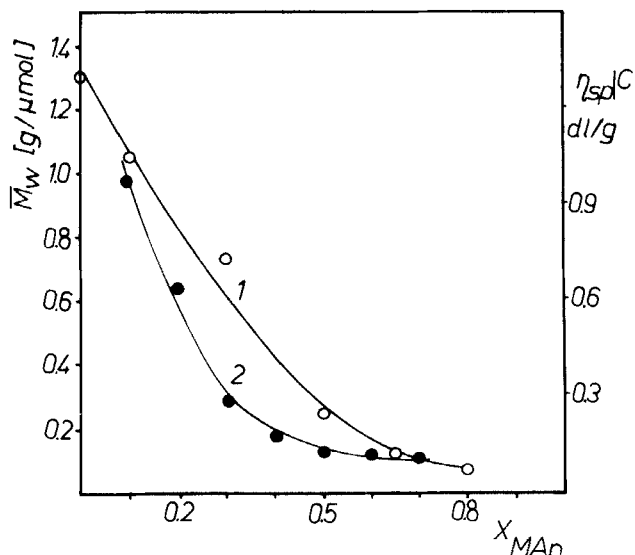


FIG. 2. Dependence of molecular weight, \bar{M}_w , for EA/MAN (1) and reduced viscosity η_{sp}/c for AN/MAN copolymers (2) on x_{MAN} .

Figure 2 demonstrates that the molecular weights (EA/MAN) and the reduced specific viscosities in solution (AN/MAN), like the ν_{Br} values, decrease with increasing MAN. The AN/MAN copolymers are of increasing oily-sticky consistency.

Figure 3 shows that, with introduction of more MAN into the monomers, there is only a slight increase in MAN in the copolymers. The reactivity ratios found by Kehlen and Tüdos [8] and Erzriev [9] are given in Table 1 for comparison with data from the literature and the values calculated from Q and e values. It shows that the experimentally ascertained r_1 values for EA/MAN are in good agreement with those calculated from Q and e , while larger differences occur in the case of AN/MAN. The negative r_2 values lie within the error range, and it is assumed that $r_2 = 0$. The r_2 value for AN/MAN points to the possibility of MAN addition to a MAN chain end.

For further characterization of the kinetic behavior of this nonalternating system of MAN copolymerization, the exponents of the initiators, the initial velocity, and the radical efficiency were obtained for EA/MAN by variation of the monomer composition. As expected from the general ν_{Br} equation, $\nu_{\text{Br}} = k_{\text{Br}}[\text{M}_1]^x[\text{M}_2]^y[\text{I}]^z$, increasing values of the initiator exponents Z were ob-

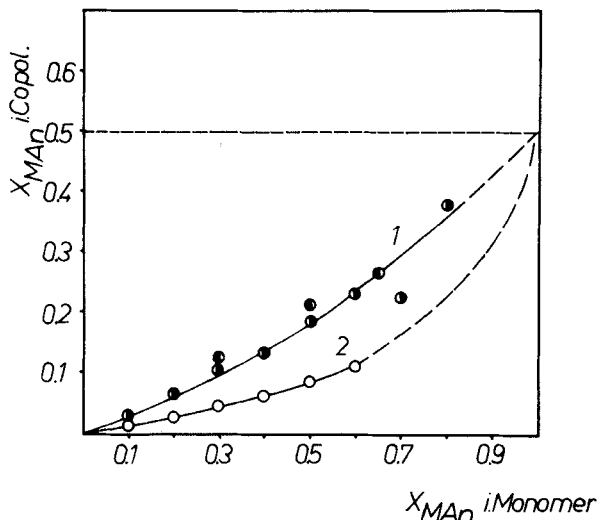


FIG. 3. Copolymerization of the monomer pairs EA/MAN (1) and AN/MAN (2).

tained with increasing MAN contents. For EA/MAN 80/20, 50/50, and 20/80, Z was 0.59, 0.64, and 0.83, respectively. The magnitude of these values is only partly reduced to microheterogeneity in the products because the conversion/time curves show no effect of acceleration. Degradative chain transfer to MAN is assumed to cause the strong decrease in molecular weight with increasing MAN content.

The initial rate constant, k_{St} , was obtained by measurements of inhibition using the dependence of the Koelsch radical concentration on the molar fraction x_{MAN} . This inhibitor radical has been found suitable for investigations of the initial styrene/MAN copolymerization [10]: whereas the concentration of the inhibitor in the absence of initiator is not decreased by the monomers, strong inhibition appears. The obtained k_{St} values show only a slight change with the monomer composition, which is caused, among other things, by a slight increase in the decomposition constant, k_Z values of the pure components were determined volumetrically, the intermediate values were additionally calculated from the compositions [11]. Since the k_{St} values from inhibition measurements give only an estimate of the amount of radical, k_{St} was also determined by use of ^{14}C -containing AIBN initiator. Figure 4 shows a comparison of the values obtained by both methods. The k_{St} values, deter-

TABLE 1. Parameters of Copolymerization for the Copolymerization with MAn (M_2)

M_1	Solvent	r_1	r_2	Ref.
MMA		3.5	0.03	1
	Ethyl acetate	4.5	-0.18	2
MA	Benzene	6.7	0.02	3
	Benzene	2.8	0.02	3
EA	1,2-Dichloroethane	3.69 ± 0.14	-0.08	a
		3.53^b	0.004^b	
AN	Benzene	7.23 ± 0.3	0	5
	1,2-Dichloroethane	7.52 ± 0.39	0	5
	Ethyl acetate	7.72 ± 0.3	0	5
	Dimethylformamide	5.20 ± 0.14	0	5
		6.0^b	0	10
	Acetone	7.94 ± 0.15	0.19	a
8.17 ± 0.05		-0.19	c	

^aExperimental value, interpreted according to Ref. 8.

^bCalculated from Q and e .

^cExperimental value, interpreted according to Ref. 9

mined by ^{14}C tracer, decrease with increasing amount of MAn, which demonstrates, together with the k_Z values for the AIBN decomposition, that the radical efficiency decreases with increasing amount of MAn in the monomer mixture. Hence, it follows that the initiation step via MAn proceeds more difficultly than via EA.

Using the obtained r_1 values, the decrease in ν_{B_1} can be explained as follows:



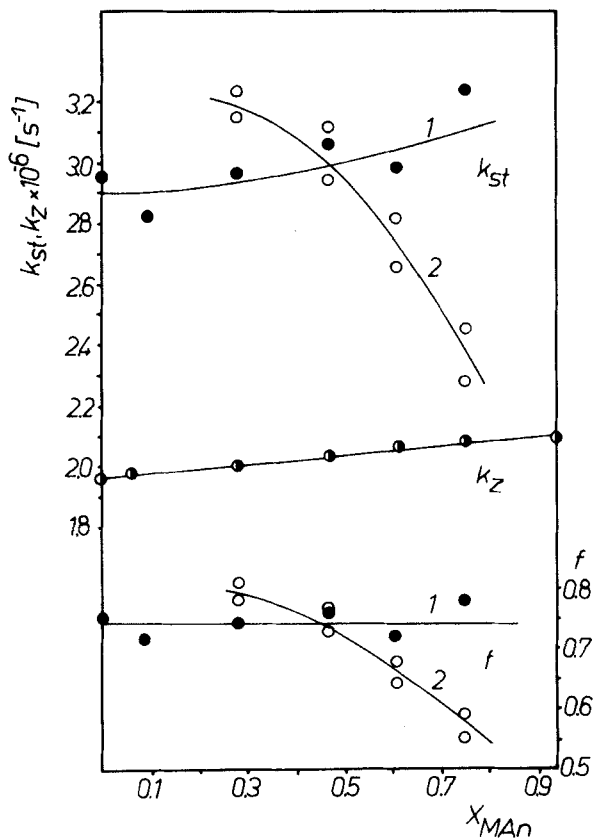


FIG. 4. Dependence of k_{st} , k_z , and f on x_{MAN} for EA/MAN copolymerization in DCE. Measurements of inhibition with (1) the Koelsch radical and (2) the ^{14}C -AIBN tracer.



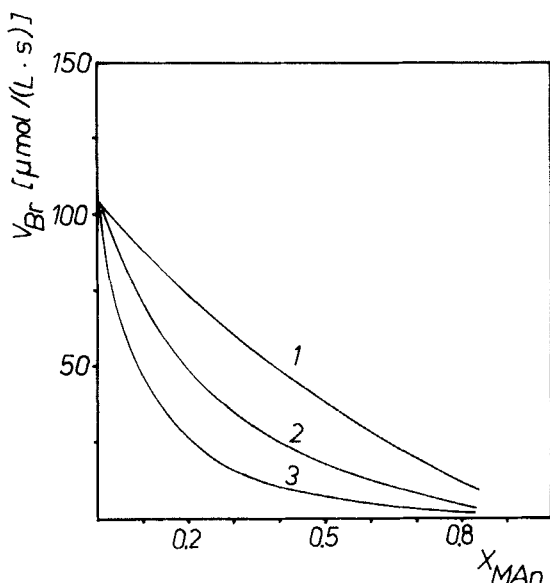


FIG. 5. Calculated rate (v_{Br}) curves for the copolymerization of EA/MAN according to Eq. (5) for various values of k_{21} . $[M_1 + M_2] = 3 \text{ mol/L}$; $[I] = 1 \text{ mmol/L}$; $k_{St} = 3 \times 10^{-6} \text{ s}^{-1}$; $k_{11} = 2 \text{ L/(mmol}\cdot\text{s)}$; $k_{12} = 55 \text{ L/(mmol}\cdot\text{s)}$; $k_a = 1 \times 10^7 \text{ L/(mol}\cdot\text{s)}$, $k_{21} = 50$ (1), 150 (2), 5 (3) $\text{L/(mmol}\cdot\text{s)}$.

Reaction (1) yields the largest contribution to v_{Br} and decreases with increasing x_{MAN} . Compared with Reaction (1), Reaction (2) is distinctly slower (r_1 values). The explanation for the v_{Br} curves includes (a) these factors, (b) an increase of the termination constant for crossed termination (k_{a12}), which we demonstrated for the copolymerization of acrylamide with styrene and which we showed to be probable for the copolymerization of acrylic amide with MAN [11], and (c) increasing degradative chain transfer to MAN. The marked change of k_{St} has only little influence on v_{Br} . Calculated v_{Br} curves for the monomer pair EA/MAN are shown in Fig. 5. The following v_{Br} equation, which assumes $k_{22} = 0$ was used:

$$v_{Br} = \left(\frac{k_{St}}{k_a} [I] [M_1] [M_2] k_{12} k_{21} \right)^{0.5} \left(\frac{k_{11} [M_1]}{k_{12} [M_2]} + 2 \right). \quad (5)$$

The shapes of the curves were obtained from experimental results and assumed k_{21} values. Contrary to expectations, k_{21} is possibly greater than k_{12} . The influence of degradative chain transfer was not considered in these calculations.

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