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THE FREE-RADICAL COPOLYMERISATION OF ETHYLENE

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I. INTRODUCTION

Copolymerisation has now acquired considerable importance as a method which makes it possible to alter the properties of a polymer in a required direction. By selecting different combinations of ethylene with appropriate monomers, it is possible to vary over a wide range such properties of the polymer as its strength, elasticity, melting point, adhesive properties, solubility, etc.[1,2] Copolymers of ethylene can be prepared both by free-radical copolymerisation and by ionic copolymerisation. The free-radical process, in particular, is of considerable interest, since in this case the number of monomers which can be used with ethylene is much greater than for ionic copolymerisation. The ionic process is carried out chiefly with monoalkene and diene hydrocarbons, whereas the copolymerisation of ethylene by the free-radical mechanism can be carried out not only with these hydrocarbons but also with a large number of compounds of different types, including halogenated alkenes, vinyl esters and ethers, acrylic monomers, and even compounds which do not polymerise independently, such as sulphur dioxide and carbon monoxide[1,2]. Moreover, the presence of different functional groups (e.g. acetate and carbonyl groups) in the copolymers prepared by radical copolymerisation makes it possible to convert these polymers, by means of chemical reactions, into a number of new copolymers (binary or ternary in the case of partial replacement of the functional groups) which cannot be obtained by direct copolymerisation with ethylene.

The present review deals with copolymers of ethylene prepared by radical copolymerisation, and covers the literature up to September 1964. Work published before 1959 is mentioned only briefly, since this has been described in detail in monographs devoted to polyethylene[1,2], and more recent work is examined in greater detail.

II. GENERAL PROBLEMS OF THE COPOLYMERISATION OF ETHYLENE

Copolymers of ethylene, with such readily polymerised monomers as styrene, vinyl acetate, and acrylic acid, were first prepared as early as 1930,[3] i.e. before polymers of ethylene itself had been prepared. In the presence of peroxo-compounds under conditions of low pressure, a small quantity of ethylene was introduced into the polymer. However, the copolymerisation of ethylene with unsaturated compounds of different types[4] was described for the most part after the discovery of polyethylene. Styrene, isobutene, methyl acrylate, n-butyl acrylate, methyl methacrylate, vinyl acetate, butadiene, etc. were proposed as secondary components. The copolymerisation was carried out by a method analogous to that used for the polymerisation of ethylene, by the block method under conditions of high pressure (1000–2000 bars) and relatively high temperature (100–300°), in the presence of oxygen or peroxo-compounds as initiators[5-9]. It has been shown comparatively recently that it is possible to copolymerise ethylene under the influence of ionising radiation with alkenes[10], vinyl chloride, vinyl acetate, and carbon monoxide[11].

Colombo and Steinberg[12-14] describe the radiation copolymerisation of ethylene with a large number of monomers — propene, but-1-ene, *cis*- and *trans*-but-2-ene, isobutene, isoprene, vinyl chloride, chlorotrifluoroethylene, vinyl acetate, allyl acetate, allyl alcohol, acrylonitrile, methyl methacrylate, styrene, divinylbenzene, vinylpyrrolidone, methyl vinyl ketone, and carbon monoxide. In a number of cases, however, the data on the composition and properties of the resulting copolymers, given by Colombo and Steinberg, are of doubtful accuracy, since the copolymerisation was carried out to high degrees of conversion. On the basis of the data given below on the relative activities of monomers, it may be assumed that, in the case of copolymerisation with methyl methacrylate, methyl acrylate, vinylpyrrolidone, methyl vinyl ketone, and also possibly with propene and allyl acetate, the reaction products contained polyethylene.

Kolesnikov and his coworkers[15,16] showed that it is possible to copolymerise ethylene with certain monomers (vinyl chloride, styrene, vinyl acetate, acrylonitrile, and methyl methacrylate) under the influence of alkylborons.

The copolymerisation temperature for ethylene covers a very wide range, from -70° to 250°. The process is usually carried out at 180–250° in the case of initiation of copolymerisation by molecular oxygen[4] or within the range 50–150° for initiation by organic peroxides[5-9]. The use of γ-radiation[12] and alkylborons[16] makes it possible to carry out the copolymerisation at or below room temperature. The possibility is not excluded that at temperatures below 0° the process takes place partly or completely by an ionic mechanism. In particular, ethylene is known to polymerise by a cationic mechanism under the influence of ^{60}Co γ-radiation at -78°.[17,18]

The radical copolymerisation of ethylene is most frequently carried out at a pressure of $\sim$ 1000 bars[4,8,9]. The use of such high pressures is apparently necessary in order to produce a high concentration of ethylene to ensure sufficiently rapid reaction and to obtain copolymers of optimum

molecular mass. It may be assumed, however, that this condition to some extent applies only to the copolymerisation of ethylene with a small quantity of a second component in the gas phase. In the case of copolymerisation in the liquid phase, pressure plays a smaller part and may be reduced to 100–300 bars[5,15,16].

The process is carried out, not only by block copolymerisation, but also in low-boiling organic solvents (e.g. benzene, toluene, or isooctane)[9,15,16], in water[7,8], and in emulsion[6].

Some idea of the physical properties of copolymers of ethylene can be obtained on the basis of a comparatively simple model consisting of a polymethylene chain in which hydrogen atoms have been replaced by different side-groups. The properties of the copolymers will be determined by the nature of the second component, its concentration in the copolymer, and the nature of the distribution of monomer units of the second component along the length of the chain.

The influence of the nature of the second component involves chiefly two factors, the polarity and the dimensions of the monomer units. The presence of polar units in the polyethylene chain brings about intermolecular and intramolecular interaction between the permanent and induced dipoles, leading to an increase in the rigidity and a rise in the melting point; at the same time there is a deterioration in the dielectric properties of the polymer, and its adhesion to various materials increases.

In the molecules of ethylene copolymers containing a small quantity of the second component, the units of the latter will generally be attached only to non-polar and unpolarised methylene groups, which have no significant influence on their dipole moment. In this case the dipole moment of the units can be taken as approximately equal to that of the corresponding hydrogenated compound. The dipole moments of compounds which are the hydrogenated analogues of the second components in ethylene copolymers are given in Table 1. In conformity with the data in Table 1, the greatest rigidity and highest melting point among the known types of ethylene copolymer are shown by the copolymers with carbon monoxide and sulphur dioxide.

TABLE 1. Dipole moments of various hydrogenated analogues of second components in copolymers of ethylene[19].

Compound	Dipole moment, D
Hydrogenated analogues of methyl acrylate*, vinyl alcohol, methyl methacrylate**, ethyl acrylate, n-butyl acrylate, vinyl chloride, vinyl acetate, vinyl fluoride, and vinylidene chloride	1.7–1.9
1,1-Difluoroethane (vinylidene fluoride)	2.2
Diethyl ketone (carbon monoxide)	2.7
Acetonitrile (acrylonitrile)	3.3
Succinic anhydride (maleic anhydride)	3.8
Diethyl sulphone (sulphur dioxide)	4.4
Ethylene carbonate (vinylene carbonate)	4.7

* The dipole moment of the monomer unit of methyl acrylate attached to two monomer units of styrene in the copolymer of methyl acrylate with styrene is 1.61 D, and that of methyl methacrylate is 1.68 D. The production of induced dipoles in neighbouring phenyl groups possibly leads to a slight decrease in the dipole moments of the monomer units of methyl acrylate and methacrylate relative to those for the corresponding homopolymers[20,21].

** Shima's data[21].

The dimensions of the units of the second component influence the properties of the ethylene copolymer as follows. When side-groups whose dimensions differ little from those of the methylene groups are introduced into the polyethylene chain, the crystal structure of the polyethylene is not broken down: there is merely a change in some parameters of the crystal lattice, accompanied by a change in the physical properties of the polymer[22–25]. In particular, the melting points of these copolymers change monotonically with change in composition, from the melting point of polyethylene to that of the second homopolymer. This phenomenon, which is analogous to the formation of mixed crystals in the cocrystallisation of compounds of low molecular weight, has been termed isomorphism of monomer units in macromolecules[26]. Values of the van der Waals radii of some substituents are given in Table 2.[27] In conformity with these data, the formation of crystalline copolymers over a wide range of composition was observed in the copolymerisation of ethylene with tetrafluoroethylene and carbon monoxide†, and also in copolymers of ethylene with vinyl alcohol[22–25,28,29]. Determination of the crystal structure of copolymers of ethylene with vinyl alcohol led to a re-examination of previously held ideas on the nature of the crystallinity of high polymers[24,25].

If the dimensions of the side-groups are so great that packing of the copolymer molecules into the crystal lattice of polyethylene becomes impossible, the introduction of copolymer molecules into the polyethylene chain leads to a gradual decrease in the crystallinity of the copolymer. At a low concentration of the second component, the melting point of these copolymers falls rapidly, in agreement with Flory's formula[30]. At the same time there is a decrease in the hardness of the polymers and increases in their elasticity and solubility. At a low concentration of the second component the nature of these changes apparently depends chiefly on the quantity of added monomer and not on its nature. Thus the copolymers of ethylene with vinyl acetate, ethyl acrylate, *N*-vinylpyrrolidone, and *N*-vinylsuccinimide, obtained at 1000 bars and 70–90°, showed an approximately linear relationship between the logarithm of

TABLE 2. Van der Waals radii of substituents[27].

Substituent	Van der Waals radius, Å
H	1.17
F	1.35
O	1.35*
Cl	1.80
CH_3	1.90

* Bunn's data[24].

† The structure of the copolymer is

$$[(-CH_2CH_2-)_n-\underset{\underset{O}{\|}}{C}]_m$$

the modulus of rigidity and the molar content of the second component in the polymer, irrespective of the nature of the second component [31].

The influence of the dimensions of the unit of the second component on the crystallinity of the copolymers is clearly revealed on comparing the properties of the copolymers of ethylene with carbon monoxide and with propene (the latter copolymer was prepared on a Ziegler–Natta catalyst): the crystallinity of ethylene–carbon monoxide copolymers amounts to ~70% and is independent of the content of the second component; the crystallinity of ethylene–propene copolymers decreases linearly to zero with increase in the content of the second component from 0 to 15%. [32] This shows that carbonyl groups enter the polyethylene crystal lattice, whereas $CHCH_3$ groups break down the lattice‡.

The phenomenon of isomorphism of monomer units in macromolecules can be observed in the copolymers of ethylene and carbon monoxide. According to the data of Chatany et al. [34,35], copolymers obtained at room temperature in the gas phase have the crystal structure of polyethylene, but the lattice parameters change with increase in the carbon monoxide content.

Thus the two factors examined — the polarity and the dimensions of the unit of the second component — have opposite effects on the properties of the ethylene copolymers. If the unit of the second component is sufficiently large, steric factors predominate. For example, the copolymerisation of ethylene with small quantities of polar monomers such as vinyl acetate gives products whose rigidity and melting points are lower than those of polyethylene. On saponification of these copolymers, however, the opposite effects are observed, as a result of the replacement of the large acetate group by the comparatively small hydroxy-group, despite the fact that the dipole moment of the unit of the second component remains almost unchanged (see Table 1).

One of the most important factors influencing the properties of a copolymer is its composition. The nature of the dependence of the properties of ethylene copolymers on the relative proportions of the monomers is determined by the dimensions of the molecules of the second component. Where isomorphous crystalline structures are formed, we must expect a monotonic change in the properties of the copolymer with increasing content of the second component. If introduction of molecules of the latter leads to breakdown of the copolymer structure, the properties of the copolymer show a marked dependence on composition. The addition of even small quantities of monomers such as vinyl chloride and vinyl acetate leads to a marked fall in the melting point and the crystallinity of the copolymer. At a high concentration of the second component, the product acquires properties characteristic of the homopolymer of the second monomer. The influence of the composition of ethylene copolymers is not shown with all properties, however. In particular, the dependence of the temperatures of vitrification of ethylene copolymers on their composition is specific in character [36,37].

‡ Here and subsequently, conclusions regarding the crystallinity of copolymers are based on data obtained by X-ray structural analysis. However, structural criteria of crystallinity do not always agree with thermodynamic criteria [33]. Similarly no account is taken of the influence of intermolecular interaction in the molten state, the rigidity of the chain, and other factors on the kinetics of crystallisation and the tendency of the copolymers to undergo supercooling.

The dependence of the vitrification temperature of ordinary vinyl copolymers on their composition is described, to a first approximation, by the straight line joining the glass points of the corresponding homopolymers [38]. The vinyl chloride–vinyl acetate and vinyl chloride–acrylonitrile systems provide examples. It was to be expected that copolymers of ethylene would exhibit analogous properties, but they in fact exhibit quite different behaviour, as shown by Reding et al. [37] By means of a torsion balance and an apparatus for determining the maximum mechanical losses (Instron tester), they detected two glass points (two temperature transitions) in ethylene copolymers. The first, low-temperature transition takes place at -125° and is almost independent of the composition of the copolymers. The existence of this glass point was attributed [37] to the movement of segments comprising 3–5 CH_2 groups. The second, high-temperature transition is observed between -25° and +50°, and is independent of composition only at high ethylene contents (35–100 wt.%); at high concentrations of the second component, the glass point of the copolymer rises sharply, approaching linearly that of the corresponding homopolymer. It was not clear why the glass point of the copolymer remains unchanged over a wide range of compositions. Mandelkern et al. [39] suggested that in crystalline copolymers it is determined by the composition of the amorphous phase. Since in ethylene copolymers only the ethylene units crystallise with increase in the ethylene content, the composition of the amorphous phase remains constant, so that the vitrification temperature remains constant. A similar explanation for copolymers of ethylene with vinyl acetate was given by Nielsen [36], but, as correctly noted by Reding et al. [37], this explanation does not reflect the true situation, since with ethylene–vinyl acetate copolymers the last traces of crystallinity disappear at a content of the latter of 45 wt.%, whereas the glass point remains constant up to 65%. Reding and his coworkers suggest that the high-temperature transition in ethylene copolymers is associated with the localised movement of small segments of the main chain, attached to tertiary carbon atoms. This movement is independent of the nature of the remainder of the molecule. At a high concentration of the second component, as a result of steric hindrance or dipole–dipole interaction between the side-groups, this movement is transformed into movement of large sections of the macromolecules, including long sections of the chain and side-groups, analogous to that taking place in copolymers of the vinyl chloride–vinyl acetate type.

The two glass points of copolymers of ethylene with many monomers depend little on the nature of the second component [37].

It is evident that the properties of copolymers also depend on the distribution of the monomer units along the chain, which is determined by the product of the relative activities of the monomers (see Section III); if this quantity is close to unity, the monomer units are distributed irregularly; but with decrease in the magnitude of the product, the extent to which the monomers alternate increases. In particular, if the crystallinity of the copolymers is determined by the crystallisation of chain segments consisting of the units of only one monomer (e.g. ethylene), the crystallinity of such a copolymer increases with increase in the product of the relative activities of the monomers. This was confirmed for copolymers of ethylene with propene, having up to 10% crystallinity, obtained on Ziegler–Natta catalysts [40,41]. The crystallinity of ethylene copolymers has been studied by Killian [42].

The uses of ethylene copolymers have been dealt with in a number of reviews[43,44]. Some information on their applications is given in Section IV.

III. THE REACTIVITY OF ETHYLENE IN RADICAL COPOLYMERISATION

Because of the experimental difficulties involved in carrying out copolymerisation under high pressures, data on relative activities have until now been published only for a comparatively small number of systems containing ethylene (Table 3). We ignore the values given by Pieski[55] for the relative activities in the copolymerisation of ethylene with styrene ($r_{ethylene} = 0.0069$, $r_{styrene} = 345$), since the conditions and methods of determination are unknown.

Since there is no conjugation of the double bond, the reactivity of ethylene as a monomer is low, so that the rate of attachment of ethylene molecules to both types of copolymer radical in copolymerisation with vinyl chloride, acrylonitrile, and n-butyl acrylate is less than the rate of attachment of molecules of the second component ($r_1 < 1$, $r_2 > 1$); the opposite relationship is observed in copolymerisation with vinyl fluoride.

If we take ethylene as standard monomer, the relative rates of attachment of monomers to copolymer radicals terminating in an ethylene group, in reactions of chain growth in the radical copolymerisation of ethylene, are given by the corresponding values of $1/r_1$. In Table 4 the values of $1/r_1$ for various monomers are compared with the relative rates of attachment of the same monomers to the methyl radical in the liquid phase at 65°, calculated from Szwarc's data given in Bagdasar'yan's monograph[56]. Since the relative activities generally depend little on temperature, the values of r_1 are taken from Table 3 without correction for temperature§. The relative rate of addition of propene to the methyl radical was calculated from the data of Mandelkern and Steacie[56] for a temperature of 175° (reaction in the gas phase). It can be seen from Table 4 that the relative reactivity of monomers towards both the methyl radical and copolymer radicals terminating in an ethylene group increases in the order propene < vinyl acetate < < tetrafluoroethylene < acrylonitrile. The values do not, however, show a quantitative relationship corresponding to Szwarc's equation[57] (n not constant).

§ For vinyl acetate the value of r_1 at 70° has been taken.

TABLE 4. Relative rates of attachment of monomers to the methyl radical and to copolymer radicals terminating in an ethylene group.

Monomer (M_i)	$\frac{K_{CH_3^\cdot M_i}}{K_{CH_3^\cdot C_2H_4}}$	$\frac{1}{r_1}$	$n = \frac{\log \frac{K_{CH_3^\cdot M_i}}{K_{CH_3^\cdot C_2H_4}}}{\log 1/r_1}$
Propene	1.22	0.29	—0.16
Tetrafluoroethylene	10	6.7	1.2
Vinyl acetate*	2.2	1.3	3.0
Acrylonitrile	91	50—1000	—

* The relative rate of attachment to the ethyl radical at 90° is 2.0; $1/r_1 = 0.93$.[48]

The relative rates of addition of propene to methyl and to copolymer radicals are quite different. The rate of attachment of propene to the methyl radical is greater than that of ethylene, whereas the opposite relationship is observed in the addition of these monomers to a copolymer hydrocarbon radical. The lower reactivity of propene in the latter case does not agree with the theory of ideal radical reactivity applicable to the reactions of hydrocarbons[58]. The reasons for the above discrepancies are not clear.

According to Alfrey and Price[58], the relative activities of monomers in copolymerisation reactions can be calculated by means of constants characteristic of individual monomers — the activity factor Q and the polarity factor e — which are calculated from experimental data. The values taken for styrene are $Q = 1.0$ and $e = -0.8$. A theoretical interpretation of the method of Alfrey and Price has

TABLE 3. Experimental values of the relative activities and parameters for the copolymerisation of ethylene.

Second component	Copolymerisation conditions		Relative activities		Ref.	$r_1 r_2$	Copolymerisation parameters by methods of					
							Alfrey and Price		Kawabata et al.		Spasskii and Karas*	
	temp., °C	pressure, b	r_1 (ethylene)	r_2			Q_1	e_1	Q_1	e_1	$\alpha_1\beta_1$	ϵ_1
Propene	130—220	1000—1700	3.43±0.16	—	45	—	—	—	—	—	—	—
But-1-ene	130—220	1000—1700	3.25±0.38*	—	45	—	—	—	—	—	—	—
Oct-1-ene	130—220	1000—1700	3.66±0,15	—	45	—	—	—	—	—	—	—
Vinyl chloride	70	до 300	0.20±0.002	1.85±0.2	46	0.37	0.019	—0.79	0.02	—0.6	—	—
Ditto	90	1000	0.24±0.07	3.6 ±0.3	47,48	0.86	0.011	—0.18	0.01	0.0	—	—
Vinyl fluoride	160	1000	4.4 ±0.8	0.16±0.05	48	0.70	0.035	0.68	—	—	—	—
Tetrafluoroethylene	40—200	70—200	0.15	0.85	49	0.13	0.010**	—0.21**	—	—	—	—
Vinyl acetate	70	400	0.77±0.04	1.02±0.02	50	0.79	0.023	0.26	0.02	0.4	0.14	—0.06
Ditto	130	400	0.97±0.03	1.02±0.02	50	0.99	0.022	—0.13	0.02	0.0	0.22	—0.29
»	90	1000	1.07±0.06	0.08±0.19	47,48	1.16	0.026	—0.22	0.02	—0.1	0.23	—0.30
Acrylonitrile	20	10—45	0	4	51	0	—	—	—	—	—	—
»	18—50	100	0	7	51	0	—	—	—	—	—	—
n-Butyl acrylate	70	1000	0.03±0.01	11.9 ±2.5	48	0.36	0.015	—0.01	—	—	0.26	—0.34
Carbon monoxide	20	650	0.05	0***	13,52	0	—	—	—	—	—	—
Ditto	70	120—240	0.16±0.02	0	53	0	—	—	—	—	—	—
»	120—130	850—1000	0.15	0***	54	0	—	—	—	—	—	—
					Mean		0.020	—0.075	0.02	—0.1	0.21	—0.25

* Without correction for chain transfer via the alk-1-ene.
** Values taken from Young's summary[49].
*** Assumed by the authors of the works cited.

been given by a number of authors[60-69]. Despite certain difficulties associated with the interpretation of the physical significance of the polarity factor[66,67], this method is useful for a preliminary estimation of the behaviour of monomers in copolymerisation reactions. Table 3 gives the values of the parameters Q and e which we have calculated for ethylene; those for other monomers have been taken from Young's summary[49].

Since the Alfrey–Price method is semi-empirical in character, various modifications have been proposed. In particular, it appears more appropriate to take as standard monomer not styrene but ethylene, assuming for the latter $Q = 1$ and $e = 0$, since, of all monomers containing a carbon–carbon double bond, ethylene has the simplest molecular structure. The establishment of the true zero on the scale of polarity factors would make it possible to obtain more accurate values for the activity and polarity factors of various monomers. The relative activities for the copolymerisation of several monomers have been calculated by Zutty and Burkhart[47,48], using a $Q-e$ scale based on ethylene. Allowance must be made for the fact that these values correspond only to a pressure of about 1000 bars, at which the copolymerisation of ethylene was carried out, since the relative activities and hence the activity and polarity factors depend on pressure[47].

Kawabata et al.[66,67] consider it advisable to take $e = 0$ for styrene; the same conclusion has been reached by Bamford and Jenkins[65]. Values of the activity and polarity factors for ethylene which we have calculated using the method of Kawabata et al. are given in Table 3. Price[70], however, objects to the choice of zero for the polarity factor of ethylene or styrene. In his opinion, the polarity factor for ethylene should be negative, since the double bond in the ethylene molecules carries a negative charge; the zero on the scale of polarity factors should correspond to vinyl chloride, and this corresponds to a value of e for styrene of -0.8. He refers, in particular, to the data of Zutty and Burkhart[48], who, on the basis of values of Q and e for other monomers taken from Alfrey et al.[59] and from Thompson and Raines[71], calculated for ethylene the mean values $Q = 0.03$ and $e = -0.43$. The mean value of the polarity factor which we have obtained for ethylene by the Alfrey–Price method is close to zero; at the same time, Young's summary gives for vinyl chloride $e = 0.20$. The value of the polarity factor can evidently vary over a fairly wide range, depending on the choice of data taken as a basis for the calculation.

In the method of Spasskii and Karas'[72], the activity factor Q is replaced by the product of two quantities — a factor α representing the influence of the polarisability of the π bonds, characterised by the refraction, and a factor β representing the influence of the structure of the monomer, not taken into account by the refraction. Values of the parameters for the copolymerisation of ethylene, which we have calculated by this method, are given in Table 3.

From the mean values of the activity and polarity factors for ethylene (Table 3) we have calculated, by the methods of Alfrey and Price, Kawabata et al., and Spasskii and Karas', values of the relative activities for the copolymerisation of ethylene with monomers of different classes. The results of the calculation are given in Table 5, the copolymerisation parameters of the monomers having been taken from published data[49,66,67,72]. The order of magnitude is generally the same for the relative activities calculated by different methods; discrepancies are observed only with maleic anhydride and diethyl fumarate. Comparison of the calculated (Table 5) and experimental (Table 3) values of the relative activities for the copolymerisation of ethylene shows that the methods of calculation used are sufficiently accurate.

TABLE 5. Calculated relative activities for copolymerisation with ethylene.

Second component	Relative activities by methods of: Alfrey and Price		Kawabata et al.		Spasskii and Karas'	
	r_1 (C_2H_4)	r_2	r_1 (C_2H_4)	r_2	r_1 (C_2H_4)	r_2
Styrene	0.02	25	0.02	50	0.03	33
Butadiene	0.01	43	0.02	64	0.02	58
Isoprene	0.01	41	—	—	0.01	75
Vinyl chloride*	0.44	2.1	0.32	2.5	0.28	1.3
Vinylidene chloride	0.09	9.4	0.04	6.5	0.01	5.4
1,1-Dichloro-2,2-difluoroethylene	0.41	0.02	—	—	—	—
Chlorotrifluoroethylene	0.89	0.10	—	—	—	—
Vinyl fluoride*	1.50	0.11	—	—	—	—
Tetrafluoroethylene*	0.37	0.50	—	—	—	—
Vinyl acetate*	0.78	1.26	1.00	1.00	0.98	0.99
Vinyl γ-methylvalerate	0.49	1.32	—	—	—	—
Vinyl stearate	0.61	1.29	—	—	—	—
Vinyl benzoate	0.36	2.4	—	—	—	—
Vinyl thioacetate	0.07	2.1	—	—	—	—
Ethyl vinyl ether	0.68	0.45	—	—	—	—
Methyl vinyl ketone	0.03	21	0.00	15	0.01	19
Maleic anhydride	0.07	0.06	—	—	0.01	0.41
Diethyl maleate	0.30	0.28	—	—	0.10	0.46
Diethyl fumarate	0.03	5.8	—	—	0.01	0.91
Vinylene carbonate	2.9	0.25	—	—	—	—
Acrylonitrile*	0.03	6.4	0.01	2.9	0.00	5.6
Methacrylonitrile	0.02	27	0.01	6.8	0.00	21
Methyl acrylate	0.05	11	0.01	9	0.01	20
Methyl methacrylate	0.03	31	0.01	20	0.02	33
Ethyl acrylate	0.04	24	—	—	—	—
Ethyl methacrylate	0.04	27	—	—	—	—
n-Butyl acrylate*	0.04	8.3	—	—	0.03	14
n-Butyl methacrylate	0.03	35	—	—	—	—
2-Vinylpyridine	0.02	52	0.01	23	0.03	35
N-Vinylcarbazole	0.05	4.0	—	—	—	—
N-Vinylpyrrolidone	0.16	2.1	—	—	—	—
N-Vinylsuccinimide	0.14	7.2	—	—	—	—

* The experimental values are given in Table 3.

The results of the calculations given in Table 5 naturally require experimental verification. These data may prove useful, however, in the planning of experiments on the radical copolymerisation of ethylene.

The production of a copolymer of uniform composition in high yield can be achieved only if the relative activities of the monomers used do not differ too greatly. The data in Tables 3 and 5 show that the most "convenient" monomers in this sense for copolymerisation with ethylene are fluoroalkenes, vinyl esters of aliphatic acids, and carbon monoxide.

In particular, considerable difficulties should be encountered in the copolymerisation of ethylene with small quantities of acrylic and, more particularly, methacrylic monomers. Copolymers of ethylene with ethyl acrylate, containing a small quantity of the latter, are, however, now being produced in the USA,[73] on equipment designed for the production of high-pressure polyethylene, i.e. as a continuous process. It is evident that it is much easier to keep the composition of the monomer mixture constant in this type of process than in a batch process.

Kawabata et al.[68,69], on the basis of the method proposed by Fukui and his coworkers[61,74,75] for the quantitative characterisation of the activation energy for growth reactions in vinyl polymerisation, have calculated the additional energies of conjugation in the transition state for reaction of the ethylene radical with various monomers ($E_{R\cdot M}$) and also of various radicals with ethylene ($E_{RM\cdot}$). If it is assumed, following these authors, that the preexponential factors for

the addition of different monomers to the same radical are equal, the relative activities of ethylene in copolymerisation with different monomers will be given by the equation

$$\ln r_1 = -q\frac{E_M}{RT},$$

where E_M is the difference between the additional energies of conjugation for reaction of the ethylene radical with the second component and with ethylene, and q is a proportionality coefficient. The polarity factors in reactions involving the ethylene molecule or the ethylene radical were taken as zero.

As will be seen from the results discussed below, however, the assumption that the preexponential factors for the copolymerisation of ethylene are equal is unjustified, so that the relative activities in the copolymerisation of ethylene with vinyl acetate and vinyl chloride (Table 3) do not correspond to the above equation. For many monomers, however, an approximately linear relationship is observed between E_M and the values of the activity factors calculated on the scale proposed by Kawabata et al. (Q = 1.0 and e = 0 for styrene) or on the scale based on ethylene (Q = 1.0 and e = 0 for ethylene)[68,69,76].

IV. COPOLYMERISATION OF ETHYLENE WITH VARIOUS MONOMERS

(a) Copolymerisation with Hydrocarbons

The ionic copolymerisation of ethylene with alkene, alkyne, and diene hydrocarbons has been studied in considerable detail (particularly the copolymerisation of ethylene with propene and butenes on organometallic complexes or a chromium-oxide catalyst), but the free-radical copolymerisation of ethylene with these hydrocarbons has been little studied.

In early patents on the copolymerisation of ethylene[4,5,7], the second components included such alkenes as propene, butene, and methylpropene. No reliable proof of the formation of a copolymer was given, however. Later, solid high-molecular copolymers of ethylene with a small quantity of propene or octadec-1-ene were prepared at higher pressures, of 2000–2500 bars[77]. The copolymerisation was carried out by a continuous block method at ~ 200° in the presence of oxygen as initiator. The products obtained differed from polyethylene in their high content of vinyl groups, determined by infrared spectrophotometry. Thus polyethylene prepared by the usual high-pressure method contains 0.02–0.06 double bond per 1000 carbon atoms, whereas the copolymer of ethylene with propene contains 0.2–0.6 double bond[77].

According to Boghetich et al.[45], the only way in which the unsaturation of the polymer can increase is by chain transfer via the alk-1-ene:

$$\cdots CH_2{-}CH_2^{\bullet} + CH_2{=}CH{-}CH_3 \longrightarrow \cdots CH_2{-}CH_3 + CH_2{=}CH{-}CH_2^{\bullet},$$

$$CH_2{=}CH{-}CH_2^{\bullet} + CH_2{=}CH_2 \longrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2^{\bullet},$$

since none of the four growth reactions in the copolymerisation of ethylene with alk-1-enes leads to an increase in the content of double bonds in the copolymer.

Boghetich et al.[45] give convincing proof of the copolymerisation of ethylene with alk-1-enes by a radical mechanism. Formation of a copolymer was confirmed by carrying out the copolymerisation of ethylene with ^{14}C-labelled propene, but-1-ene, and oct-1-ene, and then determining the activity of the product. The copolymerisation was carried out at 1050–1750 bars and 130–200° under the influence of t-butyl peroxide and acetoxime. The values of the relative activity of ethylene in copolymerisation with different alk-1-enes (Table 3) are close to one another and lie in the range 3.4–3.6, with a correction for chain transfer; in other words, under the conditions studied, ethylene is a more active monomer than the alk-1-enes. Chain transfer was estimated from the decrease in molecular mass and the increase in unsaturation of the polymer with increase in the alk-1-ene content of the original mixture. The values of the chain-transfer constants are given in Table 6. Comparison of the data on the unsaturation and on the radioactivity of the copolymers shows that only a small quantity of alk-1-ene (< 10%) enters the copolymer by chain transfer, and that the predominant reaction is copolymerisation.

Study of the continuous copolymerisation of ethylene with propene in the presence of oxygen as initiator at 1500–1800 bars in the range 170–240° showed that the process can be carried out at a concentration of propene in the original mixture not greater than 15%.[78]

As stated in Section II, ethylene copolymerises under the influence of ^{60}Co γ-radiation with alkenes, styrene, isoprene, and divinylbenzene[10,12–14].

The copolymerisation of ethylene with styrene has also been carried out under the influence of tributylboron at 18–50°[15] and of triisobutylboron between -70° and 18°.[16] In the latter case, ethylene copolymerises with styrene much more slowly than with vinyl chloride and acrylonitrile. The low yield of copolymer was attributed to the fact that styrene, which is the more active monomer, does not polymerise readily in solution in the presence of alkylborons. Copolymers of ethylene with styrene dissolve readily in toluene, dichloroethane, and tetralin at room temperature, and have vitrification temperatures in the range 55–95°.[16] The copolymerisation of ethylene with 9-methylenefluorene has also been described[79].

The free-radical copolymerisation of ethylene with acetylene and diene hydrocarbons is carried out at high pressures (of about 1000 bars) and temperatures up to 200° under the influence of oxygen, organic peroxides[7,9,80–82], and ^{60}Co γ-radiation[10,12,13]. Among diene hydrocarbons, butadiene, isoprene[7,9,12,13,81], and norbornadiene[82] have been used. According to our calculations (Table 5), the relative activity of monomers such as butadiene and isoprene is much greater than that of ethylene, which is zero. Thus the content of the second component in the copolymer will always be greater than its content in the original mixture. A characteristic feature is that the copolymers of

TABLE 6. Chain-transfer constants for the copolymerisation of ethylene with alk-1-enes[45] (pressure 1400 bars, temperature 130°).

Alk-1-ene	Chain-transfer constant from	
	infrared spectrophotometry	decrease in molecular mass
Propene	0.011±0.003	0.015±0.003
But-1-ene	0.033±0.007	0.047±0.002
Oct-1-ene	—	0.036±0.002

ethylene with acetylene and diene hydrocarbons contain double bonds, by means of which vulcanisation can be carried out. The molecular mass of the ethylene–acetylene copolymers decreases with increase in the content of the latter [80].

Mortimer and Arnold [83] have shown that ethylene does not copolymerise with benzene in the presence of t-butyl peroxide at 1400 bars and 130°.

(b) Copolymerisation with Halogenated Alkenes

According to many patents, ethylene copolymerises with halogen-containing alkenes of different types: the comonomers are chlorine- and fluorine-containing compounds, and alkenes containing one, two, or more halogen substituents may be used. Copolymerisation is carried out chiefly at high pressures (700–1500 bars) and temperatures of 50–200° under the influence of peroxide initiators in the presence of water or in block. Under these conditions, copolymers of ethylene have been obtained with vinyl chloride [84,85], vinylidene chloride [86], vinylidene fluoride [87–89], tetrafluoroethylene [90], chlorotrifluoroethylene [91], 1-chloro-1-fluoroethylene [92], 1,1-dichloro-2,2-difluoroethylene [93], 3,3,3-trifluoropropene [94], and hexafluorocyclobutene [95]. With some monomers (tetrafluoroethylene [96] and 3,3,3-trichloropropene [97]) the copolymerisation initiated by organic peroxides was carried out at a relatively low pressure (up to 200 bars).

Ethylene copolymerises with vinyl chloride and chlorotrifluoroethylene under the influence of ^{60}Co γ-radiation [11–14,98]. The copolymerisation is usually carried out at room temperature. With chlorotrifluoroethylene, development of an explosive reaction is observed at a definite dose rate, of about 3000 J kg^{-1} h^{-1}. [13,98] In the separate polymerisation of ethylene and chlorotrifluoroethylene under analogous conditions, no explosion was observed. Tabata and his coworkers [28,29,99,100] have shown that it is possible to carry out the radiation copolymerisation of ethylene and tetrafluoroethylene in the liquid state at -78°. They suggest that under these conditions the reaction proceeds in a homogeneous medium. A characteristic feature is that the copolymerisation takes place by a radical mechanism, whereas at this temperature ethylene polymerises only by a cationic mechanism [17,18].

The copolymerisation of ethylene with a number of halogen-containing alkenes (vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, and chlorotrifluoroethylene) has been carried out under the influence of alkylborons, e.g. triethylboron and tributylboron [16,101–105]. An important feature is that in this case the copolymerisation is carried out at extremely low temperatures, between -70° and -80°. [16,102]

Experimental relative activities for the copolymerisation of ethylene with vinyl chloride [46,48], vinyl fluoride [48], and tetrafluoroethylene [49] are given in Table 3; calculated values for copolymerisation with other halogen-containing alkenes are given in Table 5. A noteworthy feature is that the relative activity of vinyl fluoride and also, apparently, chlorotrifluoroethylene and dichlorodifluoroethylene, is much lower than that of ethylene, whereas the relative activity of vinyl chloride is much greater than that of ethylene. It may be assumed that vinylidene chloride has an even higher relative activity than vinyl chloride.

Duntov and Erusalimskii [46,106] have studied the copolymerisation of ethylene with vinyl chloride under the influence of azoisobutyronitrile at 70° and pressures up to 300 bars. According to their data, copolymerisation in the ethylene–vinyl chloride system is homogeneous under the conditions studied. The order of the initial reaction rate with respect to initiator at an equimolar monomer ratio is 0.5, indicating that the ethylene–vinyl chloride–initiator system is homogeneous. When the reaction was carried out to a high degree of conversion at a vinyl chloride content of 5 mole % (in this case the proportion of vinyl chloride in the copolymer varied between 13% and 17%, and the melting point of the copolymer, determined from thermomechanical curves, was 52–53°), the degree of copolymerisation was found to increase with increase in the degree of conversion; this is explained by the heterogeneity of the monomer–polymer system at the given monomer ratio. The relative activities determined by these authors are close to those established by Zutty and Burkhart [47] for the process at 90° and 1000 bars.

Kolesnikov et al. [16] studied the copolymerisation of ethylene with vinyl chloride in the presence of triisobutylboron at an ethylene pressure of 98 bars and temperatures from -70° (initial) to 18° (final) in toluene medium. The yield of copolymer increases with increase in the ethylene content of the original mixture. Their statement that under the conditions of this process ethylene is a more active monomer than vinyl chloride is open to doubt, since the composition of the original mixture of monomers was, in fact, unknown (the experiments were carried out over a wide temperature range, for the most part below the critical temperature of ethylene).

We must also expect differences in the properties of the copolymers of ethylene with fluorinated and with chlorinated alkenes. As noted above, replacement of hydrogen atoms in the polyethylene chain by fluorine atoms can take place without breakdown of the polyethylene lattice. Thus, for example, copolymers of ethylene with tetrafluoroethylene are crystalline throughout the composition range [28,29,99,100]. Analogous properties may be expected for copolymers of ethylene with other fluorine-substituted ethylenes. But the introduction of chlorine atoms into the polyethylene chain, because of their large dimensions (Table 2), should lead to breakdown of the crystal structure. Thus in the case of the copolymer of ethylene with vinyl chloride [16,84,85], the rigidity first decreases with increase in the vinyl chloride content, and then increases. Rubberlike products are formed in the intermediate composition range. The addition of small quantities of copolymer phasticises poly(vinyl chloride) [107].

The melting points of the copolymers of ethylene with tetrafluoroethylene rise sharply with increase in the content of the latter within the composition range close to polyethylene. An interesting feature is that, for the same fluorine content, the melting points of the copolymers are 100–140 deg higher than those of poly(vinyl fluoride) and poly(vinylidene fluoride) [28,29].

Thermostable oils are obtained by the copolymerisation of ethylene with tetrafluoroethylene in a tertiary hydrocarbon (telogen) medium under the influence of peroxo-compounds [108].

Tarutina [109] has studied the thermal aging of copolymers of ethylene and tetrafluoroethylene at 200°, 240°, and 290°. The infrared spectra of these copolymers indicate the presence of side-branches with terminal methyl groups. It was established that the rate of aging depended on the number of branches. It is suggested [109] that aging takes place chiefly at the tertiary carbon atom, without influencing the number of methyl groups, since the intensity of the bands

due to the CH_3 groups remains unchanged on aging. Thus to obtain products with a high stability towards aging it is necessary to prepare copolymers having a predominantly linear structure.

(c) Copolymerisation with Vinyl Acetate and Other Vinyl Esters

The copolymerisation of ethylene with vinyl esters opens up extensive possibilities for the preparation of a variety of polymers, since in this case, in addition to the products formed directly during copolymerisation, it is possible to bring about conversion to a number of different macromolecular compounds by polymer-analogue reactions involving the ester group.

Vinyl acetate is one of the most readily available vinyl esters, and the copolymerisation of ethylene with this compound has been studied in greatest detail. Copolymers of ethylene with vinyl acetate can be obtained in block, solution, and emulsion; organic peroxides, alkylborons, and ionising radiation are used to initiate the reaction.

The composition of an ethylene–vinyl acetate copolymer determines its properties, and the possibilities of further modification and application. A number of patents [110-117] deal with the preparation of copolymers of low vinyl acetate content, up to 20 mole %. These copolymers can be obtained by polymerisation at 800–1500 bars and 50–150° under the influence of peroxide initiators in aqueous medium [110,111] or in emulsion [112].

A continuous process operating under the same conditions but in a propane, benzene, or cyclohexane medium has been described [113]. Continuous emulsion copolymerisation has been carried out in the presence of redox initiators at 30°. [114]

Ethylene copolymers of low vinyl acetate content can also be prepared at a pressure of 400–600 bars. [115-117] The use of low temperatures (60–70°) and solvents having low chain-transfer constants makes it possible to obtain copolymers with a fairly high molecular mass; in this case a satisfactory reaction rate is ensured by using initiators which exhibit a high activity at these temperatures, such as lauryl peroxide, peroxodicarbonates, and azoisobutyronitrile.

Although the preparation of copolymers of low vinyl acetate content requires the use of high pressure, this is not the case for the copolymerisation of ethylene with a large quantity of vinyl acetate [118,119]. Thus even at a pressure of 50–60 bars, under the influence of free-radical initiators, it is possible to prepare copolymers of fairly high molecular mass, containing more than 50% of vinyl acetate [118]. Liquid copolymers of low molecular mass containing 60–75% of vinyl acetate are obtained either by carrying out the copolymerisation in chain-terminating solvents such as ethyl methyl ketone, ethyl acetate, and acetone, or by adding to the reaction mixture a small quantity of a chain-terminating agent, such as an aldehyde or a thiol [120].

The present reviewers, together with Rysakov [50], have studied the copolymerisation of ethylene with vinyl acetate throughout the whole range of compositions of the original mixture. The copolymerisation was carried out at 400 bars in benzene medium at 70° in the presence of azoisobutyronitrile, and at 130° under the influence of t-butyl peroxide. The observed values of the relative activities (Table 3) show that the relative activity of ethylene increases with increase in the temperature of the process, whereas that of vinyl acetate remains constant. Thus at 130° both relative activities are close to unity. Data obtained for the relative activities at 90° and 1000 bars (Table 3) [48] indicate that, as with temperature, a marked increase in pressure leads to an increase in the relative activity of ethylene.

The temperature dependence of the relative activity is given by the equation [59]

$$r_1 = \exp\left(\frac{\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger}}{RT}\right),$$

where $\Delta S_{11}^{\ddagger}$, $\Delta S_{12}^{\ddagger}$, $\Delta H_{11}^{\ddagger}$, and $\Delta H_{12}^{\ddagger}$ are the activation entropies and enthalpies in reactions of the radical M_1 with molecules of the monomers M_1 and M_2.

Since the relative activity of vinyl acetate remains unchanged with increase in the temperature of the process, the differences in the heats and entropies of activation of the reactions of growth of the vinyl acetate radical are zero. For the ethylene radical

$$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger} = 4530 \text{ J mole}^{-1},$$

$$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger} = 10.9 \text{ J mole}^{-1} \text{ deg}^{-1},$$

The rate of copolymerisation of ethylene with vinyl acetate, throughout the range of monomer ratios at 70° and 130°, increases monotonically with increase in the vinyl acetate content of the original mixture. The intrinsic viscosity of the copolymers, determined in *p*-xylene solution at 85°, has a minimum value at a vinyl acetate content of 40–60 mole %. [50]

Analogous relationships are observed for the block process carried out at a pressure of 500 bars and temperatures of 60°, 100°, and 150° in the presence of various initiators of the peroxide type: dicyclohexyl peroxodicarbonate, benzoyl peroxide, and t-butyl peroxide. The fact that the nature of the dependence of the copolymer composition on the original monomer ratio is the same in each case indicates that the ethylene–vinyl acetate system is homogeneous under the conditions studied [122].

Interesting results have been obtained in a study of the influence of the benzene concentration on the rate and degree of copolymerisation at vinyl acetate contents in the original mixture of 10 and 50 mole % and temperatures of 70° and 130°. For both these monomer ratios at 70° and for the equimolar ratio at 130°, a decrease in the rate and degree of copolymerisation with increase in the benzene concentration is observed, as a result of the homogeneity of the monomer–solvent–initiator system, in which increase in the relative quantity of solvent leads to a decrease in the total molar concentration of the monomers. A quite different pattern is observed in the copolymerisation of ethylene with 10 mole % of vinyl acetate at 130°: the rate and the degree of copolymerisation increase considerably with the addition of benzene to the system, the optimum molar ratio of benzene to monomers being 0.2–0.25. This phenomenon can be explained as follows. Under these conditions the reaction mixture apparently consists of molten copolymer saturated with all the components, and a gas phase consisting of monomers and initiator. In this case the addition of benzene and increase of its concentration to a definite limit will facilitate the diffusion of monomers into the molten copolymer, accelerating the growth of the macroradicals. The decrease in the rate and degree of copoly-

merisation with further increase in the benzene concentration is due to the decrease in the total molar concentration of monomers in the homogeneous system [119].

The dependence of the rate of copolymerisation in block and in solution on the ratio of the monomers is almost linear throughout the concentration range, indicating that the probability of chain-termination reactions is the same between radicals of different types and between radicals of the same type [119].

The properties of copolymers of ethylene and vinyl acetate show the following changes with increasing content of the latter [50]: copolymers containing up to 10–12 mole % of vinyl acetate are strong plastics, similar to high-pressure polyethylene, but differing from the latter in their higher elasticity and transparency and lower melting point. At vinyl acetate contents of 13–25% the products are rubberlike, and at 30–80% they are resins which are soft and sticky at room temperature. Copolymers containing more than 80% of vinyl acetate are again rigid and strong. The solubility of the copolymers in solvents such as benzene, xylene, carbon tetrachloride, alcohol, and acetone increases with increase in the vinyl acetate content, the copolymers becoming soluble in alcohol and acetone at vinyl acetate contents greater than 40%. [50,121]

X-Ray structural analysis of copolymers of ethylene with vinyl acetate has shown that their crystallinity decreases with increase in the vinyl acetate content [36,122] (Fig. 1). The density of the copolymer at first decreases, and then increases, approaching the value 1.2 characteristic of poly(vinyl acetate) [122]. The dependence of the tensile strength and the relative elongation of the copolymer on the vinyl acetate content is shown in Fig. 2. [122]

Data have been published [36,37,123] on the glass points of copolymers of ethylene with vinyl acetate and vinyl propionate.

The frost-resistance of copolymers of ethylene with low vinyl acetate content is almost independent of the monomer ratio. All specimens, irrespective of composition, withstand a temperature of -70° (bending test method) [121].

According to published data [36,121], the melting point of ethylene–vinyl acetate copolymers falls with increase in the content of the latter in the range 0–20 mole %, in accordance with Flory's formula [30]. The similarity in the curves giving the dependence of the melting point on the number of carbon atoms in normal paraffins and in polyethylene units of average length in the copolymers shows that the melting point of the copolymers is determined by [the melting point of crystals containing polyethylene sequences whose lengths are near] the average [sequence] length of the polyethylene units in the copolymers [36].

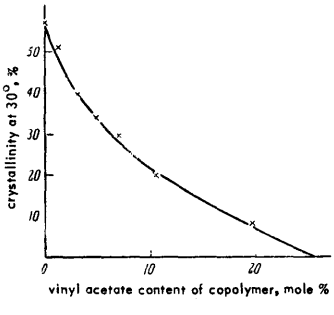


Fig. 1. Dependence of the crystallinity of copolymers of ethylene and vinyl acetate on composition (from Nielsen's data [36]).

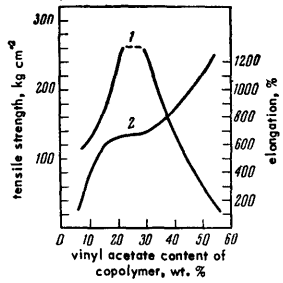


Fig. 2. Dependence of the tensile strength and relative elongation of copolymers of ethylene and vinyl acetate on composition [122]: 1) tensile strength; 2) relative elongation.

Copolymers of ethylene and vinyl acetate show strong adhesion to various synthetic materials (e.g. to polyethylene and to polyester films), wood, metal, and paper [124,125], and can be used as components in a variety of adhesives [126–128]. These copolymers mix readily with many resins, rosin, paraffin wax, and other waxes [124,129–132], poly(vinyl chloride) [133], and mineral oils containing more than 40% of aromatic hydrocarbons [134]. They can be used as elastomers in mixtures with fillers [134–136].

When ethylene–vinyl acetate copolymers are heated to 280–320°, acetic acid is split off with the formation of double bonds between neighbouring carbon atoms; no breakdown of the polymer chain was observed [137]. When the copolymers are heated above 350°, acetic acid and methane are split off; with further rise in temperature to 490°, the quantity of methane increases but the acetic acid remains constant [138]. This indicates that at 350° the removal of acetic acid from the copolymer is almost complete. This made it possible to develop a method for determining the composition of copolymers of ethylene and vinyl acetate by gas-chromatographic analysis of the pyrolysis products, from the quantity of acetic acid removed [138]. Good agreement is observed between the results obtained by this method and data obtained by high-resolution nuclear magnetic resonance and neutron activation analysis [139]. When combined with differential thermal analysis, this method can be used to establish the nature of the distribution of the monomer units in the copolymer [140].

The properties of copolymers of ethylene with vinyl acetate are altered appreciably when the copolymer molecules are cross-linked; this may be brought about by the action of peroxides [122,141–143], polycarboxylic acids [141,144], or ionising radiation [121,145]. The cross-linking of these copolymers by means of peroxo-compounds, and the properties of the products obtained in admixture with various fillers, have been described in detail by Bartl and Peter [122]. The degree of cross-linking increases with increase in the vinyl acetate content of the copolymer; it is suggested that cross-linking of the macromolecules takes place at the tertiary carbon atoms of the main chain and also at the primary

carbon atoms of the acetate groups. Vulcanised ethylene–vinyl acetate copolymers exhibit a number of valuable properties, such as high resistance to heat, aging, the action of light and ultraviolet rays, ozone, oxygen, and atmospheric conditions, together with excellent mechanical properties. It is suggested that these products are of particular interest to the rubber industry, since their addition to certain types of rubber produces a marked improvement in the properties of the latter [122]. Vulcanised elastomers based on a copolymer of ethylene and vinyl acetate can also be obtained by pyrolytic elimination of acetic acid followed by vulcanisation of the product at the double bonds [137].

According to data obtained by the reviewers [121], the action of ^{60}Co γ-radiation leads to a considerable increase in strength and melting point, with a comparatively small decrease in the relative elongation and frost-resistance, of the ethylene–vinyl acetate copolymer.

There are reports [128,146,147] that copolymers of ethylene and vinyl acetate are produced on the industrial scale and are used as elastomers, plastics, coatings, adhesives, etc.

Copolymers of ethylene and vinyl acetate are readily hydrolysed with the formation of copolymers of ethylene and vinyl alcohol or, in the case of partial hydrolysis, three-component ethylene–vinyl acetate–vinyl alcohol copolymers [148-151]. The hydrolysed copolymers are of considerable practical interest, since they exhibit valuable properties such as strength, rigidity, and resistance to common solvents; a significant advantage over poly(vinyl alcohol) is their insolubility in water [148-154]. The range of application of hydrolysed copolymers of ethylene with vinyl acetate can be extended considerably by chemical modification of these products [155-167].

Ethylene copolymerises with other vinyl esters besides vinyl acetate. Almost all the patents cited above mention, in addition to vinyl acetate, esters such as vinyl propionate, vinyl butyrate, and vinyl benzoate. Ethylene can be copolymerised also with vinyl esters of branched carboxylic acids (vinyl $\alpha\alpha$-dimethylpropionate, vinyl $\beta\beta$-dimethylbutyrate, etc.) [168], vinyl esters of thio-acids [169], methyl vinyl ether and ethyl vinyl ether [170,171], divinyl ether [172], 2,2′-vinyloxyethoxyethanol [173], 2-vinyloxyethanol [174], and divinyl and diallyl oxalate and sebacate [175]. The copolymerisation of ethylene with all these vinyl esters and ethers is generally carried out at high pressures (1000-2000 bars) under the influence of oxygen or peroxide initiators. Calculation (Table 5) shows that the relative activities of the monomers in the copolymerisation of ethylene with vinyl esters of aliphatic acids are close to one another.

Kurian and Muthana [176] showed that copolymerisation of ethylene with vinyl γ-methylvalerate is possible at 50–200 bars and 80° under the influence of benzoyl peroxide. According to their results, vinyl γ-methylvalerate under these conditions shows a higher relative activity than ethylene.

Copolymers of ethylene with vinyl and allyl salicylate are of considerable interest because of their ability to form chelate compounds [177].

Three-component copolymerisation involving ethylene and vinyl acetate has been described in a number of patents [174,177-181]. Vinyloxyalkanols [174,179], vinyl and allyl salicylates [177], alkyl acrylates [178], and carbon monoxide [180,181] have been used as third component. The copolymerisation of ethylene, vinyl acetate, and ethyl acrylate [178] is of particular interest. The process was carried out at 800–1500 bars in benzene medium under the influence of azoisobutyronitrile or a peroxide. The copolymerisation products were hydrolysed to give copolymers consisting of 25–60 mole % of ethylene, 10–30% of vinyl alcohol, and 25–60% of acrylic acid; the tensile strength of these copolymers reached 300–400 kg cm^{-2}.

(d) Copolymerisation with Vinylene Compounds

Known copolymers of ethylene with monomers of the vinylene type include compounds with maleic acid derivatives, diethyl fumarate, and vinylene carbonate. Copolymerisation of ethylene with maleic anhydride is carried out at comparatively low pressure under the influence of free-radical initiators in various organic solvents [182,183]. Copolymers of high maleic anhydride content and low molecular weight are formed at 20–30 bars under the influence of peroxide initiators in the presence of a chain-terminating agent such as cumene or an aldehyde [184-188]. The relative activities of this pair of monomers are apparently less than unity (Table 5). Copolymers of ethylene and maleic anhydride are soluble in water [189]. They are now produced on the industrial scale as the anhydride, acid, or ammonium maleamate, and are used in the production of transparent films, adhesives, fungicides, paint thickeners, etc. [147,189-197]. Ethylene copolymerises also with monoesters of maleic acid [198].

Hopff and Stark [199,200] have shown that the emulsion copolymerisation of ethylene with diethyl fumarate is possible, with the formation of products whose softening temperatures are lower than room temperature. The molecular mass (determined by the osmotic method) of the fraction with highest molecular mass was 41 000. According to our calculations (Table 5), diethyl fumarate should have a much greater relative activity than ethylene.

An interesting feature of the copolymerisation of ethylene with vinylene carbonate is the apparently much greater relative activity of ethylene compared with vinylene carbonate (Table 5). Their copolymerisation under high pressure in the presence of free-radical initiators gives products which are at least as valuable as polyethylene and have a number of advantages, such as high strength, stability during processing, satisfactory flow properties, absence of cross-linked molecules, transparency, and gloss [201]. Copolymers containing up to 30 wt. % of vinylene carbonate can be used as additives to poly(vinylidene chloride fluoride) [202], polyvinylformal [203], and styrene–acrylonitrile copolymers [204], to improve their quality. The addition of small quantities (up to 10%) of a copolymer of ethylene and vinylene carbonate during the polymerisation of styrene gives a polymer with an increased tensile strength [205].

The hydrolysis of copolymers of ethylene with vinylene carbonate gives compounds of the ethylene–vinyl alcohol copolymer type, in which the hydroxy-groups are present on neighbouring carbon atoms [201]. Copolymers of ethylene with hydroxy-groups in the side-chains can also be prepared directly by the copolymerisation of ethylene with allyl or methallyl alcohol at high pressure, but in this case the products are waxlike, with low molecular mass of ~ 1500. [206]

(e) Copolymerisation with Acrylic Monomers

Ethylene copolymerises readily with acrylic compounds such as acrylic acid, acrylonitrile, and acrylic and meth-

acrylic esters [3-7,9]. The reaction can be initiated by oxygen, organic peroxides [5-7], ^{60}Co γ-radiation [12-14], and alkylborons [15,16]. Copolymers with perfluoroacrylonitrile have also been prepared [207].

Table 5 gives the calculated values of the relative activities for the copolymerisation of ethylene with various acrylic and methacrylic monomers. On the basis of these data it may be assumed that compounds of this type have a much greater relative activity than ethylene, the relative activity of the latter being close to zero. Thus copolymers with acrylic monomers will always be enriched in the second component. These conclusions agree with the experimental relative activities for acrylonitrile and n-butyl acrylate (Table 3).

The copolymerisation of ethylene with acrylonitrile has been studied in greatest detail. The radiation copolymerisation of these monomers has been investigated by Gromov et al. [51] The process is carried out in toluene solution at an ethylene pressure of 10–44 bars, an absorbed dose rate of 1080 J kg^{-1} h^{-1}, and a temperature of 20°. The yield of copolymer for acrylonitrile concentrations in the monomer mixture of 10 and 50 mole % depends linearly on the duration of polymerisation up to 40% conversion; at an acrylonitrile concentration of 70%, the rate increases with time (up to 25% conversion), and this is attributed to the heterogeneous character of the process. This is indicated also by the fact that the intrinsic viscosity of the copolymer increases with increase in the degree of conversion. The rate of copolymerisation and the intrinsic viscosity of the products increase with increase in the acrylonitrile content in the original monomer mixture.

γ-Irradiation of a mixture of acrylonitrile and liquid ethylene at -78° leads to formation of only the acrylonitrile homopolymer; and when the acrylonitrile content of the mixture is low, polymerisation takes place exclusively at the $-C\equiv N$ bond. In solutions with a moderate concentration of acrylonitrile in ethylene, polymerisation takes place both at the $-C\equiv N$ bond and at the $\rangle C=C\langle$ bond [208,209].

Kolesnikov et al. [16] studied the copolymerisation of ethylene with acrylonitrile under the influence of triisobutylboron at an ethylene pressure of 98 bars in solvent naphtha medium. As in the case of radiation copolymerisation, increase in the concentration of acrylonitrile in the original monomer mixture leads to an increased yield of copolymer; at the same time, however, a decrease in its intrinsic viscosity is observed. With increase in the triisobutylboron concentration from 1 to 2 wt. %, the yield of copolymer increases from 10 to 25%; further increase in catalyst concentration, however, leads not to an increase in the yield but to a slight decrease. Lowering the initial temperature of polymerisation from 18° to -70° results in an increased content of ethylene units in the copolymer; this effect is observed for the most part at considerable concentrations of ethylene in the original mixture. In all cases decrease in the initial temperature leads to an increase in the yield of copolymer.

Good agreement is observed between the values of the relative activities calculated by Gromov et al. [51] from published data [16] and those established in radiation copolymerisation (Table 3). This may indicate that the copolymerisation process initiated by alkylborons takes place by a radical mechanism.

An interesting feature is that copolymerisation of ethylene with acrylonitrile does not take place on organometallic complexes [210].

There is almost no published information on the properties of copolymers with acrylonitrile. It is known [16] merely that the copolymers are soluble only in dimethylformamide and that X-ray structural analysis indicates a high degree of order inside the chain bundles; their vitrification temperature is almost independent of the monomer ratio and the reaction temperature, and lies in the range 60–70°.

Copolymers of ethylene with alkyl acrylates (e.g. ethyl acrylate and n-butyl acrylate) can be obtained by a continuous process in a tubular reaction vessel at 1500–2000 bars and 100–200° in the presence of oxygen or organic peroxides [211,212]. The copolymerisation was carried out at very low concentrations of the comonomers in the original mixture (0.2–1.5 mole %), apparently because of their extremely high relative activity (see Tables 3 and 5).

The composition of copolymers of ethylene with ethyl acrylate can be determined by gas chromatography of the pyrolysis products [138], high-resolution nuclear magnetic resonance [139], neutron activation analysis [139], infrared spectrophotometry, and hydrolysis [213]. In the last case, to obtain satisfactory results, the analytical reaction must be carried out in a homogeneous medium. The distribution of the monomer units in the copolymer can be established by a combination of gas chromatography of the pyrolysis products and differential thermal analysis [140,214].

Liquid copolymers of ethylene with a content of ~ 30 mole % of an alkyl acrylate or alkyl methacrylate are formed by copolymerisation under the influence of peroxide initiators at about 300 bars in hexane, cumene, etc. medium [215]. Other known compounds include copolymers of ethylene with esters of hydroxybenzophenones and acrylic or methacrylic acid [216] and with ω-methacrylamidoundecanoic acid [217], and three-component copolymers of ethylene, ethyl acrylate, and vinyl acetate [178] and of ethylene, an alkyl acrylate, and a monoester of maleic or fumaric acid [218], prepared under approximately analogous conditions.

The alkyl acrylate most widely used as comonomer with ethylene is ethyl acrylate; copolymerisation with this compound is now carried out on the industrial scale [73,219]. Published data [73,219-233] show that these copolymers exhibit properties such as flexibility over a wide temperature range, high resistance to cracking under stress, high strength at low temperatures, and excellent engineering properties. An extremely important advantage of these copolymers over polyethylene is their low embrittlement temperature, which in some specimens reaches -100°. The copolymers exhibit high adhesion and mix well with paraffin wax [224] and polyethylene [218], whose mechanical properties are improved by the addition of small quantities of copolymers of ethylene and ethyl acrylate containing up to 8 mole % of the latter.

The dependence on composition of the glass point of copolymers of ethylene with ethyl acrylate and n-butyl acrylate is shown in Fig. 3. [37] A characteristic feature of these copolymers, which distinguishes them from those of ethylene with vinyl chloride or vinyl acetate, is the decrease in their glass point (particularly in the case of the copolymers with n-butyl acrylate) with increase in the content of the comonomer.

(f) Copolymerisation with Heterocyclic Compounds

According to data given in patents, ethylene copolymerises with *N*-vinyl compounds such as *N*-vinylphthalimide, *N*-vinylsuccinimide [225], and *N*-vinylcarbazole [226] at

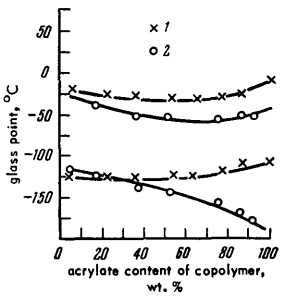


Fig. 3. Dependence on composition of the vitrification temperature of copolymers of ethylene with: 1) ethyl acrylate; 2) n-butyl acrylate. (Upper curves constructed from measurements on Instron tester; lower curves from data obtained with a torsion balance.)[37]

1000–2000 bars and 50–150° under the influence of organic peroxides or azo compounds, in water or a hydrocarbon solvent. The radiation copolymerisation of ethylene with *N*-vinylpyrrolidone has been carried out[12].

On the basis of the calculated values of the relative activities for the radical copolymerisation of ethylene with *N*-vinylcarbazole, *N*-vinylpyrrolidone, and *N*-vinylsuccinimide (Table 5) it may be assumed that these compounds have a much higher relative activity than ethylene.

The rigidity of copolymers of ethylene with small amounts of *N*-vinylsuccinimide and *N*-vinylpyrrolidone decreases with increase in the content of these compounds[31]. Copolymers containing 5–30 wt.% of *N*-vinylcarbazole have a much higher strength, elasticity, resistance to solvents, and better adhesion properties than high-pressure polyethylene[226].

According to data given in patents, copolymers of ethylene can be obtained with alkylene 1,2-oxides (e.g. ethylene oxide)[227,228], β-propiolactone[229], but-3-eno-3-lactone[230], and vinyloxoisochromans[231]. The copolymerisation is carried out at high pressures (500–1500 bars) and 50–200° under the influence of peroxide initiators. In the first two cases, however, the mechanism of the process is not clear.

(g) Copolymerisation with Compounds Incapable of Homopolymerisation

Compounds which are unable to undergo homopolymerisation but which form copolymers with ethylene include carbon monoxide, carbon dioxide, and sulphur dioxide.

1. Copolymerisation with carbon monoxide. Copolymers of ethylene with carbon monoxide were first prepared by one of the reviewers and his coworkers[232,233]. Copolymerisation of the monomers at 2000–2500 bars and 300° gave macromolecular products, consisting of viscous liquids or solids depending on the conditions of the experiment and the proportions of the original components. Copolymerisation was apparently initiated by molecular oxygen. Subsequently, methods have been described for the copolymerisation of ethylene and carbon monoxide under the influence of molecular oxygen[180], orthosilicates[234], complex nickel cyanides[235–237], alkali metals, their hydrides, and organic derivatives[238], Friedel–Crafts catalysts, carbonyl-forming heavy metals and their derivatives[239] (in the last two works cited, the process was initiated by traces of oxygen[240]), and ^{60}Co γ-radiation[11–14,34,52,53,241]. The greatest amount of work has been done on copolymerisation initiated by organic peroxides[54,180,234,242–259].

In the case of radiation copolymerisation in the gas phase at 70° and 160–180 bars, the rate of the process is proportional to the absorbed dose rate (rate of initiation) to the power 1.3. The fact that the rate of radical polymerisation is not proportional to the square root of the rate of initiation has been attributed to the heterogeneous character of the process[53].

The copolymerisation of ethylene with carbon monoxide takes place in the range 75–275° and also at room temperature in the case of initiation by γ-radiation. At high temperatures the process is complicated by side-reactions[260]. In the initiation of copolymerisation by peroxides at a pressure of 600 bars, increase in temperature from 200° to 260° led to a decrease in the molecular mass of the products of the reaction by a factor of about 3.[54] The maximum rate of radiation copolymerisation at 120–300 bars was observed at 70–120°.[53]

The copolymerisation pressure was varied over a wide range, from 14 to 2500 bars. At pressures below 100 bars, only products of low molecular weight are formed[180,257,258]. Copolymerisation under the influence of peroxide initiators was carried out in most cases at 600–1000 bars, and radiation copolymerisation at 120–300 bars and at 650–700 bars[12–14].

Copolymerisation initiated by peroxides has been carried out in the gas phase[54,180,246,248] and also in different reaction media, such as isooctane, benzene, cyclohexane, dioxan, water, etc.[54,180,243–258] In the presence of chlorinated hydrocarbons, isopropanol, thiols, ketones, esters, and chlorine, telomers of low molecular weight are formed[258,261–263]. Telomerisation was carried out at 30–8000 bars and 75–130° under the influence of peroxides or nitriles of azo-acids; under these conditions hydrogen sulphide inhibits copolymerisation[263]. The radiation copolymerisation of ethylene and carbon monoxide has generally been carried out in the gas phase.

The copolymerisation of ethylene and carbon monoxide is carried out both by batch and by continuous methods[32,54,234]. To prevent the formation of iron carbonyl during the reaction, it is recommended that the reaction vessel be lined with aluminium[53], silver, or other inert material[180].

The values of the relative activities of this pair of monomers (Table 3) show that the relative activity of carbon monoxide is in all cases zero¶. This means that, in the course of chain growth, the carbon monoxide molecules add only to radicals terminating in methylene groups. Thus the resulting copolymer contains no α-dicarbonyl groups, and the carbon monoxide content cannot exceed 50% (mole and weight percentages identical). This pair of monomers exhibit a high tendency to alternate, so that the composition of the copolymer depends little on the original monomer ratio over a wide range of original monomer concentrations.

¶ The values of the relative activities calculated by Gromov et al.[51] from the data of Brubaker et al.[257] — $r_{C_2H_4} = 0.57$ and $r_{CO} = 0.25$ — are incorrect, since no allowance was made for soluble monomers. An analogous error has been made by Steinberg and Colombo[13,52].

The composition of copolymers of ethylene and carbon monoxide shows a marked temperature dependence: the carbon monoxide content of the copolymer decreases with increase in the reaction temperature. The temperature dependence of the relative activity of ethylene corresponds to the equation given above [Section IV (c)] in the range 70–150°.[53] The parameters of this equation are

$$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger} = 19300 \pm 1700 \text{ J mole}^{-1},$$

$$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger} = 41.9 \pm 3.8 \text{ J mole}^{-1} \text{ deg}^{-1}.$$

According to the data of Coffman et al.[54], in the temperature range 200–260°,

$$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger} = 36000 \text{ J mole}^{-1},$$

$$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger} = 67 \text{ J mole}^{-1} \text{ deg}^{-1}.$$

As noted above, side-reactions take place at these high temperatures, and this possibly explains the marked discrepancy in the above data.

A noteworthy feature is the unusually large differences in the activation entropies and enthalpies of addition of ethylene and carbon monoxide to a radical terminating in a methylene group (see, for example, the data given by Alfrey et al.[264]).

An interesting feature of the copolymerisation of ethylene and carbon monoxide is the pressure dependence of the copolymer composition. Data have been published[257] indicating that, with increase in pressure in the reaction system from 14 to 1000 bars, the carbon monoxide content of the copolymer increases from 13 to 45% (the copolymerisation was carried out in cyclohexane solution in the presence of t-butyl peroxide at 135° with a carbon monoxide content in the original mixture of 42%). An explanation for this fact was put forward by Barb[265,266]†, who considered that carbon monoxide takes part in the copolymerisation not directly but in the form of an unstable equimolecular complex with ethylene, by a process similar to that occurring in the copolymerisation of alkenes with sulphur dioxide[237].

A consequence of this assumption is that the following relationship should be observed between the ratio n of the numbers of molecules of ethylene and carbon monoxide in the copolymer and the carbon monoxide concentration [CO] in the reaction system

$$n = 1 + \frac{\text{const}}{[CO]}.$$

As shown by Walling[268–270], this relationship can also be obtained on the assumption that one of the elementary reactions of chain growth is reversible

$$RCH_2CH_2 + CO \rightleftarrows CH_2CH_2CO^{\cdot}, \qquad (1)$$

Using the experimental data of Brubaker and his coworkers, Barb showed that the above relationship is in fact observed at pressures up to 300 bars. Barb, however, assumed without justification that the solubility coefficients for ethylene and carbon monoxide in cyclohexane are constant up to partial pressures of 200 bars, and that the ideal gas laws are applicable to the ethylene–carbon monoxide system at partial pressures of ethylene greater than the critical pressure. It is possible that the change in the composition of the copolymer with change in the total pressure in the system is due to a change in the relative solubilities of ethylene and carbon monoxide in cyclohexane‡. Evidence in support of this suggestion is provided, in particular, by the fact that in the case of copolymerisation in the gas phase at 70°, no change was observed in the relative activity of ethylene with change in the total pressure from 120 to 270 bars, or with change in the concentration of carbon monoxide in the reaction system from 0.2 to 6.3 mole dm^{-3}.[53]

It is nevertheless possible that at higher temperatures the composition of the copolymer does depend on pressure because of the reversibility of reaction (1). This may explain the following facts — (1) the considerable decrease in the carbon monoxide content of the copolymer with increase in the temperature of copolymerisation, (2) the decrease in the yield and molecular weight of the copolymers with increase in temperature, and (3) the increase, unusual for radical copolymerisation, in the tendency of the monomers to alternate in the polymer with increase in pressure (at 120° and 220–230 bars, $r_{C_2H_4} = 0.33$;[53] at 120–130° and 850–1000 bars, $r_{C_2H_4} = 0.15$[54]). Further studies are required to clarify this question.

The rate of radiation copolymerisation increases with increase in the concentration of carbon monoxide in the original mixture[53].

Copolymers of ethylene and carbon monoxide have the structure of linear polyketones. This has been proved by infrared spectrophotometry[12,257,260] and also by the chemical reactions of the copolymers[257]. The composition of the copolymer can be determined by elementary analysis or by infrared spectrophotometry (from the intensity of absorption of the carbonyl group[272] or from the ratio of the intensities of absorption of the methylene groups attached and unattached to carbonyl[260]).

Copolymers of ethylene and carbon monoxide of sufficiently high molecular mass are crystalline[32,180]. X-Ray structural analysis indicates a high degree of order in copolymers obtained by radiation copolymerisation in the gas phase at 25–70°.[34,35,53] As noted above, these products retain the crystal structure of polyethylene. The structure of the orthorhombic cell of polyethylene and of two copolymers with different carbon monoxide contents is shown in Fig. 4.[35]

Natta et al.[26] point out that the absorption bands in the infrared spectra of homopolymers, usually related to the crystallinity of the specimen, disappear rapidly even on isomorphous replacement of the units in the polymer chains. This phenomenon is observed, in particular, in the spectra of copolymers of ethylene and carbon monoxide. Thus the spectrum of a copolymer containing 21% of carbon monoxide still shows the 730 cm^{-1} band associated with the crystalline structure of polyethylene. This band disappears with increase in the carbon monoxide content to 43%; at the same time the appearance of a band at 1338 cm^{-1} and splitting of the band due to stretching vibrations of the carbonyl group are observed. These phenomena are related to the crystal structure of the polyketone[260].

The melting points of ethylene–carbon monoxide copolymers of high molecular weight lie in the range 90–200°. With increase in the carbon monoxide content, the melting point falls slightly, possibly owing to a decrease in the molecular mass[53] or the heat of fusion of the copolymer[32].

† Speculations regarding the mechanism of the process have also been put forward by Curphy[259] and by Vatsulik[267].

‡ Gonikberg[271] considers that increase in pressure produces an extremely marked increase in the rate of attachment of –CO– groups to the growing polymer chain.

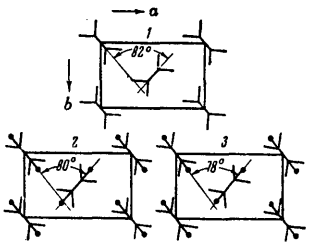


Fig. 4. Crystal structure of polyethylene and of copolymers of ethylene with carbon monoxide[35]: 1) polyethylene; 2) copolymer containing 31% of carbon monoxide; 3) copolymer containing ~50% of carbon monoxide.

With further increase in the carbon monoxide content, the melting point of the copolymer increases. A copolymer containing 10–20% of carbon monoxide has a vitrification temperature in the range between -25° and -125°.[37]

Copolymers of ethylene and carbon monoxide, obtained in the gas phase at 25–120° under the influence of ^{60}Co γ-radiation, are almost insoluble in paraffinic and naphthenic hydrocarbons, *m*-cresol, and pyridine[13,14,53]. The density of these copolymers lies in the range 1.1–1.2 (these are close to the calculated values)[13,14,34,35,53]. The density of copolymers obtained at 200–250° and 700–1100 bars increases from 0.92 to 1.02 with increase in the carbon monoxide content from 3 to 23%.[32] Copolymers of ethylene and carbon monoxide blend well with paraffin wax and other waxes[252], polyurethane elastomers[258], and chlorine-containing polymers[261]; the compatibility of the latter with the copolymers increases with increase in the carbon monoxide content of the copolymers. A disadvantage of copolymers of ethylene and carbon monoxide, which restricts their possible applications, is their brittleness. The optimum combination of mechanical properties is apparently shown by copolymers with a very low carbon monoxide content[180].

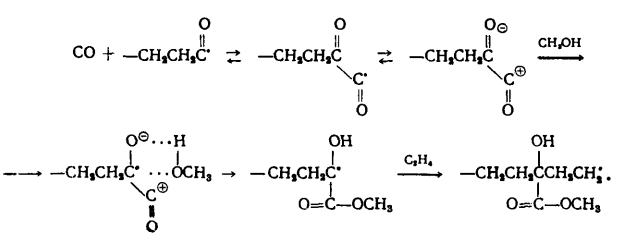
A characteristic property of copolymers of ethylene and carbon monoxide is their thermal reactivity[180,234,259,260]. When these products are heated above their melting points in air or *in vacuo*, they are rapidly converted into hard, brittle, infusible, insoluble substances, which soften when heated. This casts doubt on the accuracy of conclusions[32,257] based on the viscosity of the molten copolymers. The changes in the copolymers are accompanied by the liberation of water. The reaction rate increases sharply with temperature. It has been suggested[259,260] that this process involves the thermal initiation of crotonic condensation. The possibility of reaction is determined to a considerable extent by the mobility of the molecular chains, so that the rate of the process increases sharply on fusion of the copolymer. The process apparently takes place by an intermolecular mechanism, as indicated by the autoretardation of the reaction and the infusibility and insolubility of the products[260]. The polyketones can undergo condensation also under the influence of alkali[180,243,247,250,259,273,274].

The cross-linking of copolymers of ethylene and carbon monoxide by peroxides[180,275], chloramine[275], and nitrogen-containing bases[180,248] leads to an increase in their strength, a rise in their softening temperature, and a decrease in their solubility.

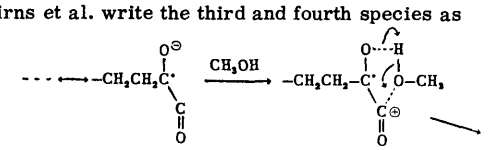
The high reactivity of the polyketones opens up extensive possibilities of chemical modification of these products and their utilisation for the preparation of macromolecular compounds of different classes — polyoximes[180,257], hetero-chain polyamides and polytetrazoles[160,276,277], poly-α-ketone oximes and dioximes[278] and chelate compounds based on them[279], allyl derivatives[181], phosphorus-containing polymers[256], polyketo-nitriles and polyketo-acids[180,242,280], polycyanhydrins[251,257], polyhydantoins[255], polyalcohols[180,245,253,257,281–284], polyurethanes[245,253,282–287], polythiols and polysulphides[254], and polyamines and their derivatives[249,259,285–296]. The oxidation of copolymers of ethylene and carbon monoxide with nitric acid gives a mixture of dicarboxylic acids, whose composition yields information on the distribution of carbonyl groups in the copolymer chain[180,246,257].

In addition to copolymers of ethylene and carbon monoxide, patents describe the preparation of three-component copolymers of ethylene and carbon monoxide with propene[180,181,240,245,248,253,261,262], methylpropene[180,181,240,261], butadiene[180,181], vinyl acetate[180,181], diethyl maleate[180,181,247], diallyl phthalate[180], and sulphur dioxide[297]; and also the four-component copolymer of ethylene, carbon monoxide, vinyl acetate, and diethyl maleate[180]. The conditions of copolymerisation do not differ in principle from those for the copolymerisation of ethylene and carbon monoxide. The three-component copolymers can be subjected to the same chemical changes as those of ethylene and carbon monoxide.

If the copolymerisation of ethylene with carbon monoxide at high pressures is carried out in the presence of alcohols or alkyl formates, the molecules of these substances combine chemically with the copolymer and modify its structure (the copolymerisation was carried out at 130° in the presence of t-butyl peroxide)[298,299]. The quantity of chemically combined alcohol increases with increase in pressure; thus the copolymer obtained in the presence of methanol at 1000 bars contains 7% of methoxy-groups, whereas that obtained at 8000 bars contains 27%. Increase in the concentration of carbon monoxide in the original mixture decreases the yield and increases the concentration of alkoxy-groups in the copolymer. Chemical and spectroscopic data indicate that these copolymers contain the groups $-CH_2-CH_2-$, $-CO-$, and $-C(OH)(COOR)-$.[289,299] Special experiments showed that copolymers of ethylene and carbon monoxide do not react with carbon monoxide and methanol under the conditions of this reaction, so that the molecules of the alcohol combine with the copolymer directly during copolymerisation. Cairns et al.[299] suggested the following reaction mechanism§



§ Cairns et al. write the third and fourth species as



(Ed. of Translation).

This reaction mechanism is difficult to reconcile with the fact that α-dicarbonyl groups are not formed in the copolymerisation of ethylene and carbon monoxide.

Products obtained by chemical transformation of the copolymers (hydrolysis, oxidation, hydrogenation, and treatment with formaldehyde and peroxides [298-300]) have also been described.

The catalytic hydrocondensation of ethylene and carbon monoxide is an unusual free-radical process: hydrogenation of the carbon monoxide gives methylene radicals, which copolymerise with the ethylene [301].

2. Copolymerisation with carbon dioxide. According to data given in patents [302], ethylene copolymerises with carbon dioxide under the influence of peroxide initiators at elevated temperatures and pressures up to 1000 bars. Vatsulik [267] suggests the following reaction mechanism

$$CH_2{=}CH_2 + CO_2 \rightarrow \dot{C}H_2{-}CH_2{-}O{-}CO{-}CH_2{-}\dot{C}H_2 \rightarrow$$
$$\rightarrow CH_3{-}CH_2{-}O{-}CO{-}(CH_2{-}CH_2{-}O{-}CO)_n{-}CH_2{-}CH_2{-}O{-}CO{-}CH_2{-}CH_3,$$

but gives no arguments in support of this scheme.

3. Copolymerisation with sulphur dioxide. The copolymerisation of alkenes with sulphur dioxide is of considerable theoretical and practical interest, and much work has been done on this reaction. In these studies, ethylene has been assigned a modest role. Since a number of fairly detailed reviews have been published [303-310], we shall merely discuss a few papers on the copolymerisation of ethylene, and shall not deal with general problems of the copolymerisation of alkenes with sulphur dioxide.

Ethylene copolymerises readily with sulphur dioxide under the influence of peroxides [311-313], azo-compounds [314-316], sunlight [317], ultraviolet rays [317,318], and ^{60}Co γ-radiation [319-321].

The substances used as copolymerisation initiators include, in particular, the peroxide products of the autoxidation of diethyl ether and ethylbenzene [311-313]. In the latter case, liquid sulphur dioxide copolymerises at temperatures from -20° to -30° and atmospheric pressure with pure ethylene and also with the technical product containing only 50% of ethylene [312,313].

A characteristic feature of the copolymerisation of alkenes with sulphur dioxide is the existence of a limiting temperature, specific for each alkenes, above which the reaction does not take place. This temperature is independent of the nature of the initiator, but depends on the monomer concentration [310]. It has not been determined for ethylene but is much higher than for other alkenes [318,322].

The kinetics of the radiation copolymerisation of ethylene and sulphur dioxide at 0° was studied by Bray et al. [321] on the basis of the following scheme for the copolymerisation process —

initiation

$$C_2H_4 \rightarrow R_1,$$
$$SO_2 \rightarrow R_2,$$

chain growth

$$RCH_2\dot{C}H_2 + SO_2 \rightarrow RCH_2CH_2SO_2^{\cdot},$$
$$RSO_2^{\cdot} + C_2H_4 \rightarrow RSO_2CH_2\dot{C}H_2,$$

chain termination

$$R_2CH_2\dot{C}H_2 + R_2CH_2\dot{C}H_2 \rightarrow P,$$
$$R_1CH_2\dot{C}H_2 + R_2SO_2^{\cdot} \rightarrow P,$$
$$R_1SO_2^{\cdot} + R_2SO_2^{\cdot} \rightarrow P.$$

It can be seen from the above scheme that Bray et al. considered that the two values of the relative activities for the copolymerisation of ethylene and sulphur dioxide are zero (the monomers do not add on to "their own" radicals). This assumption is not strictly justified, since the studies were carried out only with an equimolar mixture of monomers (the ratio of the original molar concentrations of ethylene and sulphur dioxide lay in the range 0.9–1.4); moreover, the sulphur content of the reaction products was slightly lower than that corresponding to an equimolar monomer ratio. According to the experimental data, almost no depolymerisation of the growing radicals takes place in the copolymerisation process.

In the copolymerisation of ethylene with sulphur dioxide, linear copolymers having a polysulphone structure are formed [311]. In most cases copolymers with an equimolar monomer ratio were obtained. The structure of these copolymers can be represented by the formula

$$\left[-CH_2-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\right]_n.$$

Products of this type have a crystalline structure [323] and unusually high melting points. Thus the copolymers obtained at 0° under the influence of ^{60}Co γ-radiation melted over the range 312–341°, fusion being accompanied by decomposition of the copolymer [321]. The melting points of the copolymers generally lie above the temperatures of their thermal decomposition. Such high melting points are apparently due to the marked polarity of the sulphonyl groups (Table 1) and the regular structure of the copolymer.

Equimolecular copolymers of ethylene and sulphur dioxide do not dissolve in any known solvents, including concentrated sulphuric and nitric acids [311,324] (according to Bray et al. [321] these copolymers are very sparingly soluble in aliphatic ketones). They are stable towards powerful oxidising agents but decompose under the influence of dilute alkalis, forming salts of sulphinic acids and a small quantity of neutral products [311]. The equimolecular copolymers have high thermal stability. Staudinger and Ritzenhalter [311] noted that these copolymers broke down into the original components above 300°. According to Naylor and Anderson [315] the decomposition of copolymers of monoalkenes with sulphur dioxide takes place in conformity with a unimolecular mechanism.

Of all the equimolecular copolymers of alkenes with sulphur dioxide, those of ethylene have the highest melting point, lowest solubility, and highest thermal stability. The infusibility and the insolubility of these products make their processing extremely difficult, so that they have not found practical application. According to data given in patents, considerably improved properties are shown by polysulphones containing less than 50 mole % of sulphur dioxide [316,325]. These copolymers, which have a high tensile strength, can be processed by casting under pressure or by extrusion at 200°. The copolymers can be used as additives to drying oils [326].

Naylor and Anderson [315] describe the preparation, and give data on the rate of thermal degradation, of the three-component copolymer of ethylene, propene, and sulphur dioxide. They point out that this type of three-component copolymerisation can be carried out at temperatures lower than the limiting temperature of each alkene with sulphur dioxide. A continuous process for the ternary copolymerisation of ethylene, but-1-ene, and sulphur dioxide has also been described [327]. The ratio of the reactivities of cyclohexene and ethylene under the conditions of three-compo-

nent copolymerisation with sulphur dioxide has been determined by Hazell and Ivin[328]. The three-component copolymer of ethylene, carbon monoxide, and sulphur dioxide was mentioned above[297].

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SALTING-OUT AND SALTING-IN OF NON-ELECTROLYTES

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The problem of the effect of electrolytes on the solubility of non-electrolytes is of great theoretical and practical importance. A great deal of work[1-57] has shown that electrolytes can either decrease or increase the solubility of neutral substances in water, the phenomenon being termed *salting-out* or *salting-in* respectively.

Processes associated with salting-out are widely used in the production of dyes, amines, soaps, etc. At the present time the employment of salting-out agents in extraction is becoming especially important[58-74]. On the other hand, substances which increase the solubility of non-electrolytes in water (hydrotropic substances) are beginning to find application in industry.

McKee[75] reported the employment of alkanesulphonates of the alkali and alkaline earth metals in papermaking, and referred to the possibility of replacing organic solvents by solutions of hydrotropic salts in the electrolysis of organic substances. The presence of a second phase in the system is known to diminish the rate of many organic reactions. By the use of hydrotropic salts the system can be made homogeneous, and the rate of the process thereby increased. In addition, salts influence the course of a reaction[76-79].

The behaviour of salts in aqueous solutions of non-electrolytes is a complicated phenomenon owing to the occurrence in the water–electrolyte–non-electrolyte system of various types of interaction: water–electrolyte, water–non-electrolyte, and electrolyte–non-electrolyte.

Systematic study of the effect of salts on the solubility of neutral substances in water has revealed several regularities, which have subsequently formed a basis for theories of salting-out and salting-in. The influences of some substances on the solubility of others has been investigated by various methods — by direct measurement of solubilities, determination of partition coefficients, determination of