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## KINETICS OF COPOLYMERIZATION OF ETHYLENE AND VINYL CHLORIDE\*†

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INFORMATION on radical copolymerization of ethylene and vinyl chloride is mainly contained in patents [1, 2]. Copolymerization by the effect of boron alkyls is described by Kolesnikov *et al.* [3]. Zutty and Burkhart [4] determined relative monomer activities at a pressure of 1050 kg/cm<sup>2</sup> and 90°. There are no data available in the literature on the copolymerization kinetics of these monomer.

This paper presents the results of studying the kinetics of radical copolymerization of ethylene (M<sub>1</sub>) and vinyl chloride (VC) which has been briefly mentioned previously [5, 6].

The experiments were carried out in the presence of azobisisobutyronitrile (AIB) at 70°; the main experiments were carried out at a pressure reaching 300 kg/cm<sup>2</sup>. During copolymerization of ethylene under these conditions [7] and during bulk polymerization of VC [8] properties are observed which are due to the heterogeneity of the process. We therefore studied copolymerization both in bulk and in cyclohexanone solution.

It was shown that the phase effects in bulk copolymerization influence the variation of relative monomer activities compared with solution copolymerization.

*Experimental methods.* A device with 0.2 and 0.96 l. vibratory autoclaves was used. Thermostat control was effected with water circulating from an ultrathermostat through the jacket of the autoclave. Temperature was maintained with an accuracy of  $\pm 0.5^\circ$ . The

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initiator was placed in the autoclave from which air was evacuated (by passing ethylene through) as a solution in benzene or for solution copolymerization, in cyclohexanone. Charging conditions excluded air infiltration to the system. Monomers were measured by weight from 0.7–2.0 l. cylinders with an accuracy of  $\pm 0.5$  g. Special experiments have established that during initial heating (approx. 30 min) no polymers formed.

Copolymer composition was determined from the chlorine content. The intrinsic viscosity of the copolymers was determined in a decalin–cyclohexanone (2 : 1) mixture at 80°.

*Starting materials.* Ethylene was obtained by dehydration of ethyl alcohol. Monomer content was 99.1–99.3% by volume.

Vinyl chloride: monomer content, 99.5%, acetylene, 0.01–0.07%, 1,1-dichloroethane, 0.2%. AIB is a commercial product which has been twice recrystallized from ethyl alcohol. Cryoscopic benzene was purified, distilled and a fraction with b.p. 79.8–80.1° taken.

Cyclohexanone was distilled and the fraction of b.p. 155–156° taken.

## RESULTS AND DISCUSSION

The phase state of the ethylene–VC system was studied over the pressure range from 1 to 100 kg/cm<sup>2</sup> and the temperature range of 5–80° by recording pressure–temperature relations for different monomeric mixture compositions.\* As was shown at a pressure of over 100 kg/cm<sup>2</sup> the ethylene–VC system is homogeneous for any monomer ratio. It was also shown that the ethylene–VC–cyclohexanone system is homogeneous under conditions of copolymerization.

*Determining relative monomer activities.* Copolymerization was studied for reaction mixtures containing 6.5–82 moles-% VC. In all cases, copolymers were enriched in VC irrespective of the composition of the initial mixture. From results of experiments carried out at a small degree (up to 10%) a relation was derived between copolymer composition and the composition of the initial mixture during bulk (Fig. 1, curve 1) and solution (curve 2) copolymerization.

From the differential equation for copolymer composition relative monomer activities were determined by a method of intersecting straight lines [9].

For bulk copolymerization  $r_1$  (ethylene) =  $0.20 \pm 0.02$ ,  $r_2$  (VC) =  $1.85 \pm 0.2$ ; for solution copolymerization  $r_1$  =  $0.285 \pm 0.075$ ,  $r_2$  =  $1.13 \pm 0.32$ . Certain differences in relative activity values are apparently due to the heterogeneity of the monomeric mixture–copolymer system which becomes obvious (in the absence of solvent) in the initial stage of copolymerization. Since for of a heterogeneous process values of  $r_1$  and  $r_2$  are determined not only by the reactivity of reagents but also by the diffusion factor, the data obtained in solution are more reliable.

*Copolymerization kinetics.* The dependence of the initial rate of copolymerization on the ratio of monomers was studied in bulk and solution. To retain the constancy of the total monomer concentration, a study was made in a certain pressure range. The results are shown in Fig. 2a and in the Table.

The higher reaction rates established for bulk copolymerization are the direct consequence of the heterogeneity of the system. As is well known, when the

\* The results of investigation will be presented in a special report.

polymer is present as a separate phase, the macroradicals are entrained thus reducing the rate of breakage reaction [8, 10].

DEPENDENCE OF THE INITIAL RATE OF COPOLYMERIZATION ON MONOMER RATIO AT 70°

(Concentration (mole/l.): initiator  $5 \times 10^{-3}$ , benzene 0.3; cyclohexanone 4.0)

VC content ( $M_2$ ) in the initial mixture, mol. proportion	Total ( $[M_1] + [M_2]$ ), mole/l.	Pressure, kg/cm <sup>2</sup>	$W \times 10^4$ , mole/l. $\times$ sec	VC content in copolymer, mol. fractions	$\phi$
Bulk copolymerization					
0.000	13.20	300	1.57	0.000	—
0.000	13.20	300	1.62	0.000	—
0.090	14.01	180	0.23	0.281	493.5
0.115	13.94	180	0.22	0.321	514.0
0.222	15.79	235	0.43	0.457	206.5
0.280	14.98	155	0.45	0.520	189.3
0.495	16.08	120	2.26	0.694	16.0
0.570	15.05	218	2.26	0.748	17.0
0.590	15.09	130	2.83	0.760	9.2
0.660	15.89	215	3.85	0.805	6.0
1.000	15.50	10	5.84	1.000	—
1.000	15.50	10	5.87	1.000	—
Solution copolymerization					
0.396	12.90	155	0.61	0.572	128
0.584	13.36	190	0.91	0.695	81.3
0.608	12.85	80	1.15	0.682	49.5
0.694	13.30	200	1.37	0.735	44.9
0.718	12.88	140	1.98	0.782	17.6
1.000	13.00	—	3.42	1.000	—
1.000	13.00	—	3.82	1.000	—

Note. The concentrations were calculated in moles per litre of the reaction volume.

The results obtained made it possible to calculate the constants of cross breakage,  $\phi$ . For this purpose the equation showing the overall rate of copolymerization was used [9].

$$W = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2) \frac{W_i^{1/2}}{\delta_1}}{r_1^2[M_1]^2 + 2\phi r_1 r_2 \frac{\delta_2}{\delta_1} [M_1][M_2] + r_2^2 \left( \frac{\delta_2}{\delta_1} \right)^2 [M_2]^2}^{1/2},$$

where

$$\phi = \frac{k_{t12}}{(k_{t11} k_{t22})^{1/2}}, \quad \delta_1 = \frac{(k_{t11})^{1/2}}{k_{p11}}, \quad \delta_2 = \frac{(k_{t22})^{1/2}}{k_{p22}},$$

$k_{t11}$  and  $k_{t22}$  are the rate constants of chain termination between similar radicals;  $k_{t12}$  is the rate constant of chain termination between different radicals;  $k_{p11}$  and  $k_{p22}$  are the rate constants of growth in homopolymerization.

The rate of copolymerization and the relative activities of monomers were determined experimentally. Rates of initiation ( $W_i$ ), constants  $\delta_1$  (for ethylene) and  $\delta_2$  (for VC) were calculated as described in reference [11–13], respectively.

Values of  $\varphi$  obtained indicate the predominance of cross termination. At the same time a considerable variation of  $\varphi$  is observed with the variation of the ratio of monomers in the reaction mixture (Fig. 2b). A similar effect is observed

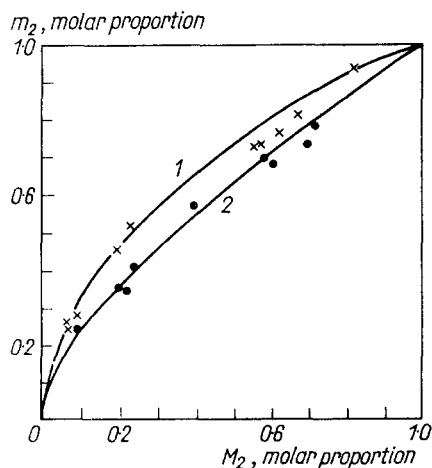


FIG. 1

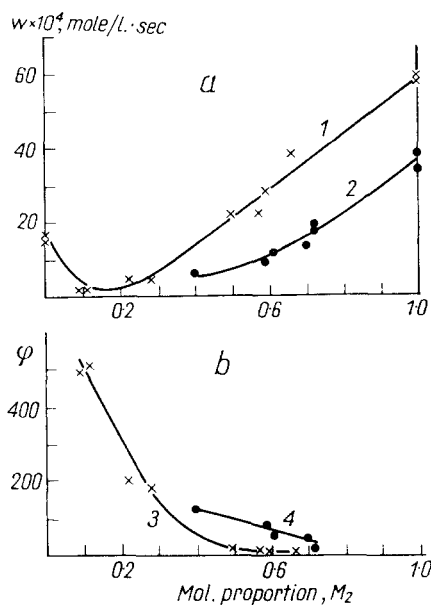


FIG. 2

FIG. 1. Dependence of copolymer composition on the composition of the initial mixture in copolymerization of ethylene with VC ( $M_2$ ) in the presence of AIB (concentration  $5 \times 10^{-3}$  mole/l.) at  $70^\circ$ : 1—bulk copolymerization, pressure 155–300 kg/cm<sup>2</sup>, 2—solution copolymerization, pressure 80–200 kg/cm<sup>2</sup>.

FIG. 2. a—Dependence of the initial rate of copolymerization on monomer ratio in copolymerization of ethylene and VC in the presence of AIB (concentration  $5 \times 10^{-3}$  mole/l.) at  $70^\circ$ : 1—bulk copolymerization, pressure 10–300 kg/cm<sup>2</sup>, 2—solution copolymerization, pressure 80–200 kg/cm<sup>2</sup>; b—Dependence of the constant of cross termination on monomer ratio: 3—bulk copolymerization, 4—solution copolymerization.

for the copolymerization of certain other monomer pairs [14–17]. The attempts to elucidate this by the effect of penultimate macroradical units [18] or by the dependence of the rate of termination on the composition of the whole polymer chain under conditions when termination is determined by diffusion [19], cannot

be considered successful. In this respect, great attention should apparently be given to the hypothesis of "hot" radicals recently proposed by Tüdös [20]. According to this hypothesis, supported by numerous experimental facts, the constants of the elementary acts of radical polymerization depend on the concentration and nature of the solvent and, in the case of copolymerization, on the  $[M_1]/[M_2]$  ratio. A natural consequence of this can be the variability of  $\varphi$  when changing the composition of the initial mixture.

Copolymerization of ethylene and VC can produce copolymers with any content of initial monomers, the products with a VC content ranging from 30 to 60% being rubber-like.

The intrinsic viscosity of copolymers having different VC contents, varies within the range of 0.2–0.35. Copolymers of a higher molecular weight with an intrinsic viscosity of 0.5–1.0 were obtained during copolymerization under a pressure higher than 1000 kg/cm<sup>2</sup>.

### CONCLUSIONS

(1) Copolymerization of ethylene and vinyl chloride was studied at 70° and pressures of up to 300 kg/cm<sup>2</sup> with varying monomer ratios, in bulk and in solution, and relative monomer activities were determined.

(2) The kinetics of copolymerization of ethylene and vinyl chloride were investigated, and constants of cross termination determined.

*Translated by E. SEMERE*

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## SPECTROPHOTOMETRIC STUDY OF N-VINYLCARBAZOLE AND METHYL METHACRYLATE COPOLYMERS\*

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VINYLCARBAZOLE polymers and copolymers are of great practical interest since they have increased thermal stability and satisfactory electrical insulating properties [1].

It was of interest to study the spectra of vinylcarbazole monomers, polymers and copolymers in order to use the spectroscopic data to examine the possibility of analysing copolymers and polymeric mixtures.

The initial substances—methyl methacrylate, carbazole, vinylcarbazole—were purified by conventional methods (repeated distillation, recrystallization) [2, 3].

The constants of the purified substances were: methyl methacrylate— $d_{20}^{20}$  0.941;  $n_D^{20}$  1.4152; b.p. 100°; carbazole—m.p. 246°; vinylcarbazole—m.p. 64°; content of pure substance 100%.

Polymerization and copolymerization of vinylcarbazole and, methyl methacrylate was effected in sealed ampoules in a nitrogen atmosphere at 70° for 6–7 hours in the presence of 0.025% azobisisobutyronitrile as initiator. The polymers and copolymers were twice precipitated from dioxane solution by methanol, in order to eliminate unreacted monomer. The residues were carefully washed with methanol and dried to constant weight at 40°.

Absorption spectra were measured in 1 cm wide quartz vessels in a SF-4 spectrophotometer in dioxane purified by conventional methods [4].

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