ADDITION POLYMERISATION AT HIGH PRESSURES

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1. Introduction.—Pressure is potentially as significant a variable as temperature in chemical reactions, and its effects are being more widely investigated as the techniques for developing controlled pressures up to 100,000 atm. become better known.

Many gas-phase reactions are considerably influenced by pressures of a few hundred atmospheres because of the increased concentrations of the reactants. Higher pressures, of a few thousand atmospheres and upwards, produce large changes in reaction rates in liquids. These are not primarily mass-action effects but are determined by the contraction or expansion accompanying the formation of the transition state from the reacting molecules, and they are intimately related to the reaction mechanisms. Measurements of the pressure-dependence of rate constants have provided fundamental information about such processes in many types of reaction, including that of addition polymerisation.

The first general studies of polymerisation at high pressures, made over thirty years ago, were prompted partly by the consideration that polymers have higher densities than the monomers from which they are produced. Conant and his collaborators[1] and Starkweather[2] subjected nearly fifty substances to pressures of 3000—12,000 atm. and found that some which formed no polymer, or small amounts, at 1 atm. gave substantial yields at the highest pressures. These were principally vinyl compounds and conjugated dienes, but included the cyclic hydrocarbon indene, the symmetrical ester diethyl fumarate, and higher aldehydes that form soft polymers unstable at ordinary pressure. Another seven olefinic substances were studied by Sapiro, Linstead, and Newitt,[3] who found α-methylstyrene to be the most responsive to pressure; and in 1933 Fawcett and Gibson discovered[4] the high-pressure polymerisation of ethylene which has become of great industrial importance.

At the time of these experiments the physical chemistry of polymerisation was in an early stage of development, and it was not possible to interpret the effects of pressure in any detail. Much more is now known about the changes caused in the separate reaction steps, largely as the result of studies of the polymerisation of styrene.

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[1] Bridgman and Conant, *Proc. Nat. Acad. Sci. U.S.A.*, 1929, **15**, 680; Conant and Tongberg, *J. Amer. Chem. Soc.*, 1930, **52**, 1659; Conant and Peterson, *ibid.*, 1932, **54**, 628.

[2] Starkweather, *J. Amer. Chem. Soc.*, 1934, **56**, 1870.

[3] Sapiro, Linstead, and Newitt, *J.*, 1937, 1784.

[4] See Perrin, *Research*, 1953, **6**, 111.

2. The Polymerisation of Styrene under Pressure.—An early attempt[5] to measure the acceleration of the polymerisation of styrene gave the huge factor of 2·24 × 10^6 at 140°/1500 atm. A re-investigation by Gillham[6] showed that it is considerably less than 10 and that experimental shortcomings, particularly failure to carry out the reaction isothermally, had led to the error. Gillham measured the polymerisation rate for styrene without initiator up to 4000 atm. at 100°. At 3000 atm. the rate was 10·1 times faster, but the molecular weight of the product was only 1·55 times greater than at 1 atm. The difference between the two factors indicates that the effect of pressure is complex. A simple acceleration of the rate of initiation of chains would not increase the polymer molecular weight, while, alternatively, an increased rate of chain growth, or a decreased rate of chain termination, would cause the overall rate and the polymer molecular weight each to increase by a similar factor.

Further measurements on styrene were made by Merrett and Norrish[7] up to 5000 atm. at 60°, using benzoyl peroxide as initiator. With improved techniques, they obtained reproducible kinetic results which have been confirmed by later workers. Their findings are illustrated in Fig. 1 which shows the logarithm of the overall rate to be nearly a linear function of pressure (with an acceleration factor at 3000 atm. of 7·2). The polymer molecular weight is approximately tripled between 1 and 3000 atm. but increases only slightly at higher pressures. The reaction order with respect to initiator concentration is 0·5 at 1 atm. but decreases a little with increas-

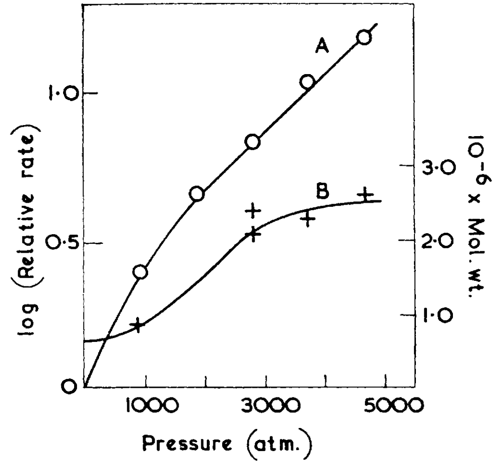

FIG. 1. *The effect of pressure on the overall rate of polymerisation of styrene* (A) *at 60°, and on the polymer molecular weight* (B) (*right-hand scale*).

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[5] Tamman and Pape, *Z. anorg. Chem.*, 1931, **200**, 113.

[6] Gillham, *Trans. Faraday Soc.*, 1950, **46**, 497.

[7] Merrett and Norrish, *Proc. Roy. Soc.*, 1951, *A*, **206**, 309.

ing pressure. An explanation of the changes in rate and molecular weight was suggested in terms of the effect of pressure on the separate steps of the reaction. For the free-radical polymerisation the rate equations are usually written:

Rate of production of radicals by initiator decomposition

$$R_d = 2fk_d[\mathrm{I}] \tag{1}$$

Rate of initiation $$R_i = k_i[\mathrm{Z}^*][\mathrm{M}] \tag{2}$$

Rate of chain growth $$R_p = k_p[\mathrm{M}][\mathrm{R}^*] \tag{3}$$

Rate of chain transfer $$R_{tr} = k_{tr}[\mathrm{R}^*][\mathrm{Y}] \tag{4}$$

Rate of termination $$R_t = k_t[\mathrm{R}^*]^2 \tag{5}$$

Equation 1 refers to the production of two radicals, Z*, from each molecule of initiator, I, by homolysis, *f* being the efficiency of the radicals in starting chains. Chain initiation is by addition of Z* to the monomer M, and chain growth proceeds by successive addition of monomer molecules to the chain radical R*. Chain transfer is a radical-displacement reaction between R* and a molecule Y (monomer, initiator, solvent, or polymer), producing a polymer molecule and the radical Y* which initiates a new chain. The kinetic chains are terminated by collisions between polymeric radicals (equation 5) which result in disproportionation or combination, the latter being strongly preferred in polymerisation of styrene.

The rate constants of liquid-phase reactions vary with pressure according to the equation:[8]

$$\partial (\ln k)/\partial P = - \Delta V^*/RT \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

in which ΔV^* is the volume change which occurs when the transition state is formed from the reacting molecules. The decomposition of benzoyl peroxide involves the stretching and breaking of the O–O bond, so that ΔV^* is likely to be positive for this reaction and k_d will be decreased by pressure. Chain growth (and initiation) are bimolecular addition processes for which negative values of ΔV^* and a consequent acceleration by pressure may be expected. Termination by combination should also have a negative ΔV^*, but Merrett and Norrish considered that this reaction between two large radicals is diffusion-controlled and is retarded at high pressure because of the increased viscosity of the medium. The transfer reactions are believed to occur through the abstraction of an atom from the molecule Y by the chain radical. Transfer does not generally affect the overall rate of polymerisation but may sometimes determine the polymer molecular weight. As transfer involves both bond-formation and bond-breaking the sign of ΔV^* is uncertain but it was assumed that the rate of transfer is increased by pressure, and later evidence supports this.

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[8] (*a*) Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; 1936, **32**, 1333; (*b*) Hamann,' 'Physico-Chemical Effects of Pressure," Butterworths Scientific Publs., London, 1957.

From the general considerations the increased molecular weight and rate of polymerisation are attributed mainly to the acceleration of chain growth by pressure, while the levelling-off of polymer molecular weight is due to an alteration in the balance between the termination and the transfer reactions. At 1 atm. most molecular chains are terminated by combination, and at first an increase in pressure causes an increase in molecular weight by slowing down this reaction. At higher pressures the accelerated transfer reactions determine the molecular weight, although kinetic termination still mainly follows equation 5.

The well-known combination of equations 1, 2, 4, and 5 gives the overall rate of polymerisation, R_0, in the steady state, as

$$R_0 = \delta k_d^{\frac{1}{2}} f^{\frac{1}{2}} [M][I]^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where $\delta = k_p/k_t^{\frac{1}{2}}$. The slight decrease in the exponent of [I] at higher pressures may indicate some participation of primary radicals Z* in termination reactions with R*.

Many organic reactions are polar in nature and the sign of ΔV^* for these is often determined by differences in the solvation of the reacting molecules and the transition state. The implicit assumptions that solvation changes are unimportant in the various stages of radical polymerisation, and that ΔV^* is simply related to alterations in the intermolecular distances and interatomic bond lengths of the reactants are reasonable but require strengthening by more direct evidence. In subsequent work Nicholson and Norrish[9] have isolated the effects of pressure on k_p, k_t, and k_d for styrene, and have confirmed most of the inferences made from the earlier results.

(*a*) *The pressure-dependence of* k_p *and* k_t. Measurements of the steady-state rate of polymerisation (equation 7) can determine only the ratio $k_p/k_t^{\frac{1}{2}}$ and additional information is needed if the two constants are to be separately evaluated. This was obtained from experiments on the photochemical polymerisation at high pressures under conditions of intermittent illumination (rotating-sector method) with the results shown in Fig. 2. k_t decreases rapidly up to 1000 atm. and then more slowly, while k_p increases exponentially with pressure. ΔV^* for the chain-growth reaction is calculated to be −13·4 c.c./mole, which may be compared with a volume difference of 22·7 c.c./mole between monomer and polymer for the polymerisation at 1 atm. The decrease in k_t is probably due to the suggested viscosity effect but this has not been independently established.

(*b*) *The pressure-dependence of* k_d. The thermal decomposition of benzoyl peroxide in carbon tetrachloride solution was studied[9] over the same pressure range at 60° and 70°. Two mechanisms are distinguishable. The first is a radical-induced chain decomposition which is accelerated by pressure but is ineffective in initiating polymerisation, and is probably

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[9] Nicholson and Norrish, *Discuss. Faraday Soc.*, 1956, **22**, 97, 104.

suppressed in the presence of monomer. The unimolecular decomposition, corresponding to equation 1, is retarded by pressure, and k_d at 3000 atm. is about half of its initial value (Fig. 2). Results have been obtained for the effect of pressure on other homolytic dissociations by Ewald[10] and by Walling *et al.*[11] The values of ΔV^* calculated from equation 6 are given in Table 1.

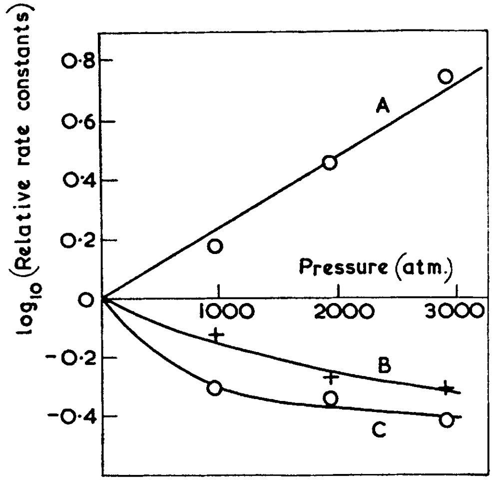


FIG. 2. *The effect of pressure on* k_p (A) *and* k_t (C) *for styrene at* 30°; *and on* k_d (B) *for the homolytic dissociation of benzoyl peroxide in carbon tetrachloride at* 70° (Nicholson and Norrish[9]).

All the dissociations are retarded by pressure, so that ΔV^* is always positive, but there are significant variations with the solvent, the values in benzene and carbon tetrachloride being roughly twice those in toluene and cyclohexene. The lower values are in agreement with approximate calcula-

TABLE 1. ΔV^* *for initiator dissociation.*

Initiator	Solvent	Temp.	ΔV^*(c.c./mole)
Benzoyl peroxide	CCl_4	60°	9·7
Benzoyl peroxide	CCl_4	70	8·6
Benzoyl peroxide	Acetophenone	80	4·8
Azoisobutyronitrile	Toluene	62·5	3·8[a]
Azoisobutyronitrile	Toluene	62·5	9·4[b]
t-Butyl peroxide	Toluene	120	5·4
t-Butyl peroxide	Cyclohexene	120	6·7
t-Butyl peroxide	Benzene	120	12·6
t-Butyl peroxide	CCl_4	120	13·3

[a] Initiator disappearance followed photometrically. [b] Rate of radical formation by iodine-scavenger technique.

[10] Ewald, *Discuss. Faraday Soc.*, 1956, **22**, 138.

[11] Walling and Pellon, *J. Amer. Chem. Soc.*, 1957, **79**, 4786; Walling and Metzger, *ibid.*, 1959, **81**, 5365.

tions of the volume effect which assume a 10% stretching of the O–O or C–N bond in the transition state, and a constant molecular cross-section (estimated from the van der Waals radii of the bonded atoms).

An explanation of the larger values found in the other solvents has been suggested[11] but is not discussed here.

(*c*) *The pressure-dependence of* k_{tr}. The effects of pressure on k_{d}, k_{p}, and k_{t} postulated by Merrett and Norrish are therefore confirmed, and the acceleration of transfer reactions by pressure has also been verified. Walling and Pellon[12] examined the polymerisation of styrene in carbon tetrachloride solution up to 6000 atm. at 60°, and found that k_{tr} for the reaction between the polymer radical and the solvent is increased to nearly the same extent as k_{p}. ΔV^* for this transfer is about -11 c.c./mole. Toohey and Weale[13] found that transfer between polystyryl radicals and triethylamine is also accelerated but that ΔV^* is apparently much smaller (~ -1 or -2 c.c./mole) than for the chain growth. The abstraction of an atom from a neutral molecule presumably occurs *via* a bimolecular transition state, formed with a contraction in volume. The contraction should be less than in the chain-growth reaction because bond-breaking occurs simultaneously; but if with some substrates the polar structures suggested by Walling[14] contribute to the transition state an additional contraction due to solvation may be expected. A variation of ΔV^* for transfer with the structure of the attacked molecule, if confirmed, could be important in the behaviour of allylic monomers (Section 4). In addition Ewald[15] has shown that transfer reactions between diphenylpicrylhydrazyl and thiols are strongly accelerated at 10,000 atm.

3. The Relation of the Pressure Effect to the Structure of the Monomer.—Kinetic data for monomers other than styrene are limited to overall rates of polymerisation under pressure. ΔV^* calculated from these is a composite quantity ($= \Delta V^*_{\mathrm{p}} + \Delta V^*_{\mathrm{d}}/2 - \Delta V^*_{\mathrm{t}}/2$ if equation 7 is valid), and its values are slightly high if, as here, they are uncorrected for increases in [M] and [I] due to compressibility. However, the compressibility corrections are generally similar in magnitude, and as ΔV^*_{p} is much the largest term the overall ΔV^* is a useful approximate guide to its variation with monomer structure. Values for styrene,[13] allyl acetate,[16] methyl methacrylate,[17] α-methylstyrene,[18] and acenaphthylene[19] are shown in Table 2.

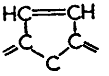
[12] Walling and Pellon, *J. Amer. Chem. Soc.*, 1957, **79**, 4776.
[13] Toohey and Weale, *Trans. Faraday Soc.*, in the press.
[14] Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 158.
[15] Ewald, *Trans. Faraday Soc.*, 1959, **55**, 792.
[16] Walling and Pellon, *J. Amer. Chem. Soc.*, 1957, **79**, 4782.
[17] Lamb and Weale, Proc. Symp. on Phys. and Chem. High Pressures, 1962.
[18] Elroy, Ph.D. Thesis, London University, 1961.
[19] Romani, unpublished results.

TABLE 2. *ΔV^* for various monomers from the overall rate of polymerisation.*

Monomer	Pressure range (atm.)	Temp.	ΔV^* (c.c./mole)
Styrene	1—3000	60°	−18
Styrene (in toluene, S/M = 4·3)	1—3000	60	−17
Styrene (in triethylamine, S/M = 3·3)	1—4400	60	−17
Allyl acetate	1—8500	80	−14
Methyl methacrylate	1—3000	40	−19
α-Methylstyrene	3000—4500	60	−17
Acenaphthylene (in toluene, S/M = 4·6)	1—2000	60	~ −10

(S/M denotes the mole ratio of solvent to monomer.)

For monomers containing the structure $CH_2{=}C<$ the substituent groups appear not to affect ΔV^*, and allyl acetate is not necessarily exceptional because the peculiar characteristics of the reaction (Section 4) may affect the apparent ΔV^*. Acenaphthylene contains the cyclic structure (I) and for this monomer ΔV^* is definitely lower. Calculations suggest[20] that the separation between radical and C=C group in the transition state is approximately the mean of the van der Waals and the covalent distance, while the C=C bond length is almost unchanged. ΔV^* for chain growth should therefore be about half the volume change for the reaction $M \rightarrow (1/n)M_n$, which is roughly true for styrene.[21]



(I)

The close similarity between ΔV^* for styrene with and without a solvent is also of interest. In many organic reactions a large negative ΔV^* is associated with a large negative entropy of activation, ΔS^*, and both result mainly from the solvation of partial ionic charges in the transition state.[8b] The considerable negative ΔV^* for styrene chain growth is also linked with a large negative ΔS^* (−35 e.u. at 1 atm.[22]) but neither can be due to charge-solvation. Conant and Peterson[1] suggested that an "alignment" of monomer molecules is favoured by pressure (*i.e.*, that compression assists formation of the transition state by reducing the translational and rotational entropy of monomer molecules), but in this case the pressure-acceleration should decrease with dilution.

4. Allylic Monomers at High Pressures.—The study of styrene has yielded much fundamental information about high-pressure polymerisation but this is restricted in some ways by the nature of the monomer. In the temperature and pressure range investigated, polymerisation of styrene is strongly favoured thermodynamically, so that depolymerisation does not occur; and chain transfer to monomer is relatively unimportant compared with chain growth. The influence of pressure on the thermodynamics of polym-

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[20] Evans, Gergeley, and Seaman, *J. Polymer Sci.*, 1948, **3**, 866.
[21] Whalley, *Discuss. Faraday Soc.*, 1956, **22**, 146.
[22] Bamford and Dewar, *Proc. Roy. Soc.*, 1948, *A*, **192**, 309.

erisation and the balance between chain transfer and chain growth is shown by recent work on monomers containing the allyl group $CH_2{:}\overset{|}{C}{\cdot}CH_2{-}$.

(*a*) *α-Methylstyrene.* There is good evidence that at 1 atm. the ceiling temperature for polymerisation of α-methylstyrene, $CH_2{:}CPhMe$, is about 60—61°. At higher temperatures depolymerisation is faster than chain growth, and polymer formation is impossible.[23] The results of Sapiro, Linstead, and Newitt[3] imply that the ceiling temperature varies with pressure, and Kilroe and Weale[24] found that it increases linearly from 61° at 1 atm. to 171° at 6480 atm. If an equation is assumed of the same form as the Clausius–Clapeyron relation, $dT_c/dP = T\Delta V/\Delta H$, and ΔH has a value[25] of $-8{\cdot}4$ kcal./mole, then the volume change for polymer–monomer equilibrium in the liquid is $-14{\cdot}7$ c.c./mole. This is of the approximate magnitude to be expected for the algebraic difference between the estimated values of ΔV^* for chain growth and depropagation.

A sharp maximum in the rate of polymerisation as a function of pressure was also observed. Elroy[18] has shown that this is due to solidification of the monomer, the freezing point of which increases linearly with pressure from $-23{\cdot}2°$ at 1 atm. to 60° at 4860 atm. The region in which polymerisation of α-methylstyrene is possible is therefore limited by the ceiling temperatures and the freezing points which both increase markedly with pressure.

The molecular weight of the polymer increases with pressure at constant temperature. At 3000 atm. the molecular weight is constant (~28,000) over much of the temperature range in which polymerisation can occur, but it rises appreciably near the freezing temperature and falls abruptly as the ceiling temperature is approached. At pressures very close to the freezing pressure polymers with molecular weights of 200,000—600,000 were obtained.

Some unsaturated liquid dimer is produced and above the ceiling temperature this is the only reaction product. The dimer probably results from transfer reactions involving abstraction of an allylic hydrogen atom from monomer, and the formation of the resonance-stabilised radical $CH_2{:}CPh{\cdot}CH_2{\cdot}$. The rate of dimer formation is accelerated by pressure but to a smaller extent than the chain growth.

(*b*) *Allyl acetate.* The polymerisation of allyl acetate ($CH_2{=}CH{\cdot}CH_2{\cdot}OAc$) has been studied[16] at 80° and pressures up to 8500 atm. The molecular weight of the polymer is low (~2000) and increases only slightly with pressure but the reaction rate increases exponentially, being 50 times greater at the highest pressure than at 1 atm. Degradative transfer with allylic hydrogen to yield an unreactive radical $CH_2{:}CH{\cdot}CH(OAc){\cdot}$ is apparently much faster, relative to chain growth, in this monomer than in α-methylstyrene. It is considered that k_{tr}/k_p is largely independent of

[23] Dainton and Ivin, *Quart. Rev.*, 1958, **12**, 61.
[24] Kilroe and Weale, *J.*, 1960, 3849.
[25] Jessup, *J. Chem. Phys.*, 1948, **16**, 661.

pressure (so that the molecular weight is nearly constant), but a part of the increase in rate is attributed to an enhanced reactivity of the allylic radicals which may restart chains at high pressures.

(*c*) *Isopropenyl acetate.* Bywater and Whalley[26] have investigated the polymerisation of α-methylvinyl acetate CH_2:CMe·OAc at 50—120° and up to 10,000 atm. Products of low molecular weight are formed up to 6000 atm., but at higher pressures the reaction is reasonably fast and yields solid polymers ($M \sim 30{,}000$). The polymerisation resembles that of α-methylstyrene rather than that of allyl acetate.

Allylic transfer appears relatively unimportant and the effect of pressure on rate and molecular weight is probably due to the acceleration of a slow chain growth and a decrease in chain termination; but the possibility of a ceiling-temperature effect at the lower pressures is not excluded.

The behaviour of these allylic monomers illustrates the effects of pressure when chain growth is relatively slow and transfer, depolymerisation, or termination competes strongly. Before monomers with other types of structure are discussed the application of the concepts used in the preceding sections to the high-pressure polymerisation of ethylene will be considered.

5. The Polymerisation of Ethylene.—The production of solid polymer ($M \geqslant 20{,}000$) from ethylene by the free-radical process is generally carried out at 1500—3000 atm. and 160—200°. Oxygen or a peroxide is the usual initiator. Many measurements of the effect of pressure, temperature, and initiator concentration on the reaction rate and polymer molecular weight have been made, but only one or two can be referred to here.

Difficulties are encountered because of the sensitivity to traces of oxygen (a few p.p.m. may initiate reaction under some conditions), the possibility of phase separation between polymer and monomer, and the large variation in the density of the system with pressure. A detailed investigation[27] between 400 and 2000 atm. with a variety of initiators showed the rate of reaction to increase rapidly with pressure, but the results could not be well expressed in a form such as equation 7. In liquid polymerisations the concentrations are readily corrected for the compression of the liquid (about 10—20% at several thousand atmospheres), but in ethylene the density may double over the experimental pressure range, and pressure, density, and fugacity each failed to represent monomer concentration satisfactorily in the rate equation. An extensive study of the oxygen-initiated polymerisation by Ehrlich and Pittilo[28] revealed features (*e.g.*, induction periods and a critical polymerisation boundary) which cannot be represented in terms of the usual steady-state kinetics. However, using propane as a diluent to ensure phase homogeneity, and t-butyl peroxide as

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[26] Bywater and Whalley, Amer. Chem. Soc., Reprints (Division of Polymer Chemistry), 1960, Vol. 1, 143.

[27] Laird, Morrell, and Seed, *Discuss. Faraday Soc.*, 1956, **22**, 126.

[28] Ehrlich and Pittilo, *J. Polymer Sci.*, 1960, **43**, 389.

initiator, Symcox and Ehrlich,[29] obtained reproducible kinetic behaviour at 130° and 1000—2500 atm. which resembles that found for liquid polymerisation.

The order with respect to initiator is between 0·5 and 0·6, indicating a close approach to binary termination (equation 5). The rate of polymerisation increases exponentially with pressure, and the order with respect to monomer is between 1 and 2. The ratio δ, calculated from equation 7, increases with pressure, so that k_p/k_t is larger. Although the ethylene–propane mixture is supercritical its density is high ($\sim$ 15 moles/l.), and the transition-state equation (6) may reasonably be applied to the system.[29] ΔV^* is thus calculated to be -23 c.c./mole, which is a feasible value though rather close to the average difference between the molar volumes of monomer and polymer over the range 1000—2500 atm. Therefore, when an initiator other than oxygen is used and phase inhomogeneity avoided, the effect of pressure appears similar in dense ethylene and in liquid olefins. Polyethylene of low molecular weight ($\sim$930) has been obtained[30] from the liquid monomer at 0° and only 40 atm. As the order of decreasing temperature-dependence is usually $k_{tr} > k_p > k_t$ the lower molecular weight accords with the view that at higher temperatures and pressures the chief effect is an increase in the ratio k_p/k_t.

6. Attempts to Polymerise Polysubstituted Olefins under Pressure.—The monomers so far discussed have all been vinyl or vinylidene compounds containing the structure $CH_2{=}C{<}$. Tri-, tetra-, and 1, 2-di-substituted ethylenes (except $CF_2{=}CF_2$) polymerise much less readily, if at all; but a few attempts to produce polymers at high pressure have succeeded.

(*a*) 1,2-*Disubstituted ethylenes.* Holmes-Walker and Weale[31] examined a number of these monomers up to 10,000 atm., generally using benzoyl peroxide as initiator. Several esters of cinnamic acid ($Ph{\cdot}CH{:}CH{\cdot}CO_2R$) give good yields of polymer containing 20—30 monomer units, in contrast to their low reactivity at 1 atm.[32] The formation of low polymer from diethyl fumarate was confirmed, but diethyl maleate is unreactive. Maleic anhydride and stilbene did not polymerise, nor did 1,2-dibromoethylene, although 1,2-dichloroethylene forms a solid polymer of unknown molecular weight at high pressure.[33] Cyclic olefins, which are formally included in this section, display varying response. Cyclohexene is unreactive,[31] indene gives low polymers,[1,31] while the formation of high polymers from acenaphthylene is accelerated at high pressure.[19] The factors governing the reactivity of monomers of this type and their dependence on pressure still remain uncertain.

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[29] Symcox and Ehrlich, *J. Amer. Chem. Soc.*, 1962, **84**, 531.
[30] Padgett and Perry. *J. Polymer Sci.*, 1959, **37**, 543.
[31] Holmes-Walker and Weale, *J.*, 1955, 2295.
[32] Marvell and McCain, *J. Amer. Chem. Soc.*, 1953, **75**, 3272.
[33] Weale, *J.*, 1952, 2223.

(*b*) *Tri- and tetra-substituted ethylenes.* Attempts to polymerise these monomers under pressure have usually been unsuccessful. Neither isopentene, $Me_2C{:}CHMe$, nor α-methylstyrene dimer, $PhMe_2C{\cdot}CH{:}CMePh$, reacts and αβ-dimethylstyrene yields only small amounts of dimer.[3] At higher pressures and temperatures (up to 30,000 atm. and 300°) Gonikberg and Zhulin[34] obtained rearranged products with up to six carbon atoms per molecule from tri- and tetra-chloroethylene; and a tetramer or pentamer, possibly of cyclic structure, from 2,3-dimethylbut-2-ene. The obvious explanation is steric hindrance between the bulky substituent groups (which is absent in the reactive polyfluorinated ethylenes). This could be so even though the dimethylbutene forms a transparent polymer[35] at $-80°$ by an ionic mechanism, since there may be less steric hindrance for the planar carbonium ion than for a radical. There is not yet sufficient evidence to exclude the possibility of radical polymerisation under pressure in at least some cases.

(*c*) 1,1-*Disubstituted ethylenes.* Although many of these monomers polymerise readily some are less reactive. 1,1 Diphenylethylene gave only dimer[3] at 5000 atm., as did methyl α-t-butylacrylate[31] at 10,000 atm. But-3-enylbenzene did not react at 5000 atm.[3] but 1-isopropenylnaphthalene yielded 54% of low polymer at 10,000 atm. and 125°.

7. The Pressure Polymerisation of Non-olefinic Monomers.—The polymerisation under pressure of substances without a $C{=}C$ bond has received little attention, but the scattered results available suggest that this field would repay further exploration. The early work on aldehydes[1] has recently been extended. Polyacetaldehyde (M 500,000) is formed at $-180°$ but an attempt to produce it at 9000 atm. and 40° was unsuccessful.[36] Novak and Whalley[37] have recently obtained high polymers of acetaldehyde, propionaldehyde, n- and iso-butyraldehyde, valeraldehyde, and chloral at 8000—9000 atm. and room temperature, and showed that they have the polyoxymethylene structure $[-CHR{\cdot}O-]_n$. All the polymers revert spontaneously to monomer at room temperature and 1 atm., and this is probably another instance of the ceiling-temperature effect discussed in connection with α-methylstyrene.

A slow reversion at room temperature (to dimer) also occurs with the high-pressure polymer of dimethylaminoborine discovered by Dewing[38]. This substance ($Me_2N{\cdot}BH_2$, an analogue of isobutene), forms a high-melting polymer at 150°/3000 atm., but diethyl- and dipropyl-aminoborine do not. The black polymer formed from carbon disulphide at

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[34] Gonikberg and Zhulin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1957, 510; 1958, 1254; 1959, 916; cf. Gonikberg, Butuzov, and Zhulin, *Doklady Akad. Nauk S.S.S.R.*, 1954, **97**, 1023.

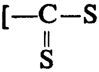
[35] Ashikari, *Kogyo Kagaku Zasshi*, 1956, **59**, 1204.

[36] Fawcett and Gibson, *J.*, 1934, 386.

[37] Novak and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 1490; *Canad. J. Chem.*, 1959, **37**, 1710, 1718.

[38] Dewing, Chem. Soc. Symposium on Inorganic Polymers, Nottingham, 1961.

45,000 atm. above 175°, which decomposes to carbon and sulphur if heated to 200° at ordinary pressure, probably has the structure



$[-\underset{\underset{S}{\|}}{C}-S-]_n$.[39]

Other polymerisable monomers in this class include epoxycyclohexane which yields a hard transparent product at 12,000 atm.,[1] and phenylacetylene which gives polymers[40] at 1000—6000 atm. Although Bengelsdorf[41] obtained a yellow solid from acetone at 320°/50,000 atm. this appears to be the result of a series of ketol condensations rather than addition polymerisation.

8. Copolymerisation at High Pressures.—The study of copolymerisation at 1 atm. has given much information about the relative reactivities of free radicals and provided a theoretical understanding of the manufacture of industrially important copolymers. The development of the high-pressure polyethylene process has been followed by many reports of the copolymerisation of ethylene with other monomers, but chiefly in patents which are uninformative about the mechanism and kinetics of the reactions. An interesting copolymer of this type is formed[42] from ethylene and carbon monoxide at 1000 atm. with t-butyl peroxide as initiator. The liquid or crystalline products ($M \leqslant 2000$) are polyketones and those with the highest carbonyl content correspond to the structure $[-CO{\cdot}C_2H_4-]_n$. Another unusual copolymer is obtained at 2000—8000 atm. from carbon monoxide, an olefin, and an alcohol.[43] The product from carbon monoxide, ethylene, and methanol contains α-hydroxy-ester groups and at the highest pressure the structure tends to $[-CMe(CO_2Me){\cdot}CH_2{\cdot}CH_2-]_n$.

Lamb and Weale[17] have recently studied the copolymerisation of some liquid monomers up to 4000 atm. The overall rates of the copolymerisations increase exponentially with pressure, the acceleration being about the same as for styrene, and the molecular weights of the copolymers increase more slowly and level off at the highest pressures. In the styrene–methyl methacrylate system the reactivity ratios, r_a and r_b, were found not to change with pressure. These are the ratios of the rate constants for chain growth, defined as $r_a = k_{paa}/k_{pab}$ (where k_{paa} is the rate constant for the addition of monomer A to a chain radical ending in monomer A, and k_{pab} is for the reaction between monomer B and a radical ending with A); and correspondingly $r_b = k_{pbb}/k_{pba}$. The constancy of r_a and r_b indicates that in each pair the two rate constants are similarly increased by pressure, and probably that ΔV^* is the same for all four reactions, in agreement with the conclusion of section 3.

[39] Whalley, *Canad. J. Chem.*, 1960, **38**, 2105.

[40] Korshak, Polyakova, and Suchkova, *Vysokomol. Soedineniya*, 1960, **2**, 1246.

[41] Bengelsdorf, in Hamann's book, ref. 8*b*, p. 187.

[42] Coffman, Pinkney, Wall, Wood, and Young, *J. Amer. Chem. Soc.*, 1952, **74**, 3391.

[43] Cairns, Coffman, Cramer, Larchar, and McKusick, *J. Amer. Chem. Soc.*, 1954, **76**, 3024.

A third important parameter is defined by $\phi = k_{tab}/(k_{taa} \cdot k_{tbb})^{\frac{1}{2}}$, in which the k_t's are the rate constants for the three possible bimolecular termination reactions between radical chains ending in A and B monomer units. In equimolar mixtures of styrene and methyl methacrylate at 1 atm. $\phi \approx 25$, so that the cross-termination reaction is strongly preferred, and in the same system ϕ appears to vary little with pressure up to 3000 atm. The persisting preference for cross-termination seems at variance with the assumption of diffusion-control for these reactions at high pressure, since both types of radical might be expected to diffuse at similar rates and ϕ to approach unity. However, it is apparent from the work of North and Reed[44] that the question of diffusion-control is complicated, even in the case of a single monomer at ordinary pressure, and no detailed study of the effect in copolymerisation has appeared.

9. Some Further Aspects of High-pressure Polymerisation.

—A few other features of high-pressure polymerisation merit a short discussion, although they have not been very thoroughly investigated.

(*i*) *Ionic polymerisation under pressure.* Most existing studies relate to radical polymerisation and little information is available for ionic reactions. The rate of formation of poly-α-methylstyrene, with trichloroacetic acid as initiator, is increased by pressure to about the same extent as the radical process,[24] and the iodine-initiated polymerisations of isobutyl vinyl ether[45] and isopentyl vinyl ether[46] are also accelerated to a comparable degree. Ionic initiation depends on the concentration and reactivity of charged complexes, which may be at least as dependent on pressure as the chain-growth, and the relative importance of the two effects has not been determined for any system. The aldehyde polymerisations may also occur by an ionic mechanism but have not been studied kinetically.

(*ii*) *The structure of high-pressure polymers.* Polymer molecules formed by the radical mechanism often have long chain branches which have developed from the site of a transfer reaction between a radical and "dead" polymer. There is some evidence that pressure has little effect on branching in polymerisation of styrene. Kobeko *et al.*[47] found the viscosity–concentration curves for solutions of polystyrenes made at 1 and 6000 atm. to be very similar, and no difference is detectable by light-scattering measurements.[48] The resemblance between the increase of molecular weight with pressure for reactions taken to 100% conversion[6] and to <20% conversion[7] also suggests that pressure causes no large increase in branching even with high concentrations of polymer. These results may reflect a difference between the effects of pressure on transfer to polymer and on transfer to monomer and solvent, but sufficiently detailed evidence is not

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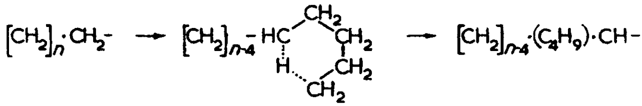
[44] North and Reed, *Trans. Faraday Soc.*, 1961, **57**, 859.
[45] Nahumy, Ph.D. Thesis, London University, 1961.
[46] Hamann and Teplitsky, *J. Phys. Chem.*, 1961, **65**, 1654.
[47] Kobeko, Kuvshinskii, and Semenova, *Zhur. fiz. Khim.*, 1950, **24**, 345.
[48] Trementozzi and Buchdahl, *J. Polymer Sci.*, 1954, **12**, 149.

available on this point. Another type of structural variation, which occurs with polydienes, appears also to be unaffected by pressure. Richardson[49] made an infrared analysis of polyisoprenes and polybutadienes produced at pressures between 5700 and 10,000 atm. and detected no important change in the proportions of *trans*-1,4- and *cis*-1,4-, or of 1,2- and 1,4-linkages present.

There is, however, a very considerable effect of pressure on the structure of polyethylene. The lower density and crystallinity of the ordinary high-pressure polymer compared with the low-pressure (Ziegler) polymer are attributed to short "pendant" side chains occurring at frequent intervals along the main chain. Roedel[50] has suggested that these arise from a cyclic internal transfer reaction (annexed), after which further chain growth continues from the secondary radical. At 7000 atm. and 50—60° the side chains are not formed and the polymers have the high density and crystallinity characteristic of the low-pressure product.[51]



It is well known that polymers of many substituted ethylenes can exist in stereoregular forms in which the configurations of successive asymmetric carbon atoms are either all identical (isotactic polymer) or alternate in some regular sequence (*e.g.*, syndiotactic polymer). If ΔV^* differs for the various modes of chain growth, pressure will affect the type of stereoregularity exhibited by the polymer. A study of poly(methyl methacrylates) produced between 1 and 7500 atm. shows the effect to exist and the ratio of the propagation constants $k_{\mathrm{iso}}/k_{\mathrm{syn}}$ to increase from 0·33 to 0·54 in this pressure range.[52] Isotactic growth requires a helical conformation of the radical and a strictly oriented approach by the monomer molecule. The larger (negative) ΔV^* for isotactic propagation is therefore probably associated with a greater decrease in entropy in the transition state.

(*iii*) *Fast radical polymerisation under pressure.* Many monomers polymerise with great rapidity if ionic initiators are used, but the products are often of low molecular weight.[53] The pressure-acceleration of radical polymerisations is accompanied by an increase in molecular weight, so that fairly high polymers might be obtained in rapid reactions under pressure. Sometimes a fast, uncontrolled reaction yields decomposition products (*e.g.*, ethylene,[54] cyclopentadiene,[55] dichloro- and trichloro-

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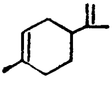
[49] Richardson, *J. Polymer. Sci.*, 1954, **13**, 321.
[50] Roedel, *J. Amer. Chem. Soc.*, 1953, **75**, 6110.
[51] Hines, Bryant, Larchar, and Pease, *Ind. Eng. Chem.*, 1957, **49**, 1071.
[52] Zubov, Kabanov, Kargin, and Shchetinin, *Vysokomol. Soedineniya*, 1960, **2**, 1722.
[53] Swarc, *J. Amer. Chem. Soc.*, 1956, **78**, 1122; Hayes and Pepper, *Proc. Roy. Soc.*, 1961 *A*, **263**, 63.
[54] Hunter, *Chem. and Ind.*, 1955, 396.
[55] Raistrick, Sapiro, and Newitt, *J.*, 1939, 1761.

ethylene[33,34]), but Klaassens and Gisolf[56] found that when styrene is compressed to 10,000 atm. at 75° the temperature rises to over 300° in a few seconds and a block of polymer is formed. Molecular weights were not reported but in more recent experiments at 2000—3000 atm. with initial temperatures of 90—100° (in which the temperature increased a little more slowly) polystyrenes with molecular weights up to ~500,000 were obtained.[57] Transfer reaction rates increase with temperature more rapidly than chain growth, so that higher molecular weights might be attained if the temperature rise was controlled.

(*iv*) *Pressure and cyclisation.* Under some conditions polymerisable monomers yield cyclic products, *e.g.*, tetrafluoroethylene $CF_2{=}CF_2$ can give the perfluorocyclobutane C_4F_8. It is possible that in some cases pressure as well as temperature may determine which reaction path is followed. This has not been demonstrated experimentally, though Walling and Peisach[58] found that when the polymerisation of isoprene is suppressed by adding trinitrobenzene the dimerisation to cyclic products such as 4-isopropenyl-1-methylcyclohexene (II) is strongly accelerated by pressure, with ΔV^* about −25 c.c./mole. When no inhibitor is present the rate of polymerisation is also greatly increased. In contrast, cyclopentadiene is not known to form linear polymers by a free-radical mechanism, but the formation of bicyclic dimer is much faster under pressure[55] ($\Delta V^* = -30$ c.c./mole). It has already been noted (section 6) that 2,3-dimethylbut-2-ene yields cyclic products rather than a linear polymer under pressure, and at 150° under pressure, butadiene, which does normally undergo a pressure-accelerated linear polymerisation, yields viscous liquid products, which are thought to be cyclic tetramers.[59]



(II)

Conclusion.—High pressures produce large effects in addition polymerisation by promoting processes which involve local decreases in volume and entropy and by opposing others. The results on the polymerisation of a few derivatives of ethylene are now fairly well understood, but some important aspects have received little attention, and the behaviour of non-olefinic monomers under pressure remains almost unexplored. The extension of detailed studies in these directions should yield novel polymers and reveal new chemical effects.

[56] Klaassens and Gisolf, *J. Polymer. Sci.*, 1953, **10**, 149.
[57] Rabbetts, unpublished results.
[58] Walling and Peisach, *J. Amer. Chem. Soc.*, 1958, **80**, 5819.
[59] Slobodin and Rachinskii, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 69.