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RADICAL COPOLYMERIZATION OF ETHYLENE WITH VINYL PHOSPHONATES UNDER PRESSURE*

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The reactivities (composition curves) found during the copolymerization of ethylene, as well as the copolymer densities as a function of composition, have been used to divide the $\text{CH}_2=\text{CHPO}(\text{OR})_2$ (M_2) monomers into 2 groups: 1) $\text{R}=\text{C}_6\text{H}_5$ and $\text{C}_2\text{H}_4\text{Cl}$ and 2) $\text{R}=\text{C}_4\text{H}_9$ and $\text{iso-C}_4\text{H}_9$. This correlates well with the polarity differences of M_2 . The first group is characterized by higher reactivities, especially when the M_2 content in the reaction mixture is high. The rapid drop of the reaction rate and of the mol. wt. of the copolymers, when the M_2 content is increased in the reaction mixture, and the relatively large rate of the M_2 homopolymerization, can be explained by the competition of the two mechanisms of chain transfer. An intramolecular reaction is dominant at the start and yields an intermediate P^* radical. Chain transfer is faster at a larger M_2 content and hydrogen will dissociate from R.

RADICAL copolymerizations of ethylene (M_1) with vinyl phosphonates (M_2) under pressure is of interest in connection with a polyethylene (PE) modification with organo-phosphorus compounds [1-3]. This problem had been tackled earlier at a low M_2 content [4-7]. In this communication we report about the study of the ethylene copolymerization with the diphenyl- (DPVP), 2,2-dichlorodiethyl- (DCEVP), dibutyl- (DBVP), or diisobutyl-vinyl phosphonate (DIBVP) over a wide range of comonomer ratios.

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EXPERIMENTAL

M_2 was produced by esterification of $CH_2=CHPOCl_2$; the b.p. $170^\circ C/1$ mmHg, m.p. $19-20^\circ C$, d_4^{20} 1.1947 g/cm³, n_D^{20} 1.5576 , purity 97% w/w (by chromatography). The DCEVP had b. p. $131-132^\circ C/3$ mmHg, d_4^{20} 1.3240 g/cm³, n_D^{20} 1.4780 . The DBVP had b. p. $101-102^\circ C/1$ mmHg, d_4^{20} 0.9759 g/cm³, n_D^{20} 1.4310 . The DIBVP had b. p. $79-80^\circ C/2$ mmHg, d_4^{20} 0.9730 g/cm³, n_D^{20} 1.4350 . The ethylene was of crude oil origin. We shall use $[M_2]$ to indicate the M_2 content of the comonomer mixture, $[m_2]$ for the $[M_2]$ present in the copolymer, while q will signify the total conversion of the monomers. A periodic action laboratory autoclave served as the copolymerization vessel; industrial grade di-*tert*.butyl peroxide ($10^{-4}-4 \times 10^{-2}$ mole/l.)

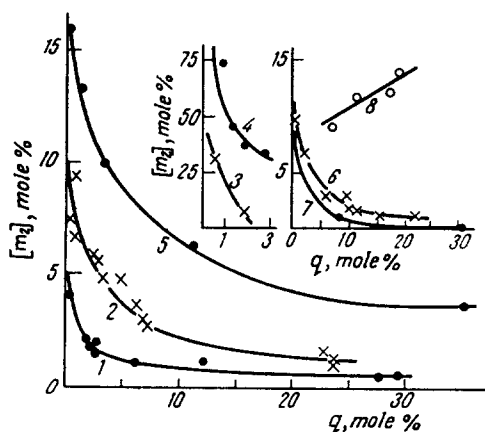


FIG. 1

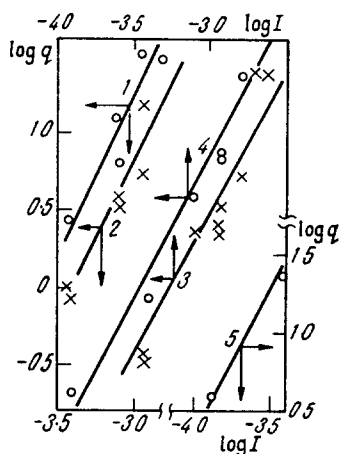


FIG. 2

FIG. 1. Copolymer composition as a function of comonomers conversion. $[M_2]$, mole %, DPVP: 1—0.2; 2—0.5; 3—4.9; 4—8.4; 5—1.6 DCEVP; 6—0.6 DBVP; 7—0.3 DIBVP; 8—10.5 DIBVP (1400 atm, $160^\circ C$, 1, 2—1300 atm; 3, 4—with 2.3 and 3.4 mole/l. benzene respectively).

FIG. 2. The comonomer conversion (mole %) as a function of initiator concentration (mole/l.): $[M_2]$, mole %: 1—0.2; 2—0.3; 3, 4—0.5 DPVP; 5—0.8 DCEVP (1300 atm, $160^\circ C$, 30 min); 5—1400 atm; 4—in the presence of 0.2 mole/l. ethyl acetate.

was used as the initiator. The pressure was normally 1400 atm at $100^\circ C$ reaction temperature [8, 9]. The majority of the experiments were carried out in bulk because of the complete solubility of M_2 in heptane and decane which were used as the model substances for liquid ethylene (DPVP $\approx 90^\circ C$, DCEVP $\approx 130^\circ C$). The reaction time was 7–120 min, and $[m_2]$ was up to 95% w/w in the case of DPVP and DCEVP, while it was up to 65% w/w for DBVP and DIBVP; some of the tests, especially where q was low, are reproduced in Tables 1–4. The M_2 mainly reacted on the double bond without change in chemical composition (a very small absorption intensity of the double bond in the IR spectra of the copolymers; the compositional agreement was calculated for the copolymers from the C- and P-analyses, e.g. 56.1 and 53.1% w/w for DCEVP, 34.7 and 31.8% w/w for DPVP, from the larger number of M_2 units per macromolecule, e.g. 10–15 units of DIBVP).

There was large variation in copolymer composition as a function of reactivity, even when q was small, the type of the $[m_2]=f(q)$ function ($[M_2]=\text{const.}$) equalled that of $[m_2]$

$=f[M_2]$ (Fig. 1). The DPVP and DCEVP contents rapidly decreased in the copolymers over a wide range of comonomer ratios when q increased (at 1400 atm and 160°C for DPVP, $[M_2]=14.0$ mole %, and $q=2.1$ and 7.0 mole %, $[m_2]=43.8$ and 43.4 mole % respectively). The copolymer composition varied in the same manner in the case of DBVP and DIBVP when $[M_2] \lesssim 5$ mole %. Where $[M_2]$ was much larger there was an increase of the DBVP and DIBVP contents in the copolymers as q increased, but the latter was approximately a linear function of the square of initiator concentration at small $[M_2]$ in the case of DPVP and DCEVP (Fig. 2, compare with [6]); the magnitude of q with respect to the initiator was about 1.5 for DPVP when used as a 5 mole/l. solution in benzene. The experimental results reproduced in Fig. 2 are for $[M_2]=0.5$ mole % DPVP (in bulk processes) and 3.9, 7.8, 11.7, 15.6 or 23.4×10^{-4} mole/l. of peroxide; they show the conversion to be 1.6, 26.4, 31.7, 48.5 and 73.6% respectively.

TABLE 1. THE ETHYLENE COPOLYMERIZATION WITH DPVP
(1400 atm, 160°C, 30 min, 140 cm³ reaction volume*)

Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %	Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %
1	0.2	3.9	0.2	4.1	8	4.9	171	0.6	31.7
2	0.3	3.9	0.2	5.1	9	8.4	69	1.2	45.8
3	0.5	3.9	0.1	8.3	10	8.4	34	0.9	74.1
4	0.6	11.7	0.8	9.3	11	13.2	210	2.1	43.8
5	1.0	11.7	1.0	8.1	12	18.5	340	12.1	51.9
6	2.0	11.7	0.2	12.9	13	24	340	10	46.3
7	3.4	6.8	0.5	26.1	14	27	375	11	51.0

* Exp. No. 1-6 at 1300 atm in 437 cm³, exp. No. 7 and 10=90 min, exp. No. 7-11 in the presence of 1.7, 2.3, 3.4 and 4.5 mole/l. benzene respectively.

The products were reprecipitated from benzene, toluene or xylene, with acetone or alcohol (the samples with a larger $[m_2]$ were precipitated with ether) and then kept under vacuum at room temperature. The composition was calculated from the C content. Any relatively large mol.wt. copolymers with $[m_2] < 10$ mole % were fraction precipitated into 10-15 fractions in a sieve tray column by dilution with a xylene-ethyl cellosolve mixture; other products were processed in the same manner with various solvents at various temperatures. The mol.wt. determination was ebullioscopic (in benzene), but also cryoscopic (in naphthalene), or viscometric ($[\eta]$ in decalin). The MWD was determined by ebulliometry. The fractions produced from the high mol.wt. copolymers had $[m_2]$ differing by not more than a few mole % for the same copolymer, e.g. fractions produced for the DIBVP bulk copolymer at $[M_2]=1.9$ mole % (giving $[m_2]$ as mole %¹ content/ $P_{n-1} + \frac{1}{2}P_n$, % w/w) were: 6.6/3, 6.9/11, 7.2/19, 7.4/28, 7.6/37, 7.7/41, 7.8/48, 8.0/58, 8.1/76, 8.2/92, 8.6/96, 10.6/98; in the case of the DIBVP bulk copolymer with $[M_2]=0.3$ mole % they were: 3.6/2, 3.9/13, 4.0/27, 4.1/31, 4.2/40, 5.0/46, 5.1/50, 5.6/61, 5.8/75, 6.0/80, 6.1/82, 6.2/86, 6.6/90, 6.8/93, 6.9/94. The fractions of the low mol.wt. copolymers also had similar composition ratios, e.g. 15.4, 14.2 and 16.1 mole % DIBVP. The MWD became more homogeneous. The DBVP bulk copolymers produced from $[M_2]=70$ mole % yielded values of (given as $M_n \times 10^{-3} / P_{n-1} + \frac{1}{2}P_n$, % w/w): 0.5/9, 1.9/22, 2.5/28, 3.5/35, 3.7/38, 4.0/41, 4.5/45, 5.1/51, 5.8/59, 6.4/66, 6.7/73, 9.2/81, 10.5/96.

The DTA curves were plotted for the 20-200°C range using high mol. wt. copolymers (2°C/min heating gradient). The DTA peaks were reproducible for all the M_2 used in consecutive heating-cooling cycles. The copolymerization constants were computed as de-

scribed by Ezrielev *et al.* [10]. The IR spectra contained intense lines typical of the organo-phosphorus groups present in the M_2 , e.g. the $P=O$ bond ($\sim 1240\text{ cm}^{-1}$), POC_6H_5 $91,170\text{ cm}^{-1}$, $C-Cl$ (770 cm^{-1}), and also of PE ($720, 730, 1370, 1470\text{ cm}^{-1}$); there were also the less intense $C=C$ bond absorption lines (1600 cm^{-1}) (an intense line around this frequency belongs to the aromatic ring in the case of DPVP). The latter is evidence of chain transfer

TABLE 2. THE ETHYLENE COPOLYMERIZATION WITH DCEVP
(1400 atm, 160°C , 30 min, 4.37 cm^3 reaction volume*)

Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %	Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %
1	0	1.3	26.5	0	10	5.4	90.2	7.8	37.5
2	0.2	5.5	1.9	0.7	11	7.5	99.7	10.1	30.2
3	0.4	1.3	6.6	6.0	12	9.4	88.2	8.2	51.7
4	0.6	5.5	3.5	5.7	13	16.9	17.1	3.7	64.2
5	0.8	1.3	3.7	7.6	14	24	27.3	4	67.8
6	1.6	3.9	0.1	15.8	15	24	17.1	7	73.1
7	2.4	3.9	0.7	22.5	16	~ 42	27.3	~ 5	79.6
8	3.2	90.2	4.2	31.4	17	~ 54	34.2	~ 4	79.9
9	3.4	90.2	1.4	27.9	18	~ 64	46.5	~ 9	74.5

* Exp. No. 2, 4, 13–18 in 100 cm^3 , exp. No. 8–12 at 1000 atm, 150°C ; exp. No. 2 and 4 in the presence of 0.5 mole/l. benzene; exp. No. 2, 6, 9 in 15, 7 and 10 min reaction time respectively.

taking place on the M_2 (or of a condensation between M_2 branches). The \bar{M}_n of the control PE was 15,000–30,000 (depending on reaction conditions). The mol.wt. of the copolymers rapidly decreased as $[m_2]$ increased. They lost their plasticity and became soft, waxy substances; they were pale yellow, sticky, translucent and resinous when $[m_2] \geq 20$ mole % ($\bar{M}_n = 1000\text{--}3000$). Those produced with DIBVP as comonomer softened earlier than those in which DBVP was used, e.g. at 60 and 80°C , where the samples contained 7.0 mole % DIBVP and 6.8 mole % DBVP respectively (thermomechanical compression tests). The copolymers were soluble in aromatic solvents and those with a large $[m_2]$ content were relatively well soluble in alkylaryl phosphates at room temperature. Gel fractions were chiefly obtainable from copolymers having a high mol.wt. and a considerable DCEVP content.

RESULTS

The high sensitivity of $[m_2]$ to the reaction efficiency greatly complicated the examination of the composition curves. Occasional ones were noticed, especially in tests at small q (Fig. 3), for which the relevant constants in the Mayo–Lewis equation were found to be: $r_1 = 0.05 \pm 0.004$, $r_2 = 0.09 \pm 1.09$ in the case of DPVP, $r_1 = 0.17 \pm 0.022$ and $r_2 = 2.85 \pm 1.94$ for DCEVP. The DBVP and DIBVP composition curves are not described by the Mayo–Lewis equation (both the constants are infinitely variable, $r_2 < 0$, $r_1 < 1$ up to the azeotropic point, while $r_1 > 1$ for the remainder of the curve). Judging from the type of $[m_2]$ change when $q \rightarrow 0$ (Fig. 1), the “true” composition curves are above those shown in Fig. 3 for DPVP and DCEVP and have a ratio in which $[m_2] > [M_2]$ over a wide range of $[M_2]$ (from 0 to about 50 mole %, possibly still broader). The “true” r_1 values are therefore

smaller and the r_2 larger than those given. In contrast, DBVP and DIBVP appear less reactive with respect to ethylene, especially at larger $[M_2]$, in which cases $[m_2] < [M_2]$.

TABLE 3. THE ETHYLENE COPOLYMERIZATION WITH DBVP
(1400 atm, 160°C, 30 min, 100 cm³ reaction volume*)

Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %	Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %
1	0	5.5	22.5	0	6	1.9	5.5	4.4	8.0
2	0.1	5.5	2.9	1.8	7	~33	3.8	~19	6.7
3	0.4	0.9	7.3	1.9	8	~48	3.8	~16	14.0
4	0.6	3.9	6.0	3.0	9	~60	3.8	~45	6.3
5	1.0	5.5	9.1	3.7	10	~70	3.8	~33	11.0

* Exp. No. 1, 2, 5 in the presence of 0.5 mole/l. benzene, exp. No. 3, 4, in 520 and 437 cm³ respectively; the DBVP conversion in exp. No. 7-10 was 3.8, 10.4, 6.6 and 5.7% respectively.

The division of M_2 into 2 groups according to reactivities (DPVP with DCEVP and DBVP with DIBVP) correlated with the polarity differences of the substituents present on the P atom.

Substituent	C_6H_5O	ClC_2H_4O	C_4H_9O	$i-C_4H_9O$	C_2H_5O	$CH_2=CH$
σ^f	-0.06	+0.03	-0.41	-0.30	-0.21	-0.68

The negative σ^f (Kabachnik constant) for C_4H_9O , $i-C_4H_9O$ and C_2H_5O (see below) indicates them to be electron donors which prevent the electron from shifting from the vinyl group to the P atom. The $\sigma^f \approx 0$ in the case of C_6H_5O and ClC_2H_4O means that these substituents can be regarded as neutral [11].

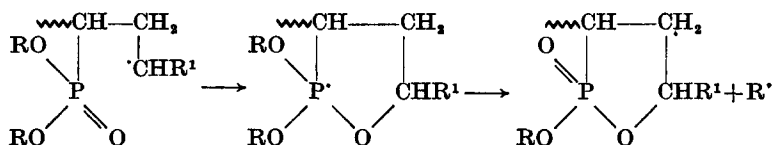
The process rates and the mol.wt. of the products quickly dropped as $[M_2]$ increased (Fig. 2), and the M_2 reacted with ethylene to the same extent as with

TABLE 4. THE ETHYLENE COPOLYMERIZATION WITH DIBVP
(1400 atm, 160°C, 15 min, 437 cm³ reaction volume*)

Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %	Exp. No.	$[M_2]$, mole %	Peroxide $\times 10^4$, mole/l.	q , mole %	$[m_2]$, mole %
1	0	1.3	15.1	0	8	3.3	1.3	1.3	13.6
2	0.6	1.3	1.9	4.1	9	10.5	17.1	6.9	9.0
3	0.9	1.3	0.2	9.8	10	19	51.4	9.8	6.0
4	0.9	15.7	2.2	6.9	11	19	52.1	22.7	21.0
5	1.2	1.3	0.1	7.9	12	23	85.6	9	14.0
6	1.6	1.3	0.1	8.9	13	~33	34.2	~5	13.2
7	2.2	1.3	0.2	7.5	14	~47	137.0	~35	20.0

* Exp. No. 2, 8, 11 with a 30 min reaction time; exp. No. 9-14 in 100 cm³; the DIBVP concentration was 12.6% in exp. No. 14.

any other comonomer [12–14]. Not one of the suggested mechanisms (conjugation $\sim\text{C}^*\text{H}-\text{PO}(\text{OR})_2 \rightarrow \sim\text{CH}-\text{PO}^*(\text{OR})_2$ [15], chain transfer by H-atom dissociation from the organo-phosphorus groups [16, 17], or intramolecular chain transfer [18]) can explain this effect, since the M_2 homopolymerization proceeds at a high rate to a low mol.wt. product [14, 16]. The reaction rate increase at larger $[M_2]$ also applies to the systems which are being examined here. Both the chain transfer reactions are probably in competition with each other and one can visualize variations of intramolecular transfer which lead to the formation of 5- and 6-membered rings; but essential is the feasibility of this mechanism in the case of $M_2M_1^*(R^1=H)$ as well as of $M_2M_2^*(R^1=\text{PO}(\text{OR})_2)$ radicals, e.g.



The rate of the intramolecular attack on the $\text{P}=\text{O}$ bond by the radical centre is thus in direct proportion to the M_2^* radical concentration, while that on the H atom present in the organo-phosphorus groups is in direct proportion to the product of radical concentration (chain transfer agents) with $[M_2]$. When $[M_2]$ is small, the chain will be mainly inactivated by the intramolecular mechanism (the proportion of M_2^* is large because $r_1 \ll 1$ in this M_2 range) and will thus yield a relatively stable P^* intermediate radical on which the free valency is located on the P atom. The chain regeneration will be slow as a consequence, and the total reaction rate will drop as well as the mol.wt. of the copolymers. The rate of the H atom dissociation will increase as a function of $[M_2]$ and the total reaction rate will increase because the process will lead directly to chain propagation, but the mol.wt. of the product will remain low.

The unusually large sensitivity of the rate of DPVP and DCEVP copolymerizations to the initiator concentration at low $[M_2]$ (Fig. 2) appears to be a secondary effect. As $[m_2] \gg [M_2]$ in this range, the acceleration of the reaction when the initiator concentration is raised will rapidly reduce the M_2 contents in the mixture and the reaction rate will increase still further.

A number of indirect data led to the theory (primarily for the lower $[M_2]$ range) that the bulk, and more so the solution reaction, will take place in most cases under single phase conditions. The M_2 solubilities in n-alkanes as models for liquid ethylene support the belief that the ethylene- M_2 systems are homogeneous under the reaction conditions. As a $[M_2]$ increase results in a rapid mol. wt. decrease of the copolymers, the majority of copolymer mixtures with monomer components will probably be in a homogeneous state (like PE of $\bar{M}_n < 20,000$, which forms a homogeneous phase with ethylene at 1400 atm/160°C [7]). Products not soluble in the monomers probably form during copolymerization due to $\text{P}-\text{O}-\text{C}$ bond condensations when more of the DCEVP is present. This

theory was confirmed by the compositional uniformity of the majority of copolymer fractions. Finally, the conditional composition curves for DPVP and DCEVP copolymers produced by the bulk and solution processes coincide with those obtained under various homogenization conditions used for the reaction medium (Fig. 3).

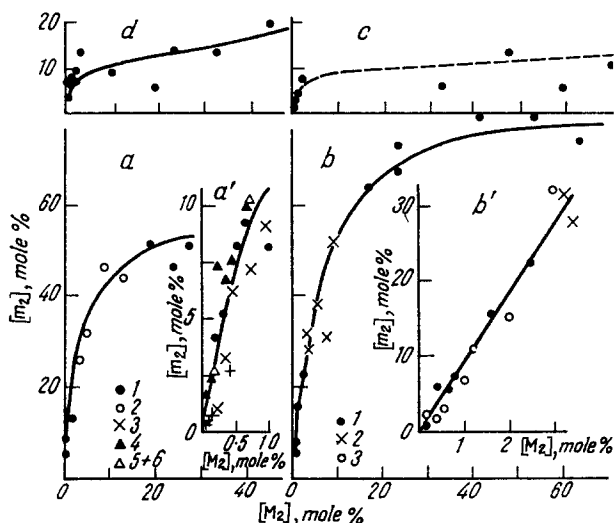


FIG. 3

FIG. 3. The ethylene and M_2 content curves: *a, a'*—DPVP: 1, 2—1300–1400 atm, 160°C; 3—1000 atm, 140°C; 4—1000 atm, 80°C; 5—400 atm, 60°C; 6—in a recycle reactor with stirring; 1—in bulk; 2–6—in solution; 3–5—data from [6]; *b, b'*—DCEVP: 1—1400 atm, 160°C; 2—1000 atm, 150°C; 3—in recycle reactor, 1300 atm, 200–220°C; *c*—DBVP, 1400 atm, 160°C; *d*—DIBVP, 1400 atm, 160°C (*b, b', c, d*—in bulk processes).

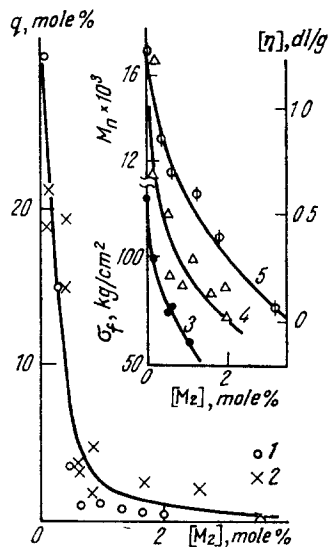


FIG. 4

FIG. 4. The dependence on M_2 content of the monomer mixture (1400 atm, 160°C, 30 min): 1—of M_2 and DPVP conversion (1.2×10^{-3} mole/l. peroxide); 2—of ethylene and DCEVP conversion (5.5×10^{-4} mole/l. peroxide, 0.5 mole/l. benzene); 3—of the tensile strength of DPVP copolymers (5.5×10^{-4} mole/l. peroxide, 0.5 mole/l. benzene); 4—of $[\eta]$ (decalin, 100°C) of the DPVP copolymers (1.2×10^{-3} mole/l. peroxide); 5—of the \bar{M}_n of DIBVP copolymers (1.3×10^{-4} mole/l. peroxide).

The melting and crystallization temperatures (according to DTA) drop when the $[m_2]$ is raised, while the copolymer density increases (Fig. 5). There is no effect of chemical composition of the substituent R on the two functions mentioned above. The nature of the density changes indicates the same two M_2 groups to be present as those found in the kinetic study, i.e. the DPVP and DCEVP copolymer densities increase noticeably faster than those of DBVP and DIBVP copolymers (and of the diethylvinylphosphonic acid [6]); the change is approximately the same within each group. The described polarity differences between the organo-

phosphorus groups present in M_2 obviously affect the chain packing in the amorphous zones of the copolymers containing M_2 chain units. The melting and crystallization temperatures decrease significantly only from $[m_2] \sim 2$ mole % onwards; the rate of the density increase also falls in this composition range. These results agree with the theory of crystal structure distortion; the latter mainly occurs after the PE chain segments become shorter on average and will then have the dimensions of the laminar folds (~ 100 CH_2 groups, which about equals 2 mole % M_2).

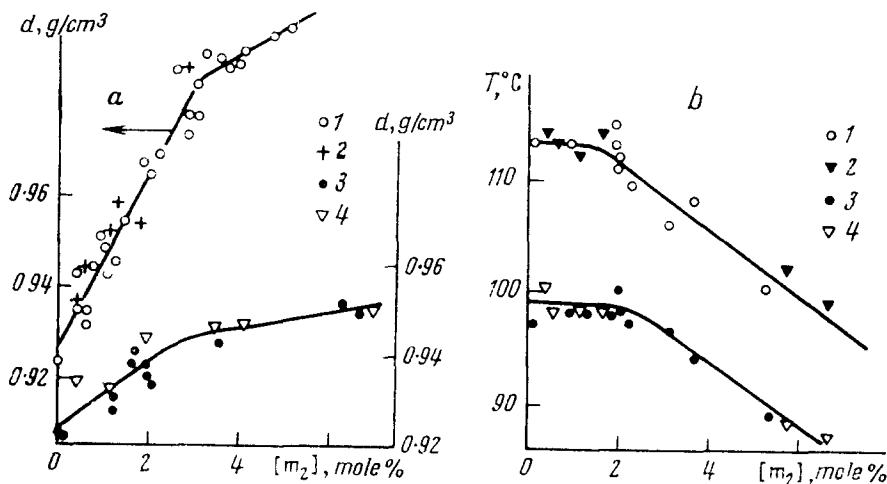


FIG. 5. *a*—The density; *b*—the melting and crystallization temperatures, as functions of ethylene- M_2 copolymer composition. *a*: 1—DPVP; 2—DCEVP; 3—DBVP; 4—DIBVP. *b*: 1, 3—DBVP; 2, 4—DCEVP (1, 2— T_m ; 3, 4— T_{cryst}).

The reactivities of the copolymers are relatively poor in P—O—C group condensations (the most reactive are the DCEVP copolymers). There is no cross-linking according to DTA when the copolymers are heated to about 200°C regardless of the type of M_2 used (which is in contrast with the behaviour of the ethylene-vinylalkoxysilane copolymers [19]). This absence of crosslinking under these conditions is also indicated by the thermochemical curves obtained with the DBVP and DIBVP copolymers.

Translated by K. A. ALLEN

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KINETICS OF THE INHIBITED OXIDATIVE POLYMERIZATION OF VINYL MONOMERS IN THE PRESENCE OF AN ANTI-OXIDANT (AO)*

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The kinetics of the polymerization of methyl methacrylate (MMA) and dimethyltriethylene glycol (TGM-3) have been studied in the presence of oxygen and of an anti-oxidant (AO). The induction period depends on the monomer concentration in a closed system and increases with the AO content only in a relatively narrow range

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