100. G.T.Morgan and W.O.Wooton, J.Chem.Soc., 91, 1311 (1907).
101. O.Dimrot, H.Leichtlin, and O.Friedmann, Ber., 50, 1539 (1917).
102. G.T.Morgan and D.A.Cleage, J.Chem.Soc., 113, 589 (1918).
103. M.S.Dinaburg, "Svetochuvstvitel'nye Diazosoedineniya i Ikh Primenenie" (Photosensitive Diazo-Compounds and Their Applications), Izd."Khimiya", Moscow, 1964, p.78.
104. P.A.S.Smith and W.L.Berry, J.Org.Chem., 26, 27 (1961).
105. G.T.Morgan and Y.M.Hird, J.Chem.Soc., 92, 1505 (1907).
106. J.Vaughan and L.Phillips, J.Chem.Soc., 1560 (1947).
107. M.S.Dinaburg, see Ref.103.
108. J.de Jonge, R.Dijkstra, and G.Z.Weggering, Rec.Trav. chim., 71, 846 (1952).
109. L.A.Kazitsyna, B.S.Kikot', B.V.Rassadin, and O.A.Reutov, Zhur.Obshch.Khim., 33, 223 (1963).
110. N.N.Kazanova, Diploma work, Lomonosov Moscow Institute of Fine Chemical Technology, 1965.
111. L.A.Kazitsyna, A.V.Upadysheva, and O.A.Reutov, Dokl. Akad.Nauk SSSR, 164, 110 (1965).
112. V.V.Ershov and G.A.Nikiforov, Dokl.Akad.Nauk SSSR, 158, 1362 (1964).
113. L.A.Kazitsyna, B.S.Kikot', L.E.Vinogradova, and O.A.Reutov, Dokl.Akad.Nauk SSSR, 158, 1369 (1964).
114. R.Huisgen and R.Fleischwann, Annalen, 623, 47 (1959).
115. G.T.Morgan and F.M.G.Micklethwait, J.Chem.Soc., 91, 1512 (1907).
116. A.M.Simonov, Zhur.Obshch.Khim., 10, 1220 (1940).
117. R.Huisgen and H.J.Koch, Annalen, 591, 200 (1955).
118. R.S.Karlinskaya and N.V.Khromov-Borisov, Zhur.Obshch. Khim., 32, 1847 (1962).
119. P.Jacobson and L.Huber, Ber., 41, 660 (1908).
120. H.Staudinger and G.Lüscher, Helv.Chim.Acta, 5, 75 (1922).
121. W.Reid and H.Appel, Z.Naturforsch., 15b, 684 (1960); Annalen, 646, 83 (1961).
122. L.R.Modling and A.Burger, J.Amer.Chem.Soc., 63, 1115 (1941).
123. R.Meldola and E.Wechsler, J.Chem.Soc., 77, 1172 (1900).
124. A.Klemenc, Ber., 47, 1407 (1914).
125. E.Kunze, Ber., 21, 3333, 3530 (1888).
126. F.K.Cameron, Amer.Chem.J., 20, 229 (1898).
127. H.H.Hodgson and S.Bartwell, J.Chem.Soc., 469 (1943).
128. N.Kornblum, in "Organic Reactions, Vol.II" (Edited by R.Adams, W.E.Bachmann, L.F.Fieser, J.R.Johnson, and H.R.Snyder) (Translated into Russian), Inostr.Lit., Moscow, 1950, p.285.
129. O.Ruff and V.Stein, Ber., 34, 1668 (1901).
130. O.Süs, Annalen, 556, 65, 85 (1944).
131. J.de Jonge, Rec.Trav.Chim., 67, 328 (1948).
132. Y.K.Stille, P.Cassidy, and L.Plummer, J.Amer.Chem. Soc., 85, 1318 (1963).
133. O.Süs and K.Möller, Annalen, 593, 91 (1955).
134. O.Süs, M.Glos, K.Möller, and H.D.Eberhardt, Annalen, 583, 150 (1953).
135. O.Süs, Z.Wiss.Photogr.Photophys.Photochem., 50, II, 476 (1955); Chem.Zentr., 11106 (1956).
136. O.Süs, H.Steppan, and R.Dietrich, Annalen, 617, 21 (1958).
137. E.Bamberger, Ber., 28, 837 (1895).
138. G.T.Morgan and J.N.Porter, J.Chem.Soc., 107, 645 (1915).
139. G.T.Morgan and F.M.G.Micklethwait, J.Chem.Soc., 89, 4 (1906).
140. L.Wolff, Annalen, 312, 119 (1900).
141. E.Bamberger, Vierteljahresschrift Naturforsch.Ges. Zuerich, 42, 136 (1897).
142. A.Hantzsch and J.Lifschitz, Ber., 45, 3011 (1912); 46, 414 (1913).
143. E.Bamberger, Annalen, 390, 154 (1912).
144. A.Angeli and A.Pieroni, Atti Accad.naz.Lincei, Rend. Classe Sci.fis.mat.nat., [5], 32, 151, 450 (1923).
145. N.V.Sidgwick, T.W.Taylor, and J.W.Baker, "The Organic Chemistry of Nitrogen", Oxford, 1937, p.423.
146. J.De Jonge, R.J.H.Alink, and D.Dijkstra, Rev.Trav.Chim., 69, 1448 (1950).
147. R.G.W.Le Fevre, J.B.Sousa, and R.L.Werner, J.Chem. Soc., 4686 (1954).
148. P.Yates and E.W.Robe, J.Amer.Chem.Soc., 79, 5761 (1957).
149. W.Reid and R.Dietrich, Annalen, 639, 32 (1961).
150. B.Glowiak, Roczniki Chem., 34, 134 (1960); Bull.Acad. polon.Sci., Ser.Sci.chim., geol., geog., 8, 1 (1960).
151. B.Glowiak, Bull.Acad.polon.Sci., Ser.Sci.chim., geol., geog., 10, 9 (1962).
152. E.Fahr, Annalen, 638, 1 (1960).
153. L.A.Kazitsyna, L.D.Ashkinadze, A.V.Upadysheva, L.E.Vinogradova, and O.A.Reutov, Dokl.Akad.Nauk SSSR, (in the press).
154. L.A.Kazitsyna, B.S.Kikot', L.D.Ashkinadze, and O.A.Reutov, Dokl.Akad.Nauk SSSR, 160, 573 (1963).
155. G.T.Morgan and H.P.Tomlins, J.Chem.Soc., 111, 497 (1917).
156. M.M.Battegay and J.Schmidt, Bull.Soc.chim.France, [4], 41, 205 (1927).
157. J.Schmidt and W.Maier, Ber., 64, 7 (1931).
158. N.N.Vorozhtsov, "Osnovy Sinteza Promezhutochnykh Produktov i Krasitelei" (Fundamentals of the Synthesis of Intermediate Products and Dyes), Goskhimizdat, Moscow, 1955, pp.431, 457.
159. T.Kunitake and C.C.Price, J.Amer.Chem.Soc., 85, 761 (1963).
160. C.L.Anderson and J.W.Steedly, J.Amer.Chem.Soc., 76, 5144 (1954).
161. C.L.Anderson and B.Manning, J.Amer.Chem.Soc., 77 3018 (1955).
162. T.S.Kikot', Candidate's Thesis, Faculty of Chemistry, Moscow State University, 1963.

Department of Organic Chemistry,
Faculty of Chemistry,
Moscow State University

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BULK POLYMERISATION OF VINYL MONOMERS AT HIGH EXTENTS OF REACTION

G.P.Gladyshev and S.R.Rafikov

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I. INTRODUCTION

The study of bulk polymerisation at high extents of reaction is of both theoretical and practical interest. Although polymerisation to high conversions is often encountered in daily practice, relatively little systematic work has been done on this problem, in contrast to the initial stages of the polymerisation reaction, mainly because of the complexity of the quantitative interpretation of the results.

Nowadays there are semiquantitative theories which explain, on the whole satisfactorily, the characteristic features of polymerisation at advanced stages of the reaction. However, many problems still remain unsolved, which, for example, makes it impossible to control the "gel effect" in the polymerisation of important vinyl monomers such as methyl methacrylate, butyl methacrylate, etc.

The present review deals with the polymerisation of vinyl compounds not accompanied by the appearance of a new phase. Problems concerning the appearance of a new phase in ω-polymerisation, polymerisation of monomers whose polymers are insoluble, etc. are not included. The literature on these problems can be found in a number of monographs [1-3].

II. GENERAL THEORY OF THE "GEL EFFECT"

At the end of the 1930's it was observed that bulk polymerisation of certain vinyl monomers involves a sharp increase of reaction rate on attainment of certain degrees of conversion of the monomer into the polymer [1-18]. This phenomenon was called the "gel effect" or the "Trommsdorff effect". In the polymerisation of methyl methacrylate the acceleration usually occurs on attainment of about 15–25% conversion. In the polymerisation of substances whose polymers are insoluble in the monomers the reaction rate increases immediately after the formation of appreciable amounts of the polymer. The shape of the kinetic curves for polymerisation with self-acceleration is determined by the nature of the monomer, the concentration of the initiator, and the reaction conditions.

Initially it was believed that the increase in reaction rate is due to the process being non-isothermal [2,16]. It was suggested that the heat evolved during polymerisation raises the temperature of the reaction mass. However, this view soon had to be rejected [13,17]. Firstly, it was shown that polymerisation under strictly isothermal conditions also involves considerable self-acceleration. Secondly, it was established that in the acceleration stage the molecular weight of the polymers formed increases, whereas according to the equation

$$\frac{d\ln P}{dT} = \left(E_r - \frac{1}{2}E_0 - \frac{1}{2}E_{in}\right)/RT^2 \qquad (1)$$

the increase in polymerisation temperature in a chemically initiated reaction should in fact lower the molecular weight.

Norrish and Smith [17] suggested that the reason for the self-acceleration is the decrease of the rate constant k_t for the chain termination reaction. They showed that an increase of the initiator concentration or temperature in the polymerisation of methyl methacrylate displaces the onset of self-acceleration towards higher degrees of conversion. Since an increase of temperature and initiator concentration results in a lowering of the molecular weight of the polymer and hence of the viscosity of the medium, it is evident that the change in k_t is associated with an increase in viscosity.

To confirm these findings, Norrish and Smith [17] studied the polymerisation of methyl methacrylate in the presence of various solvents and established that systems of low viscosity exhibit the smallest self-acceleration. As suggested, the molecular weight of the polymers increased with the viscosity of the medium. Similar ideas about the possibility of a decrease of the rate constant for chain termination were put forward by Medvedev and coworkers [18], who studied the polymerisation of chloroprene.

Somewhat later Schulz and Harborth [19] made a detailed study of the polymerisation of methyl methacrylate in the presence of benzoyl peroxide and established that the rate of reaction in the later stages can exceed the initial rate of polymerisation by several tens. By varying the concentration of the peroxide, they showed that the maximum rate of polymerisation at the self-acceleration stage is directly proportional to the initial rate. Their explanation of the phenomenon of self-acceleration was the same as that of Norrish and Smith [17].

Trommsdorff and coworkers [15] established that introduction of poly(methyl methacrylate) into the monomer causes self-acceleration at the very beginning of the polymerisation reaction. Furthermore, they showed that if the system is cooled sharply to -20° at the self-acceleration stage and then reheated to the previous temperature a long time afterwards, the rate of reaction is the same as before the freezing. These data also confirm the general theory of the "gel effect".

On the other hand, the rate of polymerisation is determined by the rate of chain growth which can also vary with the viscosity of the medium. However, if allowance is made for the fact that the molecular size of the monomer is small compared with that of the macroradicals whose interaction leads to chain termination, it may be assumed that the variation of k_p during polymerisation is slight when the degree of reaction is low. An appreciable change of k_p at a degree of reaction of the order of 50–70% might be expected. Schulz and Harborth [19], who noted a sharp decrease in the rate of polymerisation at degrees of conversion exceeding 70–80%, arrived at this conclusion.

Thus a quantitative theory of the "gel effect" was developed at the end of the 1930's and the beginning of the 1940's of the present century. A quantitative test of the theory became possible only after the development of methods for the determination of the rate constants for the fundamental reaction steps.

III. QUANTITATIVE DATA

After the rotating sector and thermometric methods began to be used to determine the ratio k_p/k_t in chain polymerisation, papers dealing with the variation of k_p and k_t with the degree of conversion appeared. Matheson and coworkers [20-22] were the first to make reliable measurements (rotating sector method) and confirmed quantitatively the treatment of the "gel effect" proposed by Norrish, Smith, Schulz, and others. The study of the polymerisation of methyl methacrylate [22] showed that at 33% conversion the chain propagation rate constant remains virtually unchanged, whereas the chain termination constant decreases by a factor of more than a hundred. On the other hand, in the study of the photopolymerisation of

methyl acrylate in the presence of diacetyl and azobisisobutyronitrile, Matheson and coworkers[22] found that the rate of polymerisation increases continuously from the very beginning of the reaction. By comparing their results with the data of other investigators, they confirmed the theory of Norrish, Smith, and coworkers. Similar results were also obtained in the polymerisation of styrene, but the change in the ratio k_p/k_t was much smaller than for methyl methacrylate. This is due to the almost complete absence of the "gel effect" in the polymerisation of styrene. The percentage conversion at which self-acceleration begins is determined by the molecular weight of the polymer formed, and hence by the viscosity of the medium. The ratios $k_p(35\%)/k_p(0\%)$ and $k_t(35\%)/k_t(0\%)$ obtained by Matheson and coworkers[22] are given in Table 1.

Naylor and Billmeyer[23] obtained interesting data on the variation of the molecular weight of poly(methyl methacrylate) with the degree of reaction in photopolymerisation. They emphasised that the observed increase in the degree of polymerisation is associated with a decrease in the rate of termination of the polymeric chain and should be accompanied by a variation of the molecular weight distribution as the monomer is converted into polymers. Examination of the "percentage conversion–(time)(intensity)$^{1/2}$" relation clearly showed that, as the intensity of irradiation increases, the onset of self-acceleration becomes more distinct and is observed at increasing degrees of conversion. At high irradiation intensities the molecular weight of the polymer is lower than at low intensities. Hence it follows that for the same degree of conversion the viscosity of the medium is smaller in the former case and the acceleration should occur at higher degrees of conversion. These authors concluded that the use of light filters makes it possible to control the "gel effect". Somewhat later Pravednikov[24,25] confirmed the theory of Norrish, Smith, and others and noted that the interpretation of the self-acceleration phenomenon as a consequence of the formation of a three-dimensional polymeric network[26] is incorrect.

Melville[27] and Bengough[28] showed, using the thermocouple method, that in the polymerisation of vinyl acetate k_t decreases by a factor of three at 50% conversion, whereas k_p remains virtually unchanged (Table 2).

TABLE 1. "Gel effect" in the polymerisation of certain monomers.

Monomer	Temperature, °C	Conversion corresponding to onset of self-acceleration, %	$\frac{k_p(35\%)}{k_p(0\%)}$	$\frac{k_t(35\%)}{k_t(0\%)}$	Degree of polymerisation, P_{init}
Vinyl acetate	25	>40	—	—	2400
Styrene	50	30	0.67	0.075	4000
Methyl methacrylate	30	15	1.12	0.0066	5000
Methyl acrylate	30	0	—	—	10000

TABLE 2. Photopolymerisation of vinyl acetate at 25° in the presence of the dinitrile of 1,1-azodicyclohexylcarbonic acid.

Conversion, %	k_p, litre mole^{-1} s^{-1}	$10^{-6}k_p$, litre mole^{-1} s^{-1}	E_p, kcal mole^{-1}	E_p, kcal mole^{-1}
4	860	240	4.2	1
23	990	126	4.2	1
46	1070	90	3.6	3.9
57	238	6.7	8.6	11.8
65	30	1.15	11.4	13.0
73	—	—	14.4	15.4

TABLE 3. Polymerisation of butyl acrylate at 25° (rate of initiation 2.1 × × 10^{-8} mole litre^{-1} s^{-1}).

Conversion, %	$10^{-6}k_p$	$10^{-8}k_t$
1	2.93	4.8
20	0.76	0.38
40	0.46	0.115
60	0.26	0.43
70	0.0044	0.0073

There is an analogous variation of the activation energy for the chain propagation and termination reactions. Similar results were obtained for butyl acrylate and methyl methacrylate. In the polymerisation of butyl acrylate it was established that the reaction rate increases slightly with the degree of conversion, the fall in rate beginning at 20–30% conversion. Table 3 presents data on the variation of k_p and k_t and shows that the decrease of k_t is accompanied by a sharp decrease of k_p. In the authors' view this fact is associated with the structure of the polymer which is responsible for the "gel effect" at degrees of conversion much smaller than 20%. In the polymerisation of methyl methacrylate it was found[27] that k_t begins to decrease at about 20% conversion, whereas the decrease of k_p does not begin until the degree of conversion is about 50%.

Later Bengough and Melville[29] showed that, for the polymerisation of methyl methacrylate, the exponent n in the equation

$$V = kI^n[M] \qquad (2)$$

(I is the intensity of irradiation or the concentration of the sensitiser) decreases from 0.5 at 0–15% conversion to about 0.3 at 15–25% conversion, and then increases again and reaches 1 when the degree of conversion is of the order of 40%. It was also found that increase of conversion from 0 to 35% (at 32°) results in an increase of $10^5k_p/k_t$ from 1.9 to 110, whereas k_t decreases from 5.7×10^6 to 8.8×10^4 (litre mole^{-1} s^{-1}). Recently Hayden and Melville[30] confirmed these data. They found that at 10–40% conversion n decreases to 0.25, the activation energy for chain termination increases appreciably, while k_p and E_p remain constant. At a conversion in excess of 50% n increases, k_t and k_p decrease, and E_t and E_p increase.

Fujii[31,32] made a novel study of the polymerisation of styrene and methyl methacrylate at high extents of reaction and demonstrated that the lifetime of free radicals in viscous media can be conveniently calculated from the photochemical after-effect. He used the equation

$$\ln\left(\frac{V_p+V_\alpha}{V_p-V_\alpha}\right) = \ln\left(\frac{V_{pL}+V_\alpha}{V_{pL}-V_\alpha}\right) + 2\frac{V_\alpha}{V_{pL}}\frac{t}{\tau}, \qquad (3)$$

derived on the hypothesis that after irradiation ceases radicals are destroyed according to the law

$$-\frac{d[R\cdot]}{dt} = k_t[R\cdot]^2 - k_i[M]^2, \qquad (4)$$

where V_α is the steady-state rate of thermal polymerisation, V_p the rate of polymerisation at the instant t after irradiation is switched off, V_{pL} the steady-state rate of photopolymerisation, and the other symbols have the usual significance.

It follows from Eqn. (3) that the plot of

$$\frac{V_{pL}}{2V_\alpha}\ln\left(\frac{V_p+V_\alpha}{V_p-V_\alpha}\right)$$

against t makes it possible to determine $1/\tau$ and hence the lifetime of free radicals and the ratio k_p/k_t. The results are presented in Table 4.

Fujii also showed that the order of the chain-termination reaction decreases from 1.9–2.1 to 1.4–1.6 when the conversion increases from about 0 to 68%. These results are consistent with the data of Melville and coworkers[29,30]. Similar results were obtained in the polymerisation of methyl methacrylate[32] (Table 5). The order of the chain termination reaction for this monomer decreases from 1.9–2.1 to 1.65–1.8 when the conversion rises from 0 to 60%. In the polymerisation of styrene[31] and methyl methacrylate[32] the apparent activation energy decreases with percentage conversion.

Miyama[33-36] used a thermistor method to determine the variation of k_p/k_t with percentage conversion in the polymerisation of vinyl monomers. Fujii and Tanaka[37] obtained interesting results by measuring the lifetime of free radicals in the photopolymerisation of styrene in the presence of carbon tetrachloride. The addition of carbon tetrachloride tends to increase the initial rate of polymerisation but at high degrees of conversion it reduces the lifetime of macroradicals.

In order to reconcile the data on the variation of k_t and k_p with the degree of polymerisation and the molecular weights obtained, Robertson[38], who studied the kinetics of the polymerisation of styrene and methyl methacrylate, assumed that the effectiveness of initiation f varies with the degree of reaction. It was shown that, as polymerisation proceeds, f for many of the initiators investigated (benzoyl peroxide, azobisisobutyronitrile, t-butyl peroxide, and lauroyl peroxide) falls sharply and becomes very small when the percentage conversion is more than 50–60%.

TABLE 4. Photopolymerisation of styrene*.

Conversion, %	Temperature, °C	k_p/k_t	$k_{t(x\%)}/k_{t(0\%)}$
0	20	$0.55\cdot10^{-6}$	
38±1	30	$2.36\cdot10^{-6}$	1
43±2	30	$6.36\cdot10^{-4}$	$3.75\cdot10^{-3}$
	30	$2.56\cdot10^{-3}$	$9.22\cdot10^{-4}$
60±2	30	$1.30\cdot10^{-2}$	$1.81\cdot10^{-4}$
70±2	30	$1.37\cdot10^{-2}$	$1.71\cdot10^{-4}$

* Intensity of irradiation 4×10^{-8} einstein s^{-1}.

TABLE 5. Photopolymerisation of methyl methacrylate*

Conversion, %	Temp., °C	k_p/k_t	$k_{t(x\%)}/k_{t(0\%)}$
0≃1	30	$1.93\cdot10^{-5}$	1
	40	$2.47\cdot10^{-5}$	
47±2	30	$9.20\cdot10^{-3}$	$2.10\cdot10^{-3}$
52±2	30	$9.33\cdot10^{-3}$	$2.07\cdot10^{-3}$
	40	$9.48\cdot10^{-3}$	
	50	$9.86\cdot10^{-3}$	
72±3	30	$2.96\cdot10^{-2}$	$6.52\cdot10^{-4}$

* Intensity of irradiation $4\times\times10^{-8}$ einstein s^{-1}.

Calculations of f in the polymerisation of styrene in the presence of azobisisobutyronitrile were also made by Nishimura[39], who used the equation

$$\bar{P}_n = \frac{[M]_0}{f[c]_0} \times \frac{x}{1-\exp(-k_d t)}, \quad (5)$$

where $\bar{P}_n$ is the cumulative degree of polymerisation, $[c]$ the initiator concentration, k_d the initiator breakdown rate constant, and x the extent of reaction. A similar calculation was also made with allowance for the change in volume with the extent of reaction. However, Nishimura believes that the variation of f is only apparent.

After many data had accumulated on the effect of the extent of reaction of vinyl monomers on the kinetic constants of the fundamental reaction steps, it became necessary to relate quantitatively the changes in these parameters to the viscosity of the medium. The first serious attempts in this field were made by Vaughan[40] and Schulz[41,42]. Schulz examined Smoluchowski's equation and showed[41] that the rate of chain termination by reaction between radicals may be determined by diffusion even in media of relatively low viscosity. The rate of chain growth should be limited by diffusion only in media of very high viscosity. The results of Schulz's theoretical study were subsequently used by a number of investigators. Fujii[31] noted that the decrease of the overall activation energy with the extent of reaction is associated with the increase of the activation energy for chain termination:

$$E = E_p - \frac{1}{2}E_0 + \frac{1}{2}E_i.$$

Using the equation proposed by Spencer and Williams[43],

$$\eta = 3.63\times10^{-10}\exp\{0.0572\sqrt{M} + \sqrt{W_2}(22.54-0.045\sqrt{M}+5000/T)\} \quad (6)$$

(where η is the viscosity of the styrene–polystyrene system in centipoises, M the molecular weight determined by the Staudinger method, and W_2 the weight fraction of the polymer), Fujii estimated the activation energy for the diffusion of polymeric polystyrene radicals for 38 and 60% conversion. He obtained 6.1 and 7.7 kcal $mole^{-1}$ respectively, which in his view is in good agreement with experiment and confirms the conclusion that the rate of the chain termination reaction is determined by diffusion. Fujii[32] also estimated the activation energy for chain termination in the polymerisation of methyl methacrylate (5.8 kcal × × $mole^{-1}$) for 52% conversion. This value is in good agreement with the data of Spencer and Williams[43] and the activation energy for viscous flow of fused polyesters, which according to Flory[44] is about 8 kcal $mole^{-1}$.

Miyama[36] made a detailed study of the effect of the viscosity of the medium on the kinetic constants for vinyl polymerisation. He expressed doubt about the correctness of the equation derived by Vaughan[40] on the basis of the theoretical study of Rabinowitch[45]. Miyama showed that the use of Smoluchowski's equation[46] for the number of collisions in solution makes it possible to obtain an expression relating the second-order rate constant to the viscosity of the medium. Comparison of the experimental values of k_p/k_t with η of the medium yields the following expressions:

$$(k_t)_{0\%}/k_t = 0.76 + 0.24\,[(\eta/\eta_0)^{0.20} \times 10^{-8}\,(\eta/\eta_0)^{1.50}] \quad (7)$$

(for vinyl acetate)

$$(k_t)_{0\%}/k_t = 0.83 + 0.17\,(\eta/\eta_0)^{0.28} \quad (8)$$

(for methyl methacrylate)

The following formula is valid for the values of $(k_p)_{0\%}/k_p$ in the polymerisation of vinyl acetate[36]:

$$(k_p)_{0\%}/k_p = 1 + 0.65 \times 10^{-6}(\eta/\eta_0) \quad (9)$$

In Eqns. (7)–(9) the subscript 0% refers to zero percentage conversion. Miyama noted that the analysis of his data on the basis of the Rabinowitch equation gives unsatisfactory results. Starting in 1959, North and others published a series of papers in which they described a thorough investigation of the effect of the medium on the rate constants for vinyl polymerisation and in which they make a comprehensive examination of the mechanism of the chain termination process whose rate is determined by diffusion[47-52]. These studies led to important conclusions.

In order to eliminate the effects of branching and cross-linking, in their attempts to elucidate the effect of viscosity on polymerisation processes Benson and North[47] studied the relevant reactions in solvents of high viscosity. The ratio k_p/k_t was determined by the photochemical after-effect method. Later they calculated the ratio k_t/k_p^2 and hence k_t and k_p on the basis of a study of the dependence of the degree of polymerisation on the rate of reaction. The earlier postulate that the viscosity of the medium affects only k_t and not k_p (in media with a viscosity exceeding by a factor of several hundred the viscosity of the monomer) was confirmed. The study showed that in the range of η values from 0.400 to 1000 cP (methyl methacrylate) there is a linear relation between k_t and the viscosity of the medium. A relation of this kind was not observed for n-butyl acrylate. Thus the rate of chain termination in the polymerisation of methyl methacrylate is determined by diffusion even in a medium of low viscosity, comparable with the viscosity of the monomer, whereas in the polymerisation of n-butyl acrylate in media of relatively low viscosity k_t is independent of the viscosity and the reaction occurs in the "kinetic" region (k_t is then the rate constant of a chemical step). Only in media with viscosities in excess of about 10 cP is the rate of chain termination determined by diffusion.

The authors examined the results obtained within the framework of a three-step mechanism of radical reaction which they proposed[47]. It was shown that this mechanism leads to the equation

$$\frac{1}{k_t} = \frac{\eta}{k_{d'}} + \frac{1}{k_{c'}} \quad \text{or} \quad k_t = k_{c'} - \frac{k_{c'}}{k_{d'}}(k_t\eta), \quad (10)$$

where $k_{d'}$ and $k_{c'}$ are constants evaluated in the derivation of the relation between k_t and $k_t\eta$. Three possible models of bimolecular reactions are examined in the same study[47]. Later North and Reed[48] confirmed the earlier data showing that the rate of the chain termination reaction in the polymerisation of certain vinyl monomers is determined by diffusion even in media of low viscosity, comparable with the viscosity of the monomer[47,53,54]. In the polymerisation of methyl methacrylate the opposite relation between k_t and the viscosity of the medium was observed[48]. This effect is not due to the chemical nature of the solvent and the shape of its molecules. The results can be explained in terms of a two-stage diffusion-dependent chain termination process. Comparison of the diffusion-dependent chain termination rate constants and the diffusion coefficients of poly(methyl methacrylate) as a function of the concentration of the latter showed that the rate-determining stage of the process is segmental diffusion of the ends of the polymeric radicals and not translational diffusion (diffusion of the centres of gravity) of the macroradicals. It was also established that the chain termination process is influenced by the molecular weight and the concentration of the polymer in solution.

The studies of North and coworkers led to the paradoxical conclusion[48] that the rate of chain termination is determined by diffusion even when the conversion is only 0%, whereas self-acceleration becomes appreciable for conversions of the order of several per cent or even several tens per cent (styrene). However, North and Reed[48] showed that this apparent paradox is caused by inadequate allowance for the viscosity of the "segment–solvent" microregions.

Recently Benson and North[49] demonstrated that the rate constant for diffusion-dependent chain termination is a function of the chain length of the reacting radicals. They examined two models of segmental diffusion. The first leads to reasonable termination rate constants but is inconsistent with kinetic data. In the examination of the second model it was assumed that segmental diffusion depends on chain length until the latter exceeds a certain characteristic value N_L. After that segmental diffusion no longer depends on the chain length. If N_L is smaller than the average length of the kinetic chain, then

$$k_t = (4P_{AB}kT/3\eta)(R_E/x_0N_L^{1/4}), \quad (11)$$

where P_{AB} is a multiplier equal to 1/8, R_E is the effective distance between the ends of the chains in the transition state, and x_0 is a proportionality constant of the order of 2.2 Å. It follows from Eqn. (11) that the chain termination rate constant is a function of T/η, i.e.

$$k_t = f(T/\eta). \quad (12)$$

Calculations by Eqn. (11) are in satisfactory agreement with experiment. For example, for a monomer of the type of styrene η = 0.5 cP (R_E/x_0 = 1.4, N_L = 100). Hence at 300°K $k_t = 1.1 \times 10^8$ litre mole^{-1} s^{-1}. If the chain length is small and ν (the kinetic chain length) $< N_L$, the polymerisation kinetics cannot be described by the usual equations.

Later North and Reed[50] yet again confirmed their theoretical findings. They showed that in the polymerisation of methyl, n-butyl, isobutyl, and 3,5,5-trimethylhexyl methacrylate in solvents of different viscosity the rate of chain termination is determined for all alkyl methacrylates by the segmental diffusion of the ends of the macroradical chains. In media with viscosities between 0.42 and 5.72 cP k_t/k_p for the polymerisation of the above monomers is proportional to η^{-n}, where n = 1 for methyl methacrylate and $n < 1$ for the other alkyl methacrylates.

Allen and Patrick[55] examined the effect of diffusion on chain propagation and chain transfer reactions for high degrees of conversion. Using the previously published data[56] they showed that the usual hypothesis according to which the rate of chain propagation (transfer) at high extents of reaction is determined by diffusion is inconsistent with the diffusion coefficients of small molecules in polymers. Indeed it is known[56] that the diffusion coefficient D of small molecules (monomer) in a polymeric network is of the order of 10^{-7} cm^2 s^{-1}, whereas a much lower value is necessary for the rate of chain propagation ($k_p < 10^3$) to be determined by diffusion.

Guzman and Tratou[57] analysed the self-acceleration in the photopolymerisation of vinyl acetate in terms of the

Rabinowitch and Smoluchowski equations and derived the following relation on the basis of experimental data:

$$\frac{k_t}{k_t^*} = 0.97 + 0.03(\eta/\eta_0)^{0.41}, \quad (13)$$

where k_t is the chain termination rate constant without allowance for diffusion and k_t^* the value of k_t found experimentally. They state that the diffusion of macroradicals becomes rate-limiting in the process when the extent of reaction is of the order of 2%.

Guertin[58] obtained kinetic equations taking into account the effect of viscosity on the chain-termination reactions in free-radical polymerisation. He also showed that chain transfer results in a decrease of the "gel effect" because the former is independent of the viscosity of the medium, like the chain termination reaction.

Ryabov and others[59,60] showed that the rate of copolymerisation of methyl methacrylate with methacrylic acid begins to increase appreciably when the viscosity of the medium is 100–500 P which in their view is evidence of a considerable decrease of the rate of diffusion of macroradicals[60]. They believe that the onset of self-acceleration is determined solely by the viscosity of the medium and is independent of the nature and concentration of the initiator.

IV. CHAIN TRANSFER REACTIONS

The general theory of the "gel effect" does not take into account the effect of the chain transfer reactions on the polymerisation at high degrees of conversion. Relatively little work has been done on this problem[23,61,62]; among the papers dealing with this question, the excellent review of Pyrkov and Frenkel'[61] may be mentioned.

As the degree of conversion of the monomer into the polymer increases, the role of the chain transfer reactions via the polymer molecules increases too. Evidently this phenomenon is associated with the increase in the concentration of the polymer in the system. Furthermore, it may be that the rate constant for chain transfer via the polymer depends on the degree of polymerisation which increases with the degree of conversion. Schulz and others[3,63,64] showed that in the polymerisation of methyl methacrylate the rate constant for chain transfer via the polymer varies significantly with the molecular weight of the polymer, decreasing as the latter increases. This phenomenon is due to the fact that chain transfer occurs mainly via the terminal groups formed in chain termination by disproportionation and not via groups containing the initiator fragment. One of the proofs of the validity of this hypothesis is that the rate constant for chain transfer via the polymer is independent of the nature of the initiator (benzoyl peroxide, azobisisobutyronitrile). The rate constants for chain transfer via inner and terminal groups may be expressed by the equations

$$\left(\frac{k_{tr}}{k_p}\right)_{\text{inner}} = 2.2 \times 10^{-4},$$

$$\left(\frac{k_{tr}}{k_p}\right)_{\text{terminal}} = 0.10.$$

We may note that the results of Schulz and others do not exclude the possibility that the initiator affects the structure of the polymers synthesised. In their study of the polymerisation of styrene, Henrici-Olivé and Olivé[65-69] noted that the degree of polymerisation is higher at high extents of reaction than would be expected from the reaction rate. This phenomenon may be explained if it is assumed that the relative contribution of the chain transfer reaction in the reaction between primary radicals and macromolecules increases with the degree of conversion:

$$R^{\cdot}_{per} + P \rightarrow RH + P^{\cdot}$$
$$P^{\cdot} + nM \rightarrow \text{branched polymer.}$$

Thus in the polymerisation of styrene in the presence of azobisisobutyronitrile at 50° the average number of initiator fragments per polymer molecule increases from 2.03 to 2.48 when the degree of conversion rises from 0.05 to 0.93. The chain transfer reactions can result in an apparent change of the effectiveness of initiation (calculated from the molecular weight of the polymer) with the degree of conversion. Chain transfer via the polymer results in an anomalous increase of the molecular weight of the latter and the value of f calculated from Eqn. (5) may be too low.

V. NEW THEORETICAL POSTULATES

Examination of the quantitative data obtained by Norrish, Smith, and Schulz shows that the problem of setting up a rigorously quantitative theory of the "gel effect" is extremely complex. Nevertheless, a number of investigators attempted to develop other semiquantitative theories[70-74]. The first serious attempt was made by Burnett and coworkers. They suggested[70] that the phenomenon of self-acceleration may be explained from the standpoint of a change in the concentration of the growing radicals in the polymerisation. Burnett and coworkers[70,71] demonstrated that the rate of polymerisation of methyl methacrylate is a linear function of percentage conversion when the latter is in the range 20–60%. The overall activation energy for the process falls initially as polymerisation proceeds and then increases sharply:

Conversion, %	0	19	30	36	41	50	57	62	67	71
E, kcal mole^{-1} (25–60°)	5.2	4.7	3.4	2.7	2.0	1.7	3.1	4.1	5.0	8.4

The exponent n in the rate equation for the reaction is initially 0.5 and then falls, it passes through a minimum at about 20% conversion, and increases again to 0.8 at about 60% conversion. These results are consistent with the data of Bengough and Melville[29] and show that chain termination is not a second-order reaction. Hence it follows that the old interpretation of the results of studies on bulk polymerisation lacks reliable justification, since the kinetic expressions used presuppose that chains are destroyed as a result of their interaction. The explanation of the "gel effect" must be sought in the change of the concentration of macroradicals during polymerisation and not only in the possible change of the rate constants for the fundamental reaction steps. Polymerisation results in an increase of the viscosity of the medium and macroradicals can no longer react with one another. At not too high extents of reaction the monomer molecules diffuse towards macroradicals and react with them. Thus the overall rate of reaction increases because of the lowering of the rate of chain termination and the increase of the rate of chain propagation. As already pointed out, the latter is more likely to be due to a change in the radical concentration than to a change in the rate constants for the fundamental reaction steps. Burnett and coworkers assumed that, starting with a certain degree of conversion, the rate of increase of the number of radicals is proportional to the

concentration of the polymer formed. Hence it follows that

$$d[R\cdot]/dx = k_1(x - x_1), \quad (14)$$

where $[R^{\cdot}]$ is the radical concentration, k_1 a constant, x the specific degree of conversion of the monomer into the polymer, and x_1 the critical degree of conversion, which depends on the molecular weight of the polymer formed in the initial stages.

Integration of Eqn. (14) gives

$$[R\cdot] - [R\cdot]_0 = \tfrac{1}{2}k_1(x - x_1)^2, \quad (15)$$

where $[R^{\cdot}]_0$ is the value of $[R^{\cdot}]$ where $x = x_1$. Eqn. (15) can be rewritten in the form

$$\frac{[R\cdot]}{[R\cdot]_0} = 1 + K_1(x - x_1)^2, \quad (16)$$

where $K_1 = \frac{1}{2}k_1(k_t/V_i)^{1/2}$ is a constant and V_i is the rate of initiation ($V_i = k_t[R^{\cdot}]^2$). Assuming that the concentration of the monomer near the growing radicals is constant, the following expression can be obtained instead of Eqn. (16):

$$(V_x/V_0 - 1)^{1/2} = K_1^{1/2}(x - x_1), \quad (17)$$

where V_x is the rate of polymerisation for a degree of conversion x and V_0 the initial rate of polymerisation.

It follows from Eqn. (17) that in the self-acceleration stage there should be a linear relation between $[(V_x/V_0) - 1]^{1/2}$ and x; the intercept made by the straight line on the abscissa should be equal to x_1 and its slope should be $K_1^{1/2}$. Eqn. (17) holds satisfactorily over a limited range of percentage conversions. At higher percentage conversions (about 50–60%) macroradicals become inaccessible to monomer molecules and the following equation then holds:

$$\frac{[R\cdot]}{[R\cdot]_0} = 1 + K_1(x - x_1)^2 - K_2(x - x_2)^2, \quad (18)$$

where x_2 is the second critical degree of conversion. Eqn. (18) can be written thus

$$[1 + K_1(x - x_1)^2 - V_x/V_0]^2 = K_2^{1/2}(x - x_2). \quad (19)$$

Hence it follows that there should be a linear relation between $[1 + K_1(x - x_1)^2 - V_x/V_0]^2$ and x. Burnett and Duncan[71] showed that this relation holds in the polymerisation of methyl methacrylate.

Similar results were obtained in the photopolymerisation of n-propyl and n-butyl methacrylates[72]. However, the polymerisation of methyl methacrylate[73] can be described by the above method only when allowance is made for additional factors characterising the possibility of the formation of branched and cross-linked structures.

The validity of the general postulates of Burnett and coworkers is evident. Clearly at high degrees of conversion a considerable increase in the lifetime of the polymeric radicals and hence an increase in their concentration may be expected. The electron spin resonance method made it possible to determine directly the concentration of radicals in viscous media. Many measurements of this kind were made[75–78]. For example, Bresler and coworkers[79], who made an ESR study of the photopolymerisation of methyl methacrylate, established that at high degrees of conversion the concentration of radicals exceeds 10^{-3} M. It should be noted that not all the radicals detected in the polymer–monomer system by the ESR method are equally stable. After irradiation ceases most of them vanish over a period of several minutes. The remaining radicals are stable and persist in the specimen at room temperature over a fairly long period.

Sawada[74] attempted to interpret quantitatively the results obtained in the study of the block polymerisation of methyl methacrylate. He started with the hypothesis that, if the radicals in a highly viscous medium become immobile and cannot disappear as a result of interaction with one another, their concentration should increase continuously as polymerisation proceeds. At a certain critical degree of conversion, the macroradicals are so firmly "stuck" in the polymer that they cannot react with the monomer.

If it is assumed that the concentration of radicals is proportional to the amount of monomer consumed since the onset of self-acceleration, the following expression holds:

$$[R\cdot] = K(x - b), \quad (20)$$

where K is a constant, x the degree of conversion of the monomer, and b the degree of conversion at which self-acceleration begins. On expressing the concentration of the monomer in terms of the critical degree of conversion a, i.e. putting

$$[M] = (a - x), \ (x < a) \quad (21)$$

and substituting the values of $[R^{\cdot}]$ and [M] from Eqns. (20) and (21) in the rate equation for the reaction, we obtain the equation

$$dx/dt = k_pK(x - b)(a - x). \quad (22)$$

Integration of Eqn. (22) yields

$$[1/(a - b)]\ln[(x - b)/(a - x)] = k_pKt + C, \quad (23)$$

where C is a constant. It follows from Eqn. (23) that $[2.3/(a - b)]\log[(x - b)/(a - x)]$ should vary linearly with time, which according to Sawada's data is borne out by experiment.

Allen and Patrick[75] examined the role of the so called "geminate chain recombination" in the kinetics of the polymerisation at high conversions.

Thus the explanation of the "gel effect" given by Norrish, Schulz, and other investigators presupposes the existence of a steady state throughout the bulk polymerisation process. However, the variation of the exponent n of the irradiation intensity in Eqn. (2) during polymerisation contradicts this hypothesis. It follows from the theory of Schulz and others that a higher value of k_t for a monomer should involve a more pronounced "gel effect". However, this is not in fact observed. Thus for styrene $(k_t)_{30\%} = 5.0 \times 10^7$ and for methyl methacrylate the corresponding value is 2.4×10^7. Nevertheless the "gel effect" in the polymerisation of methyl methacrylate is much more pronounced than in the polymerisation of styrene. The theory of Burnett and Duncan is more satisfactory. However, it is only qualitative and is based on purely empirical postulates. Although at the present time it is probably impossible to set up a rigorously quantitative theory because of the large number of factors involved in block polymerisation, a number of additional postulates must nevertheless be taken into account. Thus the majority of investigators do not consider the effect of the nature of the initiator on the polymerisation kinetics at high conversions. Also, frequently allowance is not made for the change in volume during polymerisation[80], the possible change in the rate of initiation associated with the increasing viscosity of the medium, and other factors.

At first sight it may appear that both in the initial stages and at high conversions the nature of the initiator is fairly

completely characterised by the rate constant k_d for the breakdown of the given initiator and the effectiveness of initiation f. In fact these quantities are never adequate for the description of the polymerisation process at high conversions[81]. It is well known that the following expression holds for catalysed polymerisation[1-8]:

$$-\frac{d[M]}{dt} = \frac{k_p}{k_0^{1/2}}(2k_d f)^{1/2}[c]^{1/2}[M], \quad (24)$$

where $[c]$ is the concentration of the initiator.

If the breakdown of the initiator is a first-order reaction, then obviously

$$-\frac{d[c]}{dt} = k_d[c]. \quad (25)$$

Furthermore,

$$[c] = [c]_0 e^{-k_d t}, \quad (26)$$

where $[c]_0$ is the initial concentration of the initiator. On substituting Eqn. (26) in Eqn. (24), we have

$$-\frac{d[M]}{dt} = \frac{k_p}{k_0^{1/2}}(2k_d f)^{1/2}[c]_0^{1/2}e^{-k_d t/2}[M]. \quad (27)$$

There is no doubt about the applicability of Eqn. (27) to polymerisation in many systems, both in the solid state and in solution, at low conversions[82,83]. However, Eqn. (27) no longer holds for polymerisation in viscous media. As polymerisation proceeds, the rate of initiation and the value of f in Eqn. (27) begin to vary. For example, Breitenbach and Frittum[84] showed that the rate of decomposition of the peroxide $(p\text{-}ClC_6H_4CO)_2O_2$ in polystyrene is lower than in solvents. Similar data were obtained by Haas[85-87]. Abdul-Said[2] showed that, when the viscosity of the solution is increased by a factor or ten, the rate of initiation falls by a factor of two. Dolgoplosk and coworkers[88] observed an increase in the yield of the recombination products of primary radicals in the decomposition of asymmetric diazo-compounds in viscous media. If the "gel effect" theory of Schulz and others is adopted, i.e. if allowance is made for the variation of the rate constants for the fundamental reaction steps with increasing viscosity and appropriate corrections to f are made, Eqn. (27) still need not always hold. The reason is that all the theories described above fail to take into account a number of factors. Thus allowance is not made for the possibility of chain termination when chains interact with primary radicals and for the chain transfer reaction. The possibility of chain termination by primary radicals during polymerisation has been pointed out in a number of papers[61,81,89-95]. The kinetic equations obtained with allowance for these processes differ considerably from the equations which follow from the usual theory[94,95]. Chain transfer reactions with participation of primary radicals at high conversions were studied by Henrici-Olivé and Olivé[65-69,101] and also other workers[58].

Theoretical examination shows that an increase in the viscosity of the medium lowers the rate of reactions in which large species participate (chain termination in the reaction of macroradicals) and has almost no effect (at least at 50–70% conversion) on the rate of processes involving small species (chain propagation, chain termination by primary radicals, chain transfer via initiator and low-molecular-weight inhibitor molecules, chain transfer with participation of primary radicals, etc.). Hence it follows that, as polymerisation proceeds, the relative role of processes involving the participation of small molecules should increase, which may lead to a decrease of the "gel effect"[81]. The reactivity of primary radicals will of course determine the nature of the "gel effect" on a par with other factors. However, for reasons stated above, account must also be taken of purely geometrical factors, namely the size of primary radicals which affects the diffusion coefficients.

In relatively non-viscous media the size of primary radicals has little effect on the capacity to participate in chain termination (transfer) reactions. This also applies to the value of f, which is associated with the possibility of recombination of primary radicals (cage effect). At high conversions the size of primary radicals determines both the possibility of their participation in the chain termination (transfer) reaction and the value of f. The relation between the effect of primary radical recombination and the viscosity of the medium is well known. For example, in his study of the decomposition of benzoyl peroxide in polymeric media, Haas[85-87] confirmed the postulates of the theory of primary recombination. On the other hand, it is evident that radicals such as $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, ..., $C_nH_{2n+1}^{\cdot}$ may participate in chain termination and transfer reactions to different extents because the diffusion coefficients may vary markedly with the size of the species[96].

It follows from the above considerations that the nature of self-acceleration at high conversions should be determined not only by the monomer but also by the initiator. Furthermore, the magnitude of the "gel effect" is determined by the concentration of the initiator and the experimental conditions. The "gel effect" may vary from one initiator to another[81]. Thus it has been established that bulk polymerisation of methyl methacrylate in the presence of peroxydicarbonates involves a smaller "gel effect"[97,98] compared with polymerisation in the presence of benzoyl peroxide, azobisisobutyronitrile, and other initiators. Similar results were obtained in a study of the polymerisation of methyl methacrylate activated by partial oxidation during exposure to ionising radiation[99], ultraviolet light[100], and visible light in the presence of sensitisers[101,102]. As already mentioned, such differences may be associated not only with different values of k_d and f for the given initiators but also with the different nature of the initiators themselves and the primary radicals which may participate in the chain termination and transfer reactions. The decrease of the "gel effect" at high conversions of the photo-activated monomer[100] is due to an increase of the effect of inhibitors and peroxide decomposition products formed during oxidation of the monomer. The differences in the nature of the "gel effect" during polymerisation in the presence of benzoyl peroxide, azobisisobutyronitrile, percarbonates, and hydrogen peroxide is due to the chain transfer and chain termination effects with participation of primary radicals. These conclusions were arrived at[81] by comparing the kinetic curves for polymerisation in the presence of the initiators enumerated above. Fig. 1 shows curves characterising the self-acceleration of the polymerisation of methyl methacrylate in the presence of the various initiators.

The data presented were obtained for equal concentrations of the initiators compared and therefore the differences are due to different values of k_d for the initiators and processes which are not usually taken into account by the theory. In order to eliminate the effect of k_d on the "gel effect", it is desirable to make the comparison for the same rate of initiation. Such data are presented in Fig. 2, which shows that the nature of the initiator has a significant effect on the magnitude of the "gel effect".

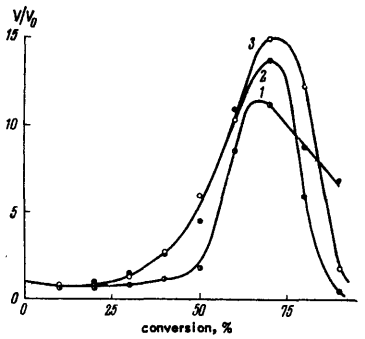


Fig. 1. Self-acceleration in the polymerisation of methyl methacrylate in the presence of various initiators at 60° and a constant initiator concentration (0.45 mole %):
1) dicyclohexyl peroxydicarbonate; 2) azobisisobutyronitrile; 3) benzoyl peroxide.

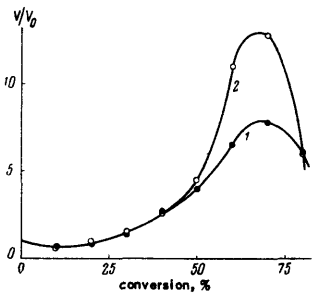


Fig. 2. Self-acceleration in the polymerisation of methyl methacrylate at 60° and constant initial rates of initiation:
1) dicyclohexyl peroxydicarbonate (0.045 mole %);
2) azobisisobutyronitrile (0.45 mole %).

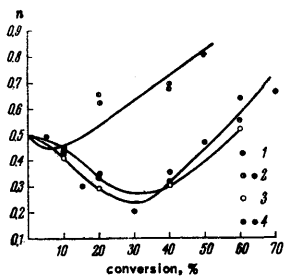


Fig. 3. Variation with the extent of conversion at 60° of the exponent n of the initiator concentration in the kinetic rate equation for the reaction, initiator — benzoyl peroxide:
1) n calculated for the initiator concentration range 0.0045–0.00045 mole %; 2) different series of experiments; 3) 0.045–0.0045 mole %; 4) 0.45–0.045 mole %.

It is difficult to allow for this effect quantitatively, but information about the chain transfer reaction may be obtained from a study of the molecular weight and polymer structure at different conversions. The possibility of chain termination by primary radicals can be assessed indirectly from the value of the exponent n of the initiator concentration (or irradiation intensity) in Eqn. (2)†. The variation of n with percentage conversion is determined by the nature of the initiator and its concentration (Fig. 3). These findings are in good agreement with the theory.

VI. OTHER STUDIES

There have been a number of investigations whose results confirm qualitatively the general theory of the "gel effect". Arbuzova and others [103] studied the photopolymerisation of acrylamide, methacrylamide, and hydroxymethylmethacrylamide in aqueous and glycerol solutions ($\lambda \simeq 3000$ Å). It was found that acrylamide and methacrylamide are polymerised only in glycerol. The rate of polymerisation of hydroxymethylmethacrylamide in glycerol is much higher than in aqueous solution. The authors explained these results on the hypothesis that the viscosity of the medium affects the rate constants for the termination of the polymeric chains. Later a similar phenomenon was observed in the polymerisation of acrylonitrile and other monomers but here initiation was effected at the interface between two phases [104]. Guzman and Delgado [105] studied the kinetics of the polymerisation of vinyl acetate at high conversions. The data obtained are consistent with the usual theory.

A number of investigators observed self-acceleration in the polymerisation of styrene [106–109]. A sharp increase in the molecular weight of the polymer was noted between 20 and 25% conversion [107,108]. The acceleration of the reaction in the case of methyl methacrylate and other acrylic esters was described by a number of investigators [106,110–115]. Burnett and coworkers [110] and also Matyska et al. [111] studied the polymerisation of n-butyl methacrylate. They established that self-acceleration occurs only after the attainment of about 40% conversion. A similar phenomenon was observed also for n-propyl methacrylate [112]. In their study of the copolymerisation of methyl methacrylate with methacrylic acid, Tarakanov et al. [113] showed that, as the methacrylic acid content of the system increases, the rate of polymerisation also rises; there is a corresponding increase in the maximum rate.

The general theory of the "gel effect" was also used in the treatment of the mechanism of three-dimensional polymerisation. Melville [27] and Melville and Hayden [30] were the first to study the effect of a three-dimensional polymer on self-acceleration at high conversions. It was shown that in the copolymerisation of methyl methacrylate with ethylene glycol dimethacrylate increase of the concentration of the latter results in onset of self-acceleration at lower conversions, while the rate of the chain termination reaction is determined by diffusion at zero conversion. Later Korolev and Berlin and coworkers made a detailed study of the three-dimensional polymerisation of a number of oligomers [116–122]; their results fully confirmed the validity of the general theory of polymerisation at high conversions. In addition, new data were obtained on the

† It should be noted that the variation of n with percentage conversion is also associated with the variation of the diffusion coefficient of macroradicals as the conversion changes [48].

characteristic features of three-dimensional polymerisation.

Thus it may be regarded as demonstrated[71,98] that the characteristic features of polymerisation at high conversions are not associated only with changes in the chain termination rate constant but with other kinetic parameters, namely the chain propagation rate constant, the rate of initiation, and the concentration of macroradicals. Furthermore, it was established that chain termination in the polymerisation of monomers such as methyl methacrylate, styrene, and others is diffusion-dependent even in the initial stages of the reaction[47,50].

At the same time the studies made in recent years show that the hypotheses described above are inadequate for the construction of a rigorously quantitative theory. For example, the available data are clearly inadequate for the interpretation of the absence of self-acceleration in the initial stages of the polymerisation of methyl methacrylate and other monomers[48]. The "paradox" considered above[48] may be explained if account is taken of the fact that in media of low viscosity not only the chain termination rate constant but also the effectiveness of initiation and the initiator breakdown rate constants vary[98,123]. The last two factors are also responsible for differences in the nature of acceleration during polymerisation in the presence of various initiators[98].

There are interesting possibilities in the study of many fundamental processes at high conversions. Thus it has been shown[124] that the study of inhibition processes in media of high viscosity permits a direct quantitative estimate of the reactivity of compounds which are relatively unreactive in radicals reactions. This cannot be done by other available methods. It is possible that further study of polymerisation at high conversions will lead not only to improved control methods for processes in which high conversions are attained[125] but also to some revision of the available data on polymerisation at low conversions[126].

1. C.H.Bamford et.al., "The Kinetics of Vinyl Polymerisation by Radical Mechanisms" (Translated into Russian), Inostr. Lit., Moscow, 1961.
2. H.Moravets, in "Formation and Trapping of Free Radicals" (Translated into Russian), Inostr.Lit., Moscow, 1962, pp.421, 430.
3. Kh.S.Bagadasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd.Akad.Nauk SSSR, Moscow, 1959.
4. G.M.Burnett, "Mechanism of High Polymer Reactions", Interscience, New York, London, 1954.
5. P.S.Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953.
6. C.Walling, "Free Radicals in Solution" (Translated into Russian), Inostr.Lit., Moscow, 1960.
7. J.C.Bevington and H.W.Melville, Uspekhi Khim., 25, 1336 (1956).
8. G.P.Gladyshev, "Polimerizatsiya Vinil'nykh Monomerov" (Polymerisation of Vinyl Monomers), Izd.Akad.Nauk Kazakh.SSR, Alma-Ata, 1964.
9. G.V.Schulz and E.Husemann, Z.phys.Chem., B36, 184 (1937).
10. G.V.Schulz and H.Staudinger, Z.phys.Chem., B39, 246 (1938).
11. G.V.Schulz, A.Dinglinger, and E.Husemann, Z.phys. Chem., B45, 105 (1939).
12. R.Norrish and E.Brookman, Proc.Roy.Soc., A171, 147 (1939).
13. G.V.Schulz and F.Bloschke, Z.Elektrochem., 47, 749 (1941).
14. E.Trommsdorff, "Colloqium on High Polymers", Freiburg, 1944, Rep.No.363, Item 22.
15. E.Trommsdorff, H.Köhle, and P.Lagally, Makromol.Chem., 1, 169 (1948).
16. G.V.Schulz and F.Blaschke, Z.phys.Chem., B50, 305 (1941).
17. R.G.W.Norrish and R.R.Smith, Nature, 150, 336 (1942).
18. S.S.Medvedev, O.Karitskaya, and E.Alekseeva, Zhur.Fiz. Khim., 17, 391 (1943).
19. G.V.Schulz and G.Harborth, Makromol.Chem., 1, 106 (1947).
20. M.S.Matheson, E.E.Auer, E.B.Bevilacqua, and E.J.Hart, J.Amer.Chem.Soc., 71, 497 (1949).
21. M.S.Matheson, E.E.Auer, E.B.Bevilacqua, and E.J.Hart, J.Amer.Chem.Soc., 73, 1700 (1951).
22. M.S.Matheson, E.E.Auer, E.B.Bevilacqua, and E.J.Hart, J.Amer.Chem.Soc., 73, 5395 (1951).
23. M.A.Naylor and F.W.Billmeyer, J.Amer.Chem.Soc., 75, 2181 (1953).
24. A.N.Pravednikov, "Voprosy Khimicheskoi Kinetiki, Kataliza i Reaktsionnoi Sposobnosti" (Problems of Chemical Kinetics, Catalysis, and Reactivity), Izd.Akad.Nauk SSSR, Moscow, 1955, p.322.
25. A.N.Pravednikov, Dokl.Akad.Nauk SSSR, 108, 495 (1956).
26. P.S.Shantarovich and S.S.Medvedev, Zhur.Fiz.Khim., 23, 1426 (1949).
27. H.W.Melville, Z.Elektrochem., 60, 276 (1956).
28. W.I.Bengough and H.W.Melville, Proc.Roy.Soc., A230, 429 (1955).
29. W.I.Bengough and H.W.Melville, Proc.Roy.Soc., A249, 445 (1959).
30. P.Hayden and H.W.Melville, J.Polymer Sci., 43, 201 (1960).
31. S.Fujii, Bull.Chem.Soc.Japan, 27, 216 (1954).
32. S.Fujii, Bull.Chem.Soc.Japan, 27, 238 (1954).
33. H.Miyama, Bull.Chem.Soc.Japan, 29, 711, 715 (1956).
34. H.Miyama, Bull.Chem.Soc.Japan, 29, 720 (1956).
35. H.Miyama, Bull.Chem.Soc.Japan, 30, 10 (1957).
36. H.Miyama, Bull.Chem.Soc.Japan, 30, 459 (1957).
37. S.Fujii and S.Tanaka, Chem.High Polymers (Japan), 14, 107 (1957).
38. E.R.Robertson, Trans.Faraday Soc., 52, 426 (1956).
39. N.Nishimura, Bull.Chem.Soc.Japan, 34, 1158 (1961).
40. M.F.Vaughan, Trans.Faraday Soc., 48, 576 (1952).
41. G.V.Schulz, Z.phys.Chem.(Frankfurt), 8, 290 (1956).
42. G.V.Schulz, Z.phys.Chem.(Frankfurt), 8, 284 (1956).
43. R.S.Spencer and I.L.Williams, J.Colloid Sci., 2, 117 (1947).
44. P.Flory, J.Amer.Chem.Soc., 62, 1057 (1940).
45. E.Rabinowitch, Trans.Faraday Soc., 33, 1225 (1937).
46. M.von Smoluchowski, Z.phys.Chem., 92, 129 (1918).
47. S.W.Benson and A.M.North, J.Amer.Chem.Soc., 81, 1339 (1959).
48. A.M.North and G.A.Reed, Trans.Faraday Soc., 57, 859 (1961).
49. S.W.Benson and A.M.North, J.Amer.Chem.Soc., 84, 935 (1962).
50. A.M.North and G.A.Reed, J.Polymer Sci., A1, 1311 (1963).
51. A.M.North, Makromol.Chem., 49, 241 (1961).
52. C.R.Patrick, Makromol.Chem., 43, 248 (1961).
53. J.Marphy and A.Wasserman, J.Polymer Sci., 14, 477 (1954).
54. G.K.Oster, G.Oster, and G.Prati, J.Amer.Chem.Soc., 79, 595 (1957).
55. P.E.M.Allen and C.R.Patrick, Makromol.Chem., 47, 154 (1961).
56. M.S.Hayes and G.S.Park, Trans.Faraday Soc., 52, 949 (1956).
57. G.M.Guzman and I.M.Tratou, Anales real Soc.españ.Fís. Quím., B58, 629 (1962).
58. A.T.Guertin, J.Polymer Sci., B1, 477 (1963).
59. A.V.Ryabov and O.G.Tarakanov, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 112 (1958).
60. A.V.Ryabov, V.V.Guzeev, and O.G.Tarakanov, Izv.Vys.

Ucheb. Zaved., Khim. i Khim. Tekhnol., 954 (1959).
61. L. M. Pyrkov and S. Ya. Frenkel', Uspekhi Khim., 32, 305 (1963) [Russ. Chem. Rev., 140 (1963)].
62. O. L. Wheeler, Ann. N. Y. Acad. Sci., 57, 360 (1953).
63. G. Henrici-Olivé, S. Olivé, and G. V. Schulz, Makromol. Chem., 23, 207 (1957).
64. G. V. Schulz, G. Henrici-Olivé, and S. Olivé, Z. Elektrochem., 60, 296 (1956).
65. G. Henrici-Olivé and S. Olivé, Makromol. Chem., 27, 166 (1958).
66. G. Henrici-Olivé and S. Olivé, Makromol. Chem., 28, 176 (1958).
67. G. Henrici-Olivé, Kunststoffe–Plastics, 5, 315 (1958).
68. G. Henrici-Olivé and S. Olivé, "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii" (International Symposium on Macromolecular Chemistry), Moscow, Sect. 3, p. 243.
69. G. Henrici-Olivé and S. Olivé, Makromol. Chem., 53, 122 (1962).
70. G. M. Burnett and L. D. Loan, Coll. Czech. Chem. Comm., 22, Spec. Issue, 113, Discuss., 188 (1957).
71. G. M. Burnett and G. L. Duncan, Makromol. Chem., 51, 154 (1962).
72. G. M. Burnett and G. L. Duncan, Makromol. Chem., 51, 171 (1962).
73. G. M. Burnett and G. L. Duncan, Makromol. Chem., 51, 177 (1962).
74. H. Sawada, J. Polymer Sci., Part B1, 305 (1963).
75. P. E. M. Allen and C. R. Patrick, Trans. Faraday Soc., 59, 1819 (1963).
76. L. A. Blyumenfel'd, V. V. Voevodskii, and A. G. Semenov, "Primenenie Elektronnogo Paramagnitnogo Rezonansa v Khimii" (Application of Electron Spin Resonance in Chemistry), Izd. Sibir. Fil. Akad. Nauk SSSR, Novosibirsk, 1962.
77. D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance" (Translated into Russian), Inostr. Lit., Moscow, 1961.
78. A. M. Bass and H. P. Broida (Editors), "Formation and Trapping of Free Radicals" (Translated into Russian), Inostr. Lit., Moscow, 1962.
79. S. E. Bresler, E. N. Kazbekov, and E. M. Sominskii, Vysokomol. Soed., 1, 132 (1959).
80. K. Murakalis, J. Soc. Org. Syn. Chem., Japan, 20, 103 (1962).
81. G. P. Gladyshev and S. R. Rafikov, "Sintez i Issledovanie Vysokomolekulyarnykh Soedinenii" (Synthesis and Study of Macromolecular Compounds), Izd. Akad. Nauk Kazakh. SSR, Alma-Ata, 1964.
82. A. V. Tobolsky, J. Amer. Chem. Soc., 80, 5927 (1958).
83. A. V. Tobolsky, C. E. Rogers, and R. D. Brickman, J. Amer. Chem. Soc., 82, 1277 (1960).
84. J. W. Breitenbach and H. Frittum, J. Polymer Sci., 29, 565 (1958).
85. H. C. Haas, J. Polymer Sci., 39, 493 (1959).
86. [Ref. 86 missing in Russian original (Ed. of Translation)].
87. H. C. Haas, J. Polymer Sci., 54, 287 (1961).
88. B. A. Dolgoplosk, B. L. Erusalimskii, E. B. Milovskaya, and G. P. Belonovskaya, Dokl. Akad. Nauk SSSR, 120, 783 (1958).
89. I. Gécry and E. Réthy, Magyar tud. akad. Kém. tud. osyt. közl., 10, 175 (1958).
90. A. Chapiro and J. Serban-Danor, J. Chim. phys., 54, 776 (1957).
91. M. Magat, Bull. Soc. chim. France, 535 (1956).
92. C. H. Bamford, A. D. Jenkins, and R. Johnston, Trans. Faraday Soc., 55, 1451 (1959).
93. C. S. Misa, A. Hafeer, and K. S. Sharma, Makromol. Chem., 51, 123 (1962).
94. P. E. M. Allen and C. R. Patrick, Makromol. Chem., 48, 89 (1961).
95. M. G. Baldwin, J. Polymer Sci., A1, 3209 (1963).
96. F. Grün, Experientia, 3, 490 (1947).
97. S. R. Rafikov, G. P. Gladishev, N. F. Khasanova, and N. V. Churbakova, J. Polymer Sci., A3, 37 (1965).
98. S. R. Rafikov and G. P. Gladishev, Preprint 299, "International Symposium on Macromolecular Chemistry", Prague, 1965.
99. B. L. Tsetlin, V. A. Sergeev, S. R. Rafikov, V. V. Korshak, P. Ya. Glazunov, and P. B. Buble, Dokl. Akad. Nauk SSSR, 126, 123 (1959).
100. S. R. Rafikov and G. P. Gladyshev, Vysokomol. Soed., 3, 1034 (1961).
101. G. P. Gladyshev and S. R. Rafikov, Vysokomol. Soed., 3, 1187 (1961).
102. S. R. Rafikov and G. P. Gladyshev, Vysokomol. Soed., 4, 1345 (1962).
103. I. A. Arbuzova, V. N. Efimova, and I. K. Uledlo, Dokl. Akad. Nauk SSSR, 112, 645 (1957).
104. G. P. Gladyshev and S. R. Rafikov, Dokl. Akad. Nauk SSSR, 137, 113 (1961).
105. G. M. Guzman and L. Delgado, Anales real Soc. españ. Fís. Quím., Ser. B56, 325 (1960).
106. G. M. Guzman, Anales real Soc. españ. Fís. Quím., Ser. B51, 69 (1955).
107. F. Patat and K. Kirchner, Naturwiss., 45, 129 (1958).
108. S. S. Ivaichev, A. I. Yurzhenko, and N. I. Solomko, Dokl. Akad. Nauk SSSR, 140, 1079 (1961).
109. H. Gerrens, Z. Elektrochem., 60, 400 (1956).
110. G. M. Burnett, P. Evans, and H. W. Melville, Trans. Faraday Soc., 49, 1096 (1953).
111. B. Matyska, I. Kössler, and V. Šrajer, Chem. Listy, 51, 2287 (1957).
112. G. M. Burnett, P. Evans, and H. W. Melville, Trans. Faraday Soc., 49, 1105 (1953).
113. O. G. Tarakanov and A. V. Ryabov, "Trudy po Khimii i Khimicheskoi Tekhnologii" (Papers on Chemistry and Chemical Technology), Vol. 2, 1958, p. 270.
114. L. K. J. Tong and W. O. Kenyon, J. Amer. Chem. Soc., 67, 1278 (1945).
115. M. H. Mackay and H. W. Melville, Trans. Faraday Soc., 45, 323 (1949).
116. G. V. Korolev, L. I. Makhonina, and A. A. Berlin, Vysokomol. Soed., 3, 198 (1961).
117. G. V. Korolev, A. A. Berlin, and T. Ya. Kefeli, Vysokomol. Soed., 4, 1520 (1962).
118. G. V. Korolev and A. A. Berlin, Vysokomol. Soed., 4, 1659 (1962).
119. G. V. Korolev, B. R. Smirnov, and A. B. Bolkhovitinov, Vysokomol. Soed., 4, 1660 (1962).
120. G. V. Korolev and N. N. Tvorogov, Vysokomol. Soed., 6, 1006 (1964).
121. G. V. Korolev and B. R. Smirnov, Vysokomol. Soed., 6, 1140 (1964).
122. G. V. Korolev, B. R. Smirnov, S. G. Bashkirova, and A. A. Berlin, Vysokomol. Soed., 6, 1256 (1964).
123. P. E. Messerle, S. R. Rafikov, and G. P. Gladyshev, Dokl. Akad. Nauk SSSR, 166, 158 (1966).
124. G. P. Gladyshev, S. R. Rafikov, and N. V. Churbakova, Dokl. Akad. Nauk SSSR, 165, 133 (1965).
125. G. P. Gladyshev, "Polimerizatsiya Vinil'nykh Monomerov pri Glubokikh Stepeniyakh Prevrashcheniya, Vystavka Dostizhenii Narodnogo Khozyaistva SSSR" (Polymerisation of Vinyl Monomers at High Extents of Reaction, Exhibition of the Achievements of the National Economy of the USSR), Moscow, 1965.
126. G. P. Gladyshev, Dokl. Akad. Nauk SSSR, 163, 1191 (1965).

Institute of Chemical Sciences,
Academy of Sciences of the
Kazakh SSR