SOME RECENT PROBLEMS IN THE THERMODYNAMICS AND REVERSIBILITY OF ADDITION POLYMERIZATION

K. J. IVIN

Department of Physical Chemistry, University of Leeds, U.K.

INTRODUCTION

The subject of this paper was reviewed in 1958 by Dainton and Ivin[1], and here I shall mainly consider the developments since that time. I shall:

(a) mention the further systems in which equilibrium (or ceiling temperature T_c) measurements have been made;
(b) consider the effect of pressure on T_c;
(c) discuss the effect of ring size on the heat of polymerization ΔH of ring compounds;
(d) summarize the position regarding entropies of polymerization ΔS, as derived by second and third law methods;
(e) say something about the effect of depropagation reactions on copolymer composition.

Before proceeding to the items listed above, it is well to recall that, in general, addition polymerization reactions differ from other chemical reactions in being aggregation processes which are characterized by a sharp temperature, known as the ceiling temperature, above which formation of high polymer will not occur. This temperature is akin to the sharp temperatures which characterize physical aggregation processes, *e.g.* melting point, Curie point. At T_c, the free energy change is zero, so that $T_c = \Delta H/\Delta S$ where ΔH and ΔS are the enthalpy and entropy changes per monomer unit under the prevailing conditions. For long chain polymer formation, these are identical with the heat and entropy changes of the propagation reaction. For most addition polymerization reactions, ΔH, ΔS and the volume change, ΔV, are negative, and T_c can be raised by increasing the monomer concentration or the external pressure, both of which cause a decrease in the numerical value of ΔS.

EQUILIBRIUM STUDIES

The theory of equilibrium polymerization has been extended by Tobolsky *et al.*[2–5]. The equilibrium monomer concentration in a particular monomer–solvent system is independent of the means of initiation, provided the polymer always has the same structure. (Very small variations are to be expected if the tacticity of the polymer varies.) The mean degree of polymerization will, however, depend very much on the initiation and termination mechanisms. Tobolsky has considered various possible cases[2],

and has applied his theory to the polymerization of caprolactam[3], sulphur[4], selenium[6] and α-methylstyrene[5]. It is interesting to note that sulphur and selenium exhibit inverted ceiling temperatures (floor temperature) on account of the unusual endothermic and endoentropic nature of their polymerizations; but whereas with sulphur this occurs at 159°, where both monomer and polymer are in the liquid state, with selenium it occurs in the solid state well below the melting point (217°) of the grey metallic form which itself has a chain structure. Specific heat data on sulphur reveal a discontinuity[7] at 159°, and the values of $(H_T° - H_{25}°)$ and $(S_T° - S_{25})$ above

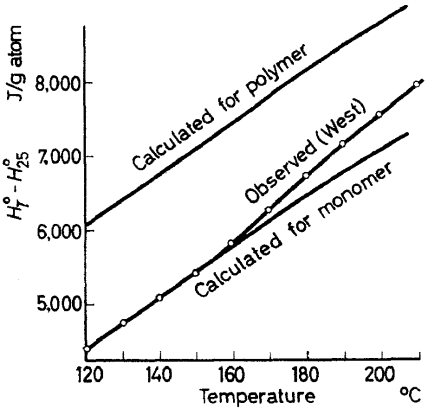


Figure 1. Calculated heat functions for monomeric (S_8) and linear polymeric sulphur and the observed function for their equilibrium mixture (by courtesy Interscience Publishers Ltd.)

159° can be divided into contributions from monomer and polymer[8] as shown in *Figure 1*. Density data[9] again show a discontinuity, from which the volume decrease on polymerization is found to be 6·15 ml (S_8 unit)$^{-1}$. Thus, although ΔH and ΔS are positive, ΔV is negative as in a vinyl polymerization.

It should be mentioned here that, if the equilibrium mixture contains appreciable amounts of dissolved polymer, then the equilibrium monomer concentration may be altered slightly[5]. The condition for equilibrium at constant temperature and pressure is:

$$\Delta \bar{G}_1 - \Delta \bar{G}_2 = \Delta G_{1c} = \text{constant}$$

where $\Delta \bar{G}_1$ and $\Delta \bar{G}_2$ are the partial molar free energies in the equilibrium mixture per mole of monomer and base-mole of polymer respectively, and ΔG_{1c} is the free energy change for pure liquid monomer going to condensed amorphous polymer.

For a 1 : 1 copolymerization of two monomers A and B in which the polymer is precipitated, we have the equilibrium condition:

$$\Delta \bar{G}_{1A} + \Delta \bar{G}_{1B} = \Delta G_{1c} = \text{constant}$$

At a particular temperature, the sum of the two partial molar free energies will have the appropriate value at two compositions of the mixture (below a certain upper temperature limit). Such a state of affairs exists in the formation of isobutene polysulphone from mixtures of isobutene, and sulphur dioxide[10], as shown in *Figure 2*. At points X and Y, the product of

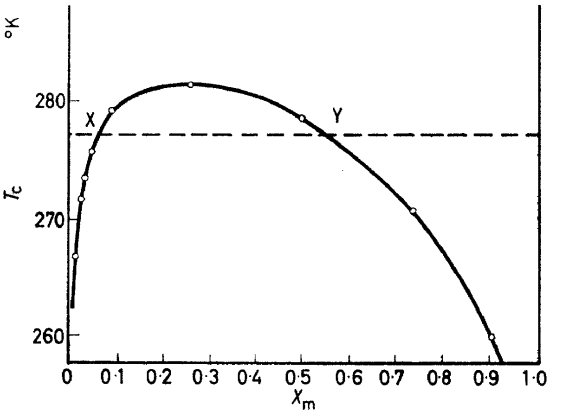


Figure 2. Formation of isobutene polysulphone from mixtures of isobutene and sulphur dioxide: variation of T_c with mole fraction of isobutene x_m (from Cook[10])

the two monomer activities should be the same. We are checking this by vapour pressure measurements, and the results can then be used to calculate ΔG_{1c} and hence ΔH_{1c} and ΔS_{1c} where these changes refer to:

$$\text{Pure A (liq.)} + \text{Pure B (liq.)} \longrightarrow \text{Polymer (solid)}$$

Other systems which have been studied over a range of temperature are styrene in cyclohexane and benzene[11] (100–150°), and formaldehyde (gas) in equilibrium with polyoxymethylene (solid)[12] (50–100°). I shall refer later to the thermodynamics of these systems. Kern and Jaacks[13] investigated the polymerization of trioxan in methylene chloride catalysed by boron trifluoride, and found induction periods due to the build-up of the concentration of formaldehyde in solution to its equilibrium value (0·06 M at 30°). Reversible equilibrium has also been shown to exist between a number of molten polymers and the cyclic oligomers derived by ring closure of two, three or four of their basic units, *e.g.* poly(ethylene terephthalate) after being held at 270° contains 1·4 per cent of the cyclic trimer[14]. Nylon 6 and nylon 66 behave similarly[15, 16].

EFFECT OF PRESSURE ON T_c;

So far, only the α-methylstyrene system has been studied quantitatively[17]. There is qualitative evidence for the existence of pressure effects in the polymerization of acetaldehyde[18], higher aldehydes[18, 19] and carbon disulphide[20].

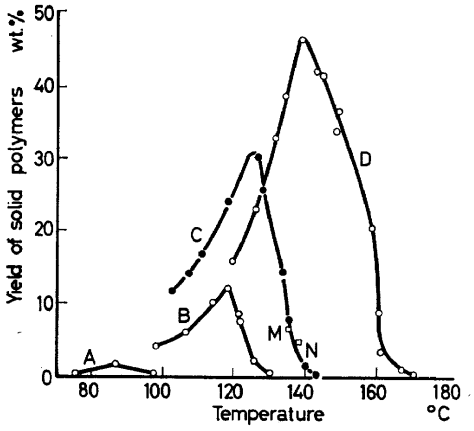


Figure 3. Effect of pressure on polymerization of α-methylstyrene (from Kilroe and Weale[17], by courtesy The Chemical Society) A, 2,200 atm; B, 4,210 atm; C, 4,860 atm; D, 6,480 atm

Kilroe and Weale's results on α-methylstyrene[17] are shown in *Figure 3.* Pure monomer was heated for 4 h in the presence of di-t-butyl peroxide at A : 2,200, B : 4,210, C : 4,860 and D : 6,480 atm. T_c increases from 61° at 1 atm to 170° at 6,480 atm, and does so in accordance with the Clapeyron–Clausius equation:

$$\frac{dT_c}{dP} = T_c \frac{\Delta V}{\Delta H}$$

as shown in *Figure 4.* The T_c values used in this plot were obtained by ignoring the high temperature " tails " in *Figure 3*, since the *DP* values were rather low (*e.g.* 5–16 for all but the last two points in curve C). The slope of *Figure 4* gives $\frac{\Delta V}{\Delta H} = 1{\cdot}73$ ml/kcal. Inserting[17] $\Delta V = -14{\cdot}1$ ml/mole,

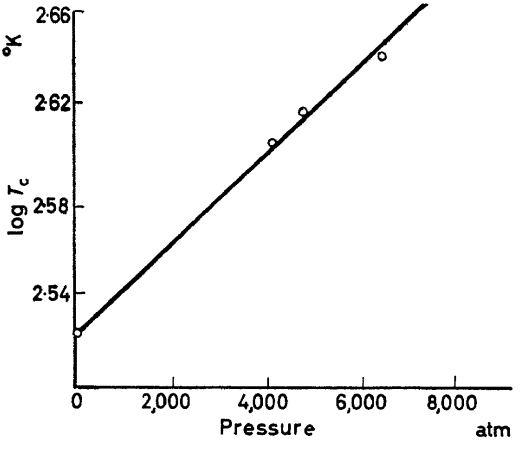


Figure 4. Variation of T_c with pressure for α-methylstyrene (from the results of Kilroe and Weale[17])

one gets $\Delta H = -8{\cdot}1$ kcal/mole, which agrees well with the values derived by calorimetry and by equilibrium measurements[1].

Of particular interest in this connection is the possibility of raising the ceiling temperature of a compound which does not normally polymerize. The free energy of a polymerization which is accompanied by a decrease in entropy and volume will vary with temperature and pressure as shown in *Figure 5*. In general, the effect of pressure on the melting point T_m is greater than that on T_c, as shown by the values of $\Delta V/\Delta H$ in *Tables 1* and *2*.

Table 1. Effect of pressure on T_c

$$\frac{dT}{dP} = T\,\frac{\Delta V}{\Delta H}$$

Monomer	$-\Delta V$ (ml/mole)	$-\Delta H$ (kcal/mole)	$\Delta V/\Delta H$ (ml/kcal)*	*Reference*
α-Methylstyrene	14·1 (20°)	8·1	1·73	17†
Styrene	19·8 (27°)	17·7	1·11	21†
Methyl methacrylate	24·5 (27°)	13·8	1·77	21†
Acrylamide/H_2O	15·9 (27°)	19·8	0·80	21
1-Oxa-4, 5-dithiacycloheptane	2·9 (27°)	2·0	1·45	22
Cycloheptane	17·8 (20°)	5·1	3·49	1
Sulphur (S_8)	6·15 (159°)	−3·17	−1·94	4, 9†
Hex-1-ene–sulphur dioxide copolymer	66·0 (27°)	20·7	3·19	23†

* 1 ml/kcal ≡ 7·27 deg/1000 atm at 25° C.
† Systems with measurable T_c or equilibrium monomer concentration.

Table 2. Effect of pressure on melting point

Substance	ΔV (ml/mole)	ΔH (kcal/mole)	$\Delta V/\Delta H$ (ml/kcal)*	*Reference*
Naphthalene	19·5	4·56	4·27	24
Diphenyl ether	16·07	4·11	3·91	23
Benzal acetone	15·2	4·50	3·38	25
Sulphur dioxide	5·89	1·769	3·33	9

* 1 ml/kcal ≡ 7·27 deg/1000 atm at 25° C.

The lines A, B and C in *Figure 5* correspond to three possible positions of zero free energy change. If the abscissa is in position B, then, by applying pressure at a temperature between T_c and T_c', one goes from an unpolymerizable liquid to a polymerizable solid. Acetaldehyde at room temperature and pressure may be represented by point D with line A as abscissa; T_c is somewhat[26] above −80° and T_c' somewhat above room temperature at 10,000 atm[18]. The polymer, which can be obtained either by reduction of temperature or increase of pressure, is unstable at normal temperature and pressure[18]; no equilibrium data exist, but they should not be hard to determine.

There are several other compounds which have not been polymerized but might resemble the aldehydes in being susceptible to polymerization

under pressure. Among these are δ-valerolactam, *N*-methyl-pyrollidone, and *N*-methylcaprolactam, all of which should have positive values of $\Delta V/\Delta H$. It must be remarked that, in many attempts to polymerize compounds by application of high pressure, the temperature has also been raised to an exceptional degree. For example, Gonikberg *et al.*[27] heated 2,3-dimethylbut-2-ene to 300° for 50 h and obtained 15 per cent dimer and 5 per cent trimer. They then heated it for 3 h at 300° under a pressure of 27,000 atm and obtained 100 per cent polymer of $\overline{\text{D.P.}} = 5$. The effect of the high pressure in reducing ΔS is probably largely compensated by the

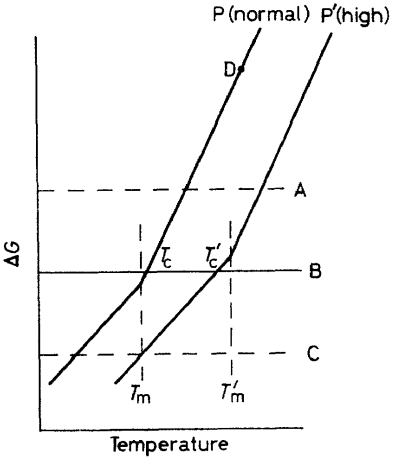


Figure 5. Diagram of the variation of the free energy of polymerization with temperature and pressure, showing effects of pressure on melting point T_m and ceiling temperature T_c

increase in temperature, so that $|T\Delta S|$ is not much reduced (*cf. Figure 5*). It would be interesting to repeat the experiment at high pressures and relatively low temperatures in the presence of suitable initiators, when there is a fair chance that polymer of reasonably high D.P. would be formed.

Increase of pressure favours polymerization not only thermodynamically but also kinetically, volumes of activation being of the order −10 to − 15 ml/mole for vinyl compounds. Much of the early work is summarized in Hamann's book[28]. A recent study is that of Walling[29]. It is also to be expected that the relative rates and equilibria for syndiotactic and isotactic addition to a given chain centre will be affected by pressure.

HEATS OF POLYMERIZATION OF CYCLIC COMPOUNDS

A fair amount of information has accumulated over the last few years, and this is summarized in *Table 3* for 5- to 8-ring compounds. These heats are a measure of the strain energy of the compounds. In several of the cases marked with an asterisk, it appears that the hypothetical heat of polymerization is not sufficient to outweigh the positive entropy term, at least under conditions which have so far been tried[1]. In these cases, polymerization might be brought about by a reduction of temperature or increase of pressure.

The considerable variation in strain energy in the 8-ring compounds provides an interesting theoretical problem. There are three interrelated factors: bond length (greater for C—S and S—S than for C—C), bond

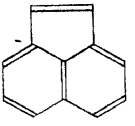
Table 3. — ΔH_{1c} for polymerization of ring compounds[30]

Repeat unit in polymer	*5-ring*	*6-ring*	*7-ring*	*8-ring*
$-(CH_2)n-$	5·2*	− 0·7*	5·1*	8·3*
$-(CH_2)n-O-CH_2-O-$	6·2	0·0*	4·7	12·8
$-(CH_2)n-CO-NH-$	1·1	2·2*	3·8	5·3
$-(CH_2)n-CO-N(CH_3)-$	0·8*	− 0·5*	2·3*	3·9
$-(CH_2)n-S-S-$(experimental)	6·3†	0·5	2·5	3·8
$-(CH_2)n-S-S-$(calculated)‡	14–18	0–2	4–5	8–10

* These have not been polymerized; the heat of formation of the polymer must be obtained by group methods in most cases.
† Indirect *ss* value.
‡ From conformation considerations[31].

angle (as affected by the different states of hybridization), and repulsion between non-bonded atoms (particularly H atoms within the ring).

In passing, it is worth mentioning a case of strain in an ethylenic monomer, since it appears to be the only one of its kind. This is the case of acenaphthylene[21]:



which polymerizes through the double bond of the 5-membered ring, with the exceptionally high heat of 24 kcal/mole. It is easy to see, by consideration of the bond lengths in naphthalene, that the 5-ring must be under some strain which is partly relieved when the double bond is opened.

ENTROPIES OF POLYMERS AND OF POLYMERIZATION

In 1958, there was not a single case in which ΔS_{1c} from equilibrium measurements could be compared with ΔS_{1c} from specific heat measurements[1]. This situation has not improved a great deal, and the comparison can still only be made for two systems, styrene and formaldehyde, with the aid of as yet unpublished data.

For styrene, equilibrium measurements[11] give $-\Delta S_{1c}$ as about 25 e.u./mole at 127° compared with the value 27·65 e.u./mole from specific heats[1]. The discrepancy of 2–3 e.u./mole can be ascribed to residual entropy in the polymer at the absolute zero which causes its third law entropy to be too low. Temperley[32] has discussed the residual entropy problem, and shown that a value of about 2 e.u./mole is to be expected for an atactic vinyl-type polymer. Part of this is configurational entropy arising from the three possible conformations of the substituents on adjacent carbon atoms, and part (up to 1·4 e.u./mole) arises from the semi-random configurations of adjacent monomer units (*d* and *l*).

For formaldehyde[33], specific heat measurements on two semicrystalline polyoxymethylenes gave S°_{298} (polymer)$_{c'}$ = 10·61 and 10·27 e.u./mole.

When combined with the accurately-known S°_{298} (monomer)$_g$ = 52·26 e.u./mole, these give $-\Delta S^{\circ}_{gc'} = 41{\cdot}65$ and 41·99 e.u./mole (25°) compared with the value of 31·02 ± 0·13 e.u./mole (80°) from equilibrium pressure measurements[12]. Here there is a serious discrepancy, too big to be explained in terms of residual entropy. The third law value is undoubtedly close to the true value, since, from Small's[34] correlation of the entropies of ethers and paraffins, the polymer entropy should have a value about 1 e.u./mode less than that of polyethylene[33] (12·4 e.u./mole). The equilibrium method must, therefore, be examined for sources of error. The original data[12] are

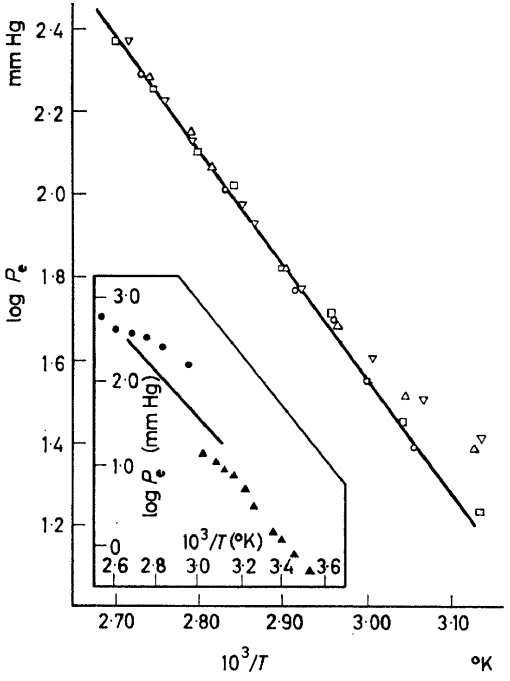


Figure 6. The equilibrium pressure (P_e) of formaldehyde over its polymer, as a function of temperature (from Dainton, Ivin and Walmsley[12], by courtesy the Faraday Society)

shown in *Figure 6* (main graph). Unfortunately, the slope cannot be checked, since there is no reliable calorimetric value for $\Delta H^{\circ}_{gc'}$ (not even the heat of formation of formaldehyde is known accurately). Three possible causes of the discrepancy can be suggested:

(a) Strong absorption of monomer by polymer in the equilibrium measurements. The correction for this effect in the methyl methacrylate system is very small (< 1 e.u./mode) and is not likely to be important here[35].

(b) The vapour at equilibrium may not consist of pure monomer, but may contain dimer and trimer in addition to water vapour derived from the end groups. Water vapour would only be expected if the starting material were of low molecular weight and if the initiation reaction were highly reversible[36]. Some preliminary mass spectrometric analyses made

by Lauder[37] indicated negligible amounts of water and only traces of dimer and trimer.

(c) There may be a first order transition between 25°, the temperature of the specific heat value, and 80° the temperature of the equilibrium measurements. Such a transition would have to be associated with an improbably large heat and entropy change to account for the major part of the discrepancy. However, it is worth noting that there is in fact a crystal-disordering process in this temperature range which has been detected by internal friction measurements[38]. Mechanical and electrical loss measurements[39] also show signs of a transition at about 60°. No data are available on the changes in ΔH and ΔS for this transition, but we may note that the entropy of fusion itself is only 3·93 e.u./mole, while the sum of two disordering changes in polytetrafluoroethylene at 20–30° amounts to less than 1 e.u./mole[40]. Further work is evidently needed to resolve the discrepancy.

The subject of polymer entropies is one which is only just developing. In 1958, it was possible to quote data on only five ethylenic polymers[1]. The lack of interest no doubt stemmed from the difficulty of obtaining perfectly crystalline polymers and the consequent problems of residual entropy at the absolute zero[32]. Dole[40] has rightly described this field as something of a scientific vacuum. That it will soon be filled[33] is due firstly, to the recent availability of polymers with a high degree of crystallinity, secondly to the theoretical interest in the C_p–T relation for crystals with chain structures[40], and thirdly, to the relatively new body of data on entropies of polymerization from equilibrium measurements which allows results to be compared and residual entropies estimated.

In concluding this section, I should like to mention some results obtained at Leeds on polyethylene[33]. A sample of 79 per cent crystallinity (X-ray) gave $S_{298} - S_0 = 11{\cdot}77$ e.u./C_2H_4 unit. A correction for the entropy of fusion of the amorphous content can be applied, and this gives $S_{298} - S_0 = 11{\cdot}77 - 0{\cdot}21 \times 3{\cdot}8 = 10{\cdot}97$ e.u./C_2H_4 unit, which, on comparison with the value of $S_{298} = 11{\cdot}35$ e.u./C_2H_4 unit, derived by extrapolation of the homologous paraffin series[1], indicates a residual entropy of about 0·4 e.u./C_2H_4 unit in the 79 per cent crystalline polymer. Similar results were obtained by comparison of isotactic (semicrystalline) and atactic polypropylene and polystyrene[33].

EFFECT OF DEPROPAGATION OF COPOLYMER COMPOSITION

The copolymerization of two monomers is generally considered in terms of four propagation steps:

$$\begin{aligned} M_1\cdot + M_1 &\longrightarrow M_1\cdot \qquad k_{11} \\ M_1\cdot + M_2 &\longrightarrow M_2\cdot \qquad k_{12} \qquad r_1 = k_{11}/k_{12} \\ M_2\cdot + M_2 &\longrightarrow M_2\cdot \qquad k_{22} \\ M_2\cdot + M_1 &\longrightarrow M_1\cdot \qquad k_{21} \qquad r_2 = k_{22}/k_{21} \end{aligned}$$

and the copolymer composition is then given by:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right)$$

Occasional deviations from this equation have been found, particularly with highly polar monomers such as acrylonitrile, and these have generally been attributed to penultimate, or antepenultimate unit effects on the rate constants[41]. Ham[42] has generalized the original penultimate unit treatment of Merz, Alfrey and Goldfinger[43], and has found satisfactory agreement with the data in certain systems at a given temperature. However, it is clear that, for systems containing a monomer at a concentration not far removed from its equilibrium value (this refers to the value in the absence of the second monomer), it may be necessary to consider certain propagation steps as *reversible*, *i.e.* the net rate of such a step must be written as the difference between two terms rather than as a single term with an altered rate constant. Lowry[44] has derived copolymer composition formulae on the basis of three different sets of assumptions (I, II, III) about the depropagation ability of different radical structures, and Hazell and Ivin[45] have added a fourth set. These assumptions are summarized in *Table 4.*

Table 4. Copolymerization mechanisms involving depropagation. — denotes that depropagation of radical is assumed not to occur; + denotes that depropagation of radical is assumed to occur

Mechanism	*Terminal radical structure* (121· denotes ~~ $M_1M_2M_1$·)								*Limiting composition* $d[M_1]/d[M_2]$ *at high* $[M_2]$, *high T*
	111·	211·	121·	221·	222·	122·	212·	112·	
I	—	—	—	—	+	+	—	—	1 : 1
II	—	—	—	—	+	—	—	—	1 : 2
III	—	—	—	+	+	—	—	—	1 : 2
IV	—	—	—	—	+	+	+	+	1 : 0

In all cases, it is assumed that the *equilibrium* concentration of M_1 is negligibly small while that of M_2 is appreciable. Lowry assumes that the main cause of reversibility is steric hindrance caused by interaction between pairs of M_2 units, not necessarily at the radical end. In all cases, he assumes that this hindrance, and, therefore, depropagation, does not occur with radicals having terminal structure 212· and 112·, the penultimate M_1 unit bringing about the relief of strain. The relative importance of depropagation in radicals with terminal structures 221·, 222·, and 122· cannot be foreseen, so that mechanisms I, II and III start from different assumptions about these three types of radical. In general, reversibility of the propagation step is associated with a low heat of reaction. When this is not caused by steric hindrance, then radicals of structure 212· and 112· are just as liable to depropagate as those of structure 222· and 122·, and so we arrive at mechanism IV.

Mechanisms I, II or III may be expected to apply to pairs of vinyl monomers in which M_2 is, say, α-methylstyrene (— 20–100°) or methyl methacrylate (100–200°). In the limit of high temperature and low $[M_2]$,

the reversible steps are highly reversed and, in effect, do not take place. Certain of Ham's equations, with appropriate reactivity ratios set equal to zero, will then apply.

It is clear that, in order to find the extent to which certain propagation steps are reversed, it is imperative to vary the temperature or $[M_2]$. As yet there has been no study of suitable systems over a sufficiently wide range of conditions to provide a proper test of mechanisms I, II or III. The kind of effects to be expected may be illustrated by the predictions of mechanism I for the case worked out by Lowry[44] and shown in *Figure 7* ($r_1 = r_2 = 1$ at

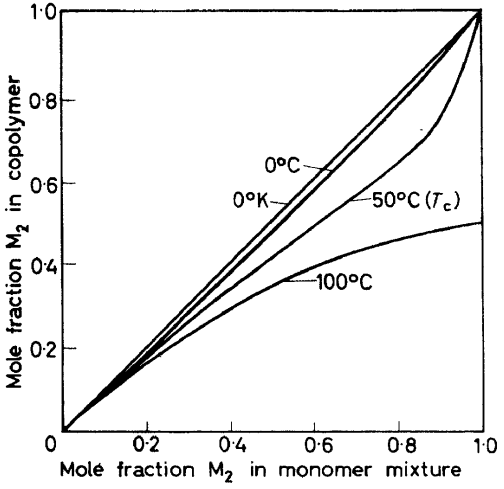


Figure 7. Effect of temperature on copolymer composition in a system containing a monomer (M_2) close to its ceiling temperature, 50°C; $r_1 = r_2 = 1$ at all temperatures, activation energies for propagation and depropagation of M_2, 2 kcal/mole and 12 kcal/mole respectively (from Lowry[44], by courtesy Interscience Publishers Ltd.)

all temperatures, ceiling temperature 50° for $M_2 = 1$ activation energies for propagation and depropagation of M_2 to its own radical equal to 2 and 12 kcal/mole respectively). At 0° there is scarcely any effect of depropagation, whilst at 100° the limiting condition has been reached and the addition of M_2 to a 12· type radical is so highly reversed that it may be regarded as not occurring. It can be seen by comparison of these curves with normal copolymerization curves that experiments at a single temperature may fail to reveal anything abnormal. Only when the temperature is varied will the depropagation effect become evident. Alternatively, a hundredfold dilution of the monomers (at 50° in the case above) will produce a substantial change in the shape of the copolymerization composition curve.

The final column in *Table 4* shows clearly how the use of high temperature and $[M_2]$ can be used to distinguish unambiguously between certain of the mechanisms. Such limiting compositions are well known[42] in systems involving monomers such as maleic anhydride (1 : 1) fumaronitrile (3 : 2(?)) and α-methylstyrene (1 : 2 or 1 : 3(?)), though in some cases, where the conditions may not have been sufficiently extreme, there is some uncertainty as to the real limit.

A good example of mechanism IV is provided by the system cyclopentene–isobutene–SO_2 which gives a regular 1 : 1 olefin–SO_2 copolymer[45]. The reaction can be regarded as a copolymerization between cyclopentene—SO_2 complexes (M_1) and isobutene–SO_2 complexes (M_2). A copolymer was prepared with a feed ratio of 1 : 4 : 40 (cyclopentene: isobutene: SO_2) at 65°. This temperature is about 60° above T_c for the M_2 system and 30° below T_c for the M_1 system. Also, it is known from low temperature experiments that under these conditions the forward reaction for isobutene is favoured by a factor of 50 over that for cyclopentene. The isobutene content of the resulting polymer was only just detectable, not more than 1 per cent of the olefin units being isobutene. This shows clearly that 212· and 112· radicals must be capable of depropagation in this system, *i.e.* mechanism IV applies.

The polysulphone systems are the only ones so far in which a systematic study has been made of the transition from " normal " copolymerization behaviour to " abnormal " behaviour, in the sense that depropagation reactions are brought into play by raising the temperature. In these systems (such as that mentioned above), the copolymerization behaviour is " ideal " at low temperature, so that the composition can be expressed in terms of a single reactivity ratio given by:

$$r = \frac{d[M_2]/d[M_1]}{[M_2]/[M_1]}$$

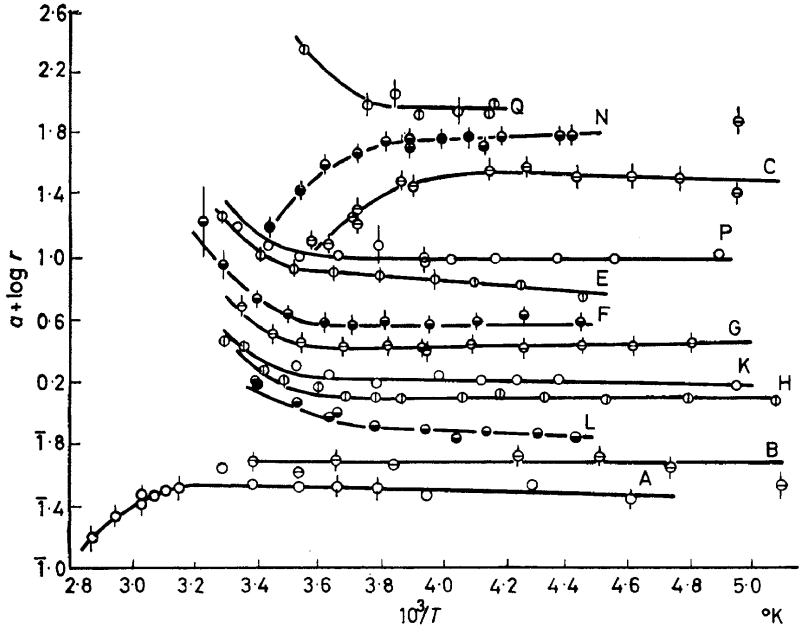


Figure 8. Effect of temperature on the apparent reactivity ratio r in systems of two olefins + sulphur dioxide. Note that where r goes up with increasing temperature, it is M_1 that is close to its ceiling temperature; a is a plotting constant for details of conditions see Hazell and Ivin[45] (By courtesy The Faraday Society)

As the temperature is raised, r begins to deviate from the true reactivity ratio r_0, as shown in *Figure 8*. For mechanism IV, the apparent reactivity ratio r_c at the ceiling temperature of M_2 is related to r_0 (obtainable by extrapolation of the Arrhenius plot at low temperature) by the equation:

$$r_c = \frac{1 + r_0 x - r_0 x \alpha_c}{\frac{1}{r_0} + x + \gamma r_0 x^2 (1 - \alpha_c)}$$

where $$\alpha_c^2 - \left(2 + \frac{1}{r_0 x}\right)\alpha_c + 1 = 0$$

$$x = \frac{[M_2]}{[M_1]}$$

and $$\gamma = \frac{k'_{12}}{k'_{22}}$$

k'_{12} and k_{22} being the rate constants forde propagation of 12· and 22· radicals respectively. In *Figure 9*, r_c is plotted against r_0 for $x = 1$ and values of γ equal to 1, 0·5 and 0 (lines (v), (iv) and (iii) respectively). The line for $\gamma = 0$ corresponds to Lowry's mechanism I, which can be regarded as a limiting case of mechanism IV. The predicted curve for mechanism II is also shown (line (ii)). The experimental points for various polysulphone systems are shown, and mostly correspond to $\gamma \sim 0{\cdot}6$. Thus, it appears that depropagation of 12· radicals is somewhat less probable than that of 22· radicals, perhaps on account of a small effect due to strain.

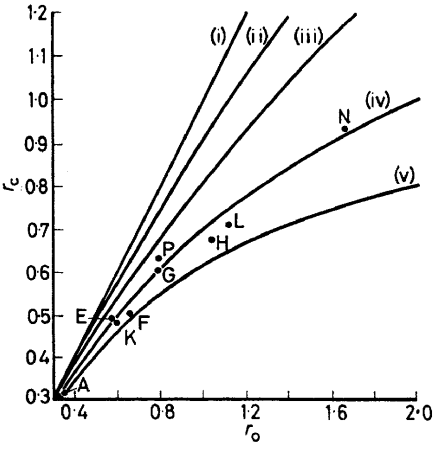


Figure 9. Relation between true reactivity r_0 and apparent reactivity r_c at the ceiling temperature for M_2; (i) no depropagation ($r = r_0$); (ii) mechanism II; (iii), (iv) and (v) Mechanism IV with γ equal to 0, 0·5 and 1·0 respectively ((iii) corresponds to mechanism I.) $[M_2]/[M_1] = 1$ throughout. Points correspond to different systems of pairs of olefins + sulphur dioxide (for details see Hazell and Ivin[45], by courtesy The Faraday Society)

The general relation between r and r_0 contains the equilibrium constant for the addition of M_2 to 12· or 22· radicals. This equilibrium constant has been derived at different temperatures for a number of systems in which cyclohexene–SO_2 is M_2, assuming $\gamma = 0{\cdot}6$. These values are plotted in *Figure 10* and give $\Delta H = -18$ kcal/mole, which is about what is expected for this reaction[45].

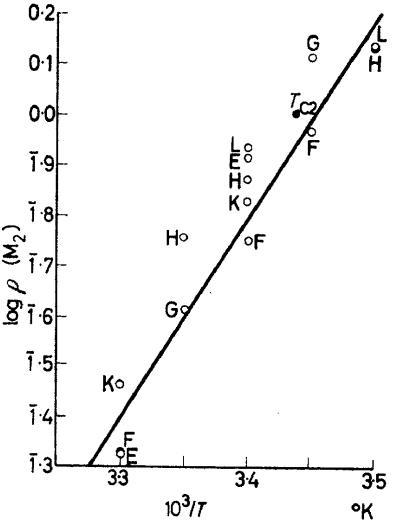


Figure 10. Effect of temperature on the equilibrium constant for the propagation reaction of the cyclohexene–SO_2 system. ($\rho = k_{22}/k_{\acute{2}2}$), [$M_2$] = constant throughout. M_1 as follows: E, hex-1-ene; F, pent-1-ene; G, but-1-ene; H, propylene; K, *cis*-but-2-ene; L, *trans*-but-2-ene (by courtesy The Faraday Society)

Summary

The developments in the field of thermodynamics and reversibility of addition polymerization over the last few years are reviewed.

The effect of pressure on the ceiling temperature of a monomer is considered, and the possibility of polymerizing previously unpolymerizable monomers is discussed.

Heats of polymerization of ring compounds are discussed in relation to polymerizability. The position regarding entropies of polymerization as derived by second law and third law methods is summarized, and the discrepancy in the case of formaldehyde is discussed.

Abnormal copolymerization behaviour is considered in relation to Ham's penultimate unit effect treatment and Lowry's depropagation effect treatment. The latter type of treatment is illustrated by reference to experimental results in systems of two olefins plus sulphur dioxide.

References

[1] F. S. Dainton and K. J. Ivin. *Quart. Revs. (London)*, **12**, 61 (1958)
[2] A. V. Tobolsky and A. Eisenberg. *J. Am. Chem. Soc.*, **82**, 289 (1960)
[3] A. V. Tobolsky and A. Eisenberg. *J. Am. Chem. Soc.*, **81**, 2302 (1959)
[4] A. V. Tobolsky and A. Eisenberg. *J. Am. Chem. Soc.*, **81**, 780 (1959)
[5] A. V. Tobolsky, A. Rembaum and A. Eisenberg. *J. Polymer Sci.*, **45**, 347 (1960)
[6] A. Eisenberg and A. V. Tobolsky. *J. Polymer Sci.*, **46**, 19 (1960)
[7] E. D. West. *J. Am. Chem. Soc.*, **81**, 29 (1959)
[8] K. J. Ivin, *J. Polymer Sci.*, **42**, 585 (1960)
[9] *Gmelin's Handbuch der anorganische Chemie*, **Vol. 9** (1953)
[10] R. E. Cook. *Ph.D. Thesis*, University of Leeds (1959)
[11] S. Bywater. Private communication
[12] F. S. Dainton, K. J. Ivin and D. A. G. Walmsley. *Trans. Faraday Soc.*, **55**, 61 (1959)
[13] W. Kern and V. Jaacks. *J. Polymer Sci.*, **48**, 399 (1960)
[14] I. Goodman and B. F. Nesbitt. *Polymer*, **1**, 384 (1960)
[15] P. H. Hermans. *Nature*, **177**, 126 (1956)
[16] C. J. Brown, A. Hill and P. V. Youle. *Nature*, **177**, 127 (1956)
[17] J. G. Kilroe and K. E. Weale. *J. Chem. Soc.*, **1960**, 3849

[18] A. Novak and E. Whalley. *Can. J. Chem.*, **37**, 1710 (1959)
[19] A. Novak and E. Whalley. *Can. J. Chem.*, **37**, 1718 (1959)
[20] E. Whalley. *Can. J. Chem.*, **38**, 2105 (1960)
[21] F. S. Dainton, K. J. Ivin and D. A. G. Walmsley. *Trans. Faraday Soc.*, **56**, 1784 (1960)
[22] F. S. Dainton, J. A. Davies, P. P. Manning and S. A. Zahir. *Trans. Faraday Soc.*, **53**, 813 (1957)
[23] F. S. Dainton, J. Diaper, K. J. Ivin and D. R. Sheard. *Trans. Faraday Soc.*, **53**, 1269 (1957)
[24] J. H. Beynon and A. R. Humphries. *Trans. Faraday Soc.*, **51**, 1065 (1955)
[25] E. J. Caule and C. C. Coffin. *Can. J. Res.*, **B28**, 639 (1950)
[26] J. Furukawa, T. Saegusa and H. Fujii. *Makromol. Chem.*, **44**, 398 (1961)
[27] M. G. Gonikberg, V. P. Butuzov and V. M. Zhulin. *Compt. rend. acad. sci. U.R.S.S.*, **97**, 1023 (1954)
[28] S. D. Hamann. *Physico-chemical Effects of High Pressure*, Butterworths, London (1957)
[29] C. Walling. *J. Polymer Sci.*, **48**, 335 (1960)
[30] Original references cited by Dainton, Ivin and Walmsley[21]
[31] A. Schöberl and H. Gräfje. *Ann. Chem. Liebig's*, **614**, 66 (1958)
[32] H. N. V. Temperley. *J. Research Natl. Bur. Standards*, **56**, 55 (1956)
[33] F. S. Dainton, D. Evans, F. E. Hoare and T. P. Melia. Unpublished results, see *Bull. Chem. Thermodynamics*, **4**, 50 (1961)
[34] P. A. Small. *Trans. Faraday Soc.*, **51**, 1717 (1955)
[35] K. J. Ivin. *Trans. Faraday Soc.*, **51**, 1273 (1955)
[36] A. Iliceto and S. Bezzi. *Chim. e Ind. (Milan)*, **42**, 728 (1960)
[37] I. Lauder. Private communication.
[38] W. H. Linton. *Plastics Inst., (London), Trans. and J.*, **28**, 131 (1960)
[39] Y. Ishida, M. Matsuo, H. Ito, M. Yoshino, F. Irie and M. Takayanagi. *Kolloid-Z.*, **174**, 162 (1961)
[40] M. Dole. *Advances in Polymer Sci.*, **2**, 221 (1960)
[41] W. G. Barb. *J. Polymer Sci.*, **11**, 117 (1953)
[42] G. E. Ham. *J. Polymer Sci.*, **45**, 169, 177, 183 (1960)
[43] E. Merz, T. Alfrey and G. Goldfinger. *J. Polymer Sci.*, **1**, 75 (1946)
[44] G. G. Lowry. *J. Polymer Sci.*, **42**, 463 (1960)
[45] J. E. Hazell and K. J. Ivin. *Trans. Faraday Soc.*, **58**, 176 (1961)