

COPOLYMERIZATION OF ETHYLENE WITH THE DIETHYL AND DIPHENYL ESTERS OF VINYLPHOSPHINIC ACID*†

R. A. TERTERYAN

All-Union Petroleum Processing Research Institute

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THERE is now a large variety of copolymers of ethylene with different monomers as a result of high-pressure radical copolymerization [1]. At the same time very little information has been published in regard to ethylene copolymerization with unsaturated heteroorganic compounds, particularly organophosphorus compounds, apart from a few patents concerning the synthesis of ethylene copolymers with phosphorus-containing monomers [2-5]. However we may assume that the introduction of organophosphorus units into the polyethylene chain may give rise not only to certain changes due to the breakdown of the crystalline structure of polyethylene but also to a number of specific properties characteristic of organophosphorus polymers in general, such as fireproofness, thermal stability, etc. [6].

This paper is based on a study of the synthesis and behaviour of copolymers of ethylene with two esters of vinylphosphinic acid, namely the diethyl (DEVP) and diphenyl (DPVP) esters. A short report on the copolymerization with one of the latter appears in [7].

EXPERIMENTAL

The copolymerization experiments were carried out with the apparatus described in [8]. The reactors were two vibratory autoclaves (200 and 625 ml) fitted with thermostat jackets and designed to operate under pressures up to 1500 kg/cm².

Air was first removed from the autoclave and then it was charged in a current of ethylene with a solution of the initiator and monomer in an inert solvent (benzene); the autoclave was next heated to the reaction temperature and the required pressure was set at the same time. The process was carried under pressures kept constant by the periodical injection of ethylene; at 500 kg/cm² the permissible pressure drop was 10 kg/cm², or 50 kg/cm² at 1000-1500 kg/cm². Temperature variations were generally less than 1°.

The amount of ethylene entering the small autoclave under the predetermined conditions was found by weighing the autoclave with the reaction mixture in a standard balance before and after the reaction. The amount of ethylene in the large autoclave was determined by means of gas hours.

The products obtained in the copolymerization were separated from the solvent and from the unreacted monomer and initiator by dissolving them in benzene with slight heating, by filtering the solutions (to remove mechanical impurities) and by precipitation with acetone followed by vacuum-drying at room temperature to constant weight. The copolymer compositions were determined by elementary analysis for phosphorus, carbon and hydrogen.

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† N. V. Fomichev and L. N. Shapkin assisted in the experiments.

The physical characteristics of the vinylphosphinic acid esters* used in the experiments (data taken from [6] are given in brackets) were as follows: DEVP—b.p. 84°/11 mm, n_D^{20} 1.4305 (1.4300), P = 18.6% (calc. 18.9%); DPVP—b.p. 174–176°/5 mm, n_D^{20} 1.5545 (1.555), P = 11.5% (calc. 11.9%).

The ethylene used in the investigation and derived from petroleum was found by chromatographic analysis to contain 99.6–99.9% ethylene and less than 0.01% methane, 0.1% ethane, 0.0001% acetylene, 0.0003% acetone and 0.0008% oxygen.

The initiators were the dinitrile of azoisobutyric acid (DAA) double recrystallized from solution in acetone, and tertiary butyl peroxide (TBP). The latter was not purified; according to iodometric analysis the peroxide contained 98% basic substance. Cryoscopic benzene was used as solvent in the copolymerization.

The molecular weight of the copolymers was found by the cryoscopic method (0.1 g of polymer in 10 g of naphthalene); the density was determined volumetrically, using water and ethanol. The tensile strength of the copolymers was tested on an RMI-5 machine, rate of deformation 100 mm/sec, using samples 200–300 μ thick pressmoulded under a pressure of 50 kg/cm² at a temperature 20–30° above the melting point of the copolymer.

DISCUSSION OF RESULTS

The results of experiments in ethylene copolymerization conducted with different monomer ratios are given in Tables 1 and 2. To ensure the homogeneity of the system a considerable amount of benzene was used as a medium for the copolymerization since we know from reference [9] that under pressures exceeding 100 kg/cm² an ethylene–benzene system forms a homogenous mixture irrespective of the temperature and the ratio of the components.

It is evident from the Tables that the copolymerization was restricted to a relatively small amount of the second component (2.5 mole %) in the initial mixture. It will be shown below that this is because of the specific nature of the monomers in question (and apparently most other organophosphorus monomers as well) which do not readily undergo radical polymerization, so that with higher concentrations of these compounds virtually no copolymerization with ethylene takes place.

It is seen from Tables 1 and 2 that there is satisfactory agreement between the number of copolymer units calculated from elementary analysis for carbon and phosphorus, and it may therefore be assumed that the copolymer macromolecules consist solely of units of the selected monomers, and that no major changes occur in the second components before and after their inclusion in the polymer chain. Seeing that analysis for the carbon content of the copolymers produced more stable results we based all further calculations on the copolymer compositions calculated on the basis of their average carbon content.

The degree of conversion in the copolymerization experiments was quite small and generally below 10% conversion of the monomer mixture. However even with these relatively low conversions it was found that the composition of the resulting copolymers is greatly influenced by the degree of conversion,

* The esters were synthesized at the Chemicotechnological Institute, Kazan, directed by Ye. V. Kuznetsov.

TABLE 1. RESULTS OF COPOLYMERIZING ETHYLENE WITH DEVP AND DPVP UNDER A PRESSURE OF 400 kg/cm² AT 80° IN THE PRESENCE OF DAA IN BENZENE SOLUTION

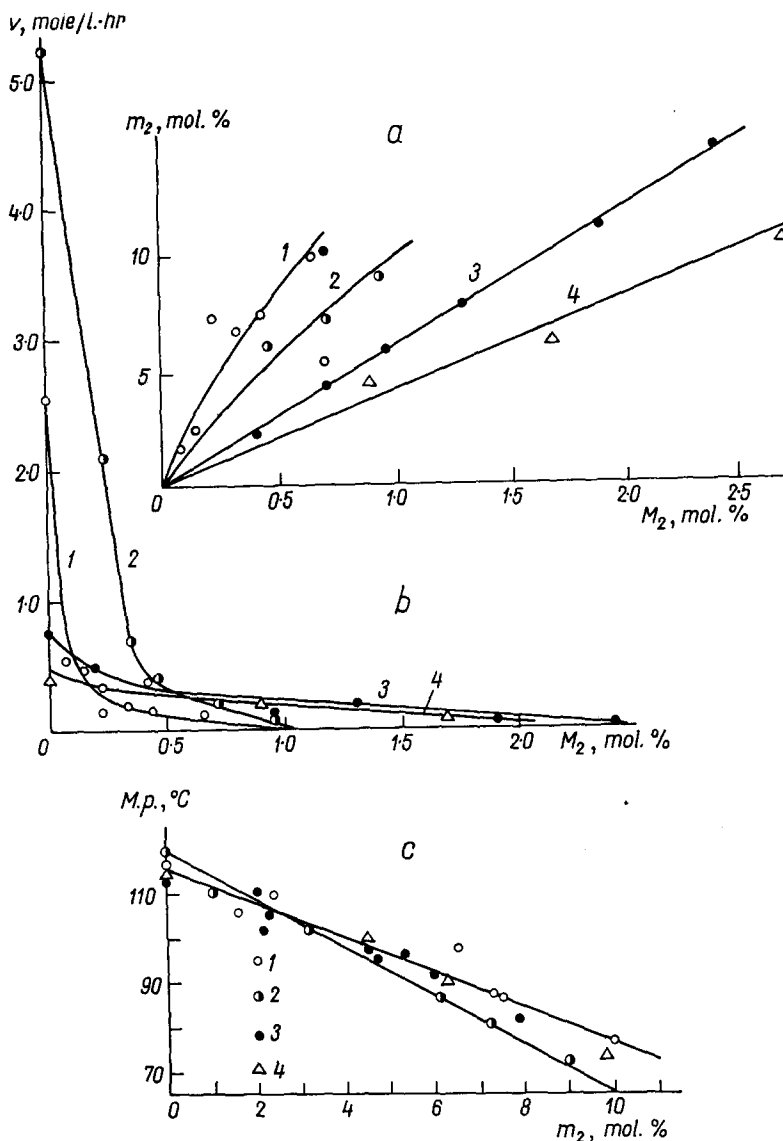
Experiment, No.	Initial concentra- tion of monomers, mole/l.		Content of M ₂ in initial mixture of monomers, mole %	Reaction time, hr	Conversion, %	Elemental analysis of copolymer, %			Number of M ₂ units in copolymer*		Molecular weight (cryoscopy)
	M ₂	M ₁				C	H	P	calculat- ing for C _{av} , mole %	calculat- ing for C _{av} , mole %	
Copolymerization with DEVP (DAA concentration 0.01 mole/l., benzene concentration 5.0 mole/l.)											
1	0.0	9.8	0.0	3	10.8	85.30	14.30	0.00	0	0	5300
2	0.085	9.3	0.9	3	5.2	76.19	13.14	3.90	4.5	4.2	2500
3	0.156	9.1	1.7	3	2.7	73.50	12.68	4.28	6.3	4.8	1000
4	—	—	—	1.5	2.0	69.14	11.84	6.33	9.8	7.8	1500
5	0.252	8.9	2.7	4	2.0	68.15	10.95	7.27	10.7	9.5	800
Copolymerization with DPVP (DAA concentration 0.02 mole/l., benzene concentration 4.5–5.0 mole/l.)											
6	0.0	9.46	0.0	1	7.9	85.20	14.27	0.00	0	0	5100
7	0.018	9.46	0.19	1	4.8	81.13	11.18	2.16	2.6	2.3	3400
8	0.035	8.57	0.41	1	4.0	81.66	11.17	2.74	2.2	3.3	3500
9	0.054	7.68	0.70	0.5	1.1	74.60	10.20	5.27	10.2	7.9	—
10†	0.054	7.68	0.70	3	4.0	78.11	11.45	3.74	5.3	4.6	3200
11†	0.054	7.68	0.70	3	4.3	78.90	11.63	3.61	4.5	4.5	3400
12	0.054	7.68	0.70	3	10.0	81.93	12.87	1.80	2.0	1.8	3200
13	0.077	8.04	0.96	3	3.3	77.54	10.78	3.91	6.0	5.0	2700
14	0.092	7.50	1.3	3	6.2	78.67	11.92	3.35	4.7	4.4	2800
15†	0.098	7.32	1.3	3	2.2	76.16	10.71	4.71	7.8	6.5	3000
16	0.144	7.50	1.9	3	2.4	74.07	10.45	—	11.2	—	—
17	0.183	7.50	2.4	3	1.1	72.60	9.05	—	14.5	—	2200

* C_{av}—average carbon content. P_{av}—average phosphorus content.

†The experiments were conducted with 0.01 mole/l. DAA.

as may be seen on comparing experiments 9 and 12, and 14 and 15 in Table 1, and also 21 and 22, 23 and 24, 25 and 26 in Table 2. This is because the copolymerization was conducted with very low concentrations of the second component in the monomer mixture. This factor together with the relative activities of the pairs of monomers investigated (close to zero) gives rise to considerable changes in the initial monomer ratio as the total degree of conversion rises, which in turn also affects the composition of the resulting copolymer. It appears

that in the present case, as also in the copolymerization of ethylene with dibutylfumarate [10] the use of the copolymerization equation in order to find the relative activities is valid only for very low conversions.



Relationship: *a*—composition of copolymers vs. initial ratios ethylene : DPVP and ethylene : DEVP (based on experiments conducted at below 4% conversion); *b*—initial copolymerization rate vs. content of comonomer in initial mixture; *c*—melting point of ethylene /DPVP and ethylene/ DEVP copolymers vs. composition: 1—DPVP, 80°, 1000 kg/cm²; 2—DPVP, 140°, 1000 kg/cm²; 3—DPVP, 80°, 400 kg/cm²; 4—DEVP, 80°, 400 kg/cm²; M_2 —content of comonomer in initial mixture; m_2 —number of comonomer units in copolymer.

The Figure *a* shows curves of copolymer composition vs. initial monomer ratio based on experiments with conversions not exceeding 4% (see Tables 1 and 2). The results of these experiments were used to find the relative activities for the pairs of monomers under review under different pressure and temperature conditions; the calculations were based on the Feinmann-Ross method [11].

The following relative activities were obtained for ethylene: in copolymerization with DEVP under the conditions stated in Table 1 $r_1 = 0.17 \pm 0.03$, in copolymerization with DPVP at 1000 kg/cm² and 80° $r_1 = 0.04 \pm 0.004$, at 1000 kg/cm² and 140° $r_1 = 0.055 \pm 0.007$, and at 400 kg/cm² and 80° $r_1 = 0.11 \pm 0.02$.

It is apparent from these copolymerization constants that the polymeric radical ending with an ethylene unit reacts with the "foreign" monomer about ten times more rapidly than with its "own" monomer. It is seen that a rise in pressure reduces the value of r_1 owing to the increased rate of this elementary reaction of propagation of the copolymer chain. A negative value was obtained for r_2 for both monomers, so we could assume that $r_2 \approx 0$ for DPVP and DEVP in the copolymerization with ethylene. In other words, in the radical copolymerization with ethylene the growing chain terminating a phosphinate unit reacts only with ethylene. This is in accordance with the low polymerizability of these monomers in homopolymerization, as well as in copolymerization with other monomers [12-15]. For example, in the copolymerization of DEVP with styrene [15] it was similarly found that the polymeric radical terminating with a DEVP unit reacts only with styrene, and the relative activity of DEVP is zero.

The Figure *b* shows curves of the copolymerization rate plotted against the ratio of the initial monomers under different reaction conditions. In every case the reaction rate is reduced with increasing contents of the second component in the monomer mixture. It is seen from the Figure *b*, however, that the curve for the rate of copolymerization conducted under a pressure of 1000 kg/cm² is very different from that for the copolymerization at 400 kg/cm². While in the latter case the copolymerization rate falls uniformly with increase in the DEVP and DPVP concentrations, and reaches zero for a comonomer content of 3 mole %, with the process conducted at 1000 kg/cm² (whether at 80 or 140°) the dependence of the rate on the comonomer concentration is still more marked: with concentrations of 0.3-0.4 mole % DPVP the rate is reduced by more than one order, becoming virtually zero for a concentration of about 1 mole %. The effect of pressure, which is very considerable in the homopolymerization of ethylene, is therefore of quite secondary importance in the copolymerization with DPVP, and the initiator concentration becomes the factor of major importance. This is apparently the reason why the copolymerization rate under a pressure of 1000 kg/cm² with a DPVP content of about 1 mole % in the initial mixture falls below the rate of the process at 400 kg/cm², and is equal to zero, whereas the copolymerization still continues under a lower pressure, but with a higher initiator concentration.

The difference in the curves obtained for the rate of copolymerization vs.

TABLE 2. RESULTS OF ETHYLENE/DPVP COPOLYMERIZATION UNDER A PRESSURE OF 1000 kg/cm²

Experi- ment No.	Initial concentration of monomers, mole/l.		Content of DPVP in initial mixture, mole %	Reac- tion time, hr	Con- ver- sion, %	Content of C in copolymer wt. % (by elemental analysis)	Number of DPVP units in copolymer, mole %	[η], 100° decalin, dl/g	Density at 20°, g/cm ³	Tensile strength, kg/cm ²	Break- ing elonga- tion, %	Melting index (at 190°), g/10 min
	DPVP	ethyl- ene										
Initiator—DAA, initiator concentration 0.005 mole/l., 80°, benzene concentration 1.8 mole/l.												
18	0	14.5	0	0.5	8.7	—	0	1.08	0.923	180	300	0.9
19	0.010	14.4	0.07	0.5	1.8	82.86	1.6	0.70	0.976	120	100	80
20	0.020	14.4	0.14	1.0	3.1	81.85	2.4	0.63	0.982	80	20	—
21	0.031	14.3	0.22	0.5	3.8	76.73	7.3	0.39	>1.000	—	—	—
22	0.031	14.3	0.22	2.0	4.5	81.50	2.6	—	0.986	70	20	—
23	0.047	14.2	0.33	2.0	2.1	77.30	6.6	0.48	>1.000	45	100	—
24	0.047	14.2	0.33	3.0	8.5	81.33	2.7	0.49	0.980	75	30	176
25	0.061	14.1	0.43	2.0	1.8	76.56	7.5	0.37	1.000	90	50	—
26	0.061	14.1	0.43	5.0	10.0	82.83	1.7	0.56	0.996	110	20	65
27	0.093	14.0	0.65	2.0	1.3	74.96	10.0	0.47	>1.000	70	70	—
Initiator—TBP, initiator concentration 0.002 mole/l., 140°, benzene concentration 1.8 mole/l.												
28	0	13.0	0	0.5	19.0	—	0	1.19	0.919	150	400	0.1
29	0.031	13.1	0.24	1.0	15.2	83.80	1.0	1.02	0.949	120	500	4.2
30	0.046	13.1	0.35	1.5	7.6	80.77	3.2	0.79	0.990	92	600	59.0
31	0.061	13.1	0.46	1.0	2.8	77.78	6.1	0.37	>1.000	20	100	—
32	0.092	12.9	0.71	2.0	2.9	76.90	7.1	0.26	—	0	0	455.0
33	0.123	12.8	0.95	2.0	0.7	75.61	9.0	—	—	2	2	—

initial monomer ratio under different pressures (Figure *b*) points to a marked rise in the cross-termination constant accompanying increase in the amount of pressure used for the process.

Besides termination reactions there is also a considerable increase in the part played by chain transfer through the comonomer as the amount of organophosphorus monomer in the reaction mixture rises. This is shown by the molecular weights of the product copolymers (see Table 1) which are lower than for the corresponding polyethylene, and also by the intrinsic viscosities of the copolymers synthesized at 1000 kg/cm² (see Table 2). Moreover, it is natural that the molecular weight of the latter should exceed that of copolymers of similar composition obtained at 400 kg/cm². For instance, the copolymers containing 7.5 and 10 mole % DPVP have MW (cryoscopy) of 6000 and 5000 respectively, while copolymers of approximately the same composition synthesized at 400 kg/cm² have MW of 2500–3000.

The introduction of organophosphorus monomer units into the polyethylene macromolecule gives rise to considerable changes in the mechanical properties of the polymer, primarily owing to the breakdown of the crystalline structure of polyethylene. Copolymers containing up to 5 mole % of the second component are solid substances that can readily be moulded into translucent films; with further increase in the comonomer content up to 15 mole % they are gradually converted into soft resinous substances. The melting points of the latter, as one would expect, fall gradually as the number of comonomer units rises. This relationship is illustrated by the Figure *c*, showing that ethylene/DPVP copolymers synthesized at 140° have rather lower melting points than copolymers of DEVP and DPVP prepared at 80°. This is probably the result of the increased role of chain transfer reactions accompanying a rise in the reaction temperature. Note that in the case of ethylene/DPVP copolymers the pressure appears to have no appreciable effect on the melting point.

It will be seen from Table 2 that the tensile strength of the copolymers is reduced with increase in the number of DPVP units they contain, and this also is probably accounted for mainly by the reduced MW. With comonomer contents of about 6 mole % ethylene/DPVP copolymers suffer complete loss of mechanical strength. The elastic properties of the copolymers obtained at 1000 kg/cm² and 140° are higher than those of polyethylene.

Table 2 contains the values of the melting index for ethylene/DPVP copolymers in relation to their composition, and a marked increase in the flow of the copolymers is seen on introducing quite a small amount of DPVP into the polyethylene chain.

Copolymers of ethylene with DEVP and DPVP differ from polyethylene on account of their higher solubility in organic solvents, and this improves as their content of comonomer units increases. Copolymers with from 5–7 mole % organophosphorus monomer in the molecule (there is no real difference in the solubility of copolymers of DEVP and DPVP of similar composition and MW)

dissolve readily with slight heating in aromatic hydrocarbons, e.g. in benzene, xylene and also in CCl_4 , but they are insoluble in acetone, alcohol, petroleum ether, heptane, and dimethylformamide. With further rise in the amount of organophosphorus comonomer the copolymers dissolve readily in the indicated solvents at room temperature.

CONCLUSIONS

(1) A study has been made of the radical copolymerization of ethylene with the diethyl and diphenyl esters of vinylphosphinic acid under pressures of 400 and 1000 kg/cm^2 at 80 and 140° in the presence of the dinitrile of azoisobutyric acid and tertiary butyl peroxide as initiators.

(2) The relative activities of the monomers have been determined; in the copolymerization with the diethyl ester of vinylphosphinic acid at 400 kg/cm^2 at 80° r_1 (ethylene) = 0.17 ± 0.03 , $r_2 \approx 0$; in the copolymerization with the diphenyl ester of vinylphosphinic acid at 400 kg/cm^2 (80°) $r_1 = 0.11 \pm 0.02$, at 1000 kg/cm^2 (80°) $r_1 = 0.04 \pm 0.004$, and at 1000 kg/cm^2 at 140° $r_1 = 0.055 \pm 0.007$, $r_2 \approx 0$.

(3) The kinetics of the copolymerization have been investigated. It has been shown that a rise in the concentration of organophosphorus monomers in the initial mixture is accompanied by a fall in the rate and in the degree of copolymerization.

(4) The behaviour of the copolymers of different composition and molecular weight has been studied. The dependence of the melting point, melting index, density and mechanical properties on the content of organophosphorus monomer in the copolymer has been noted.

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