84. V.I.Kasatochkin and B.V.Lukin, Zhur.Tekh.Fiz., 20, 1160 (1950).
85. W.Bekkedahl and L.A.Wood, Ind.Eng.Chem., 33, 381 (1941).
86. E.W.Russel, Trans.Faraday Soc., 47, 539 (1951).
87. M.F.Bukhina, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1963.
88. W.A.Gibbons, R.H.Gerke, and H.C.Tingey, Ind.Eng.Chem., Analyt., 5, 279 (1933).
89. B.V.Lukin and V.I.Kasatochkin, "Issledovaniya po Fizike i Khimii Kauchuka i Reziny" (Studies in the Physics and Chemistry of Raw and Cured Rubber), Goskhimizdat, 1950, p.77.
90. B.I.Aikhodzhaev, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1957.
91. V.A.Kargin, T.I.Sogolova, and B.I.Aikhodzhaev, Dokl.Akad.Nauk SSSR, 120, 1277 (1958).
92. A.S.Lykin and K.A.Pechkovskaya, Izv.Akad.Nauk SSSR, Ser.Fiz., 23, 725 (1959).
93. T.G.Rochow and E.G.Rochow, Science, 3, 271 (1950).
94. E.G.Rochow, "An Introduction to the Chemistry of the Silicones", New York, 1951, pp.120–130.
95. H.Kamoyawa, M.Kuriyagawa, and H.Jako, "Proceedings of the Third International Conference on Electro-Microscopy", London, 1954, p.507.
96. E.H.Andrews and M.Braden, J.Polymer Sci., 55, 787 (1961).
97. V.G.Kalashnikova, M.V.Kazhdan, Z.Ya.Berestneva, and V.A.Kargin, Dokl.Akad.Nauk SSSR, 158, 939 (1964).
98. T.S.Nikitina, E.V.Zhuravskaya, and A.S.Kuz'minskii, "Deistvie Ioniziruyushchikh Izluchenii na Polimery" (The Action of Ionising Radiation on Polymers), Goskhimizdat, Moscow, 1959.
99. I.Ya.Poddubnyi, E.G.Erenburg, and E.I.Starovoitova, Dokl.Akad.Nauk SSSR, 120, 535 (1958).
100. M.V.Kazhdan, T.N.Dyumaeva, E.Ya.Berestneva, and V.A.Kargin, Vysokomol.Soed., 8, 204 (1966).
101. V.A.Kargin, Z.F.Zharikova, Z.Ya.Berestneva, and E.V.Reztsova, Dokl.Akad.Nauk SSSR, 158, 697 (1964).
102. E.F.Zharikova, E.V.Reztsova, Z.Ya.Berestneva, and V.A.Kargin, Vysokomol.Soed., 8, 569 (1966).
103. E.V.Reztsova, Z.F.Zharikova, Z.Ya.Berestneva, and V.A.Kargin, Vysokomol.Soed., in the press.

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POLYMERISATION OF CHEMICALLY ACTIVATED MONOMERS†

V.A.Kabanov

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In a recently published paper Kargin and Kabanov[1] discussed the problem of the polymerisation of complexed and organised monomers, which may be regarded as one of the new developments in the field of macromolecular synthesis. In the present review an attempt is made to develop and justify in greater detail some of the postulates put forward by Kargin and Kabanov.

1. INTRODUCTION

The conversion of a monomer M into a polymer P can be represented by the mechanism

$$M \rightarrow R^* \rightarrow P, \qquad (I)$$

where R^* are activated intermediates (growing chains). However, this mechanism does not reflect the interaction of M, R^*, and P with the medium, which often occurs in real systems. Therefore, extending mechanism (I), one should write

$$M(X)_i \rightarrow R^*(X)_j \rightarrow P(X)_k, \qquad (II)$$

where X represents the species of the medium interacting with the monomer molecules, with the active centres of the growing chains, and with the units of the polymer being formed (i, j, $k \geqslant 0$).

If the chemical interaction of the monomer with the medium results in an increase of the absolute rates of conversion or, when several modes of polymerisation are possible, in a relative increase of the rate of conversion by a particular pathway, chemical activation is said to obtain and the corresponding monomer is chemically activated.

Chemical activation of a monomer may be due to (1) the redistribution of electron density among the intramolecular bonds caused by the interaction between M and X, which we shall call the intramolecular effect or (2) a change in the nature of the intermolecular bonds between the reacting species accompanied by a change in their distribution and mutual orientation (for example, the formation in the system of organised aggregates favouring chain growth), which we shall call the intermolecular effect.

The presence in the systems of species X interacting with the monomer often affects more than just its reactivity. The addition of a monomer molecule combined with a species X to the initial active centre may result in the formation of a new active centre which is also capable of retaining the species X. Hence the possibility arises of a change in the reactivity (for example, activation) of the growing chains and even the possibility of polymerisation mechanisms which are not characteristic of the given monomer in relatively inert media.

Finally, the interaction between the species X, the initial monomer, and the units of the polymer being produced can appreciably alter the free energy of polymerisation. Indeed if the chemical potentials of the macromolecular units and monomer molecules in the presence of X are μ_{px}

† The contents of this article were presented at the International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, September, 1966.

and μ_{mx} respectively, the change in chemical potential on polymerisation is

$$\Delta\mu = u_{px} - \mu_{mx} = \mu_p - \mu_m + \overline{\Delta G}_x = \Delta\mu_0 + \overline{\Delta G}_x. \quad (1)$$

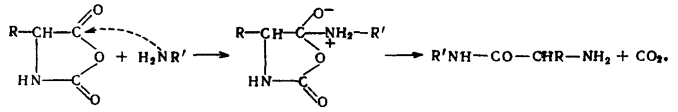
where μ_p, μ_m, and $\Delta\mu_0$ are respectively the chemical potentials of the polymer and monomer and the change in chemical potential in an inert medium. $\overline{\Delta G}_x$ is the difference between the free energies of interaction of X with the polymer units and with the monomer.

Thus "chemical activation" opens up extensive possibilities of influencing the mechanism and thermodynamics of polymerisation reactions. The above considerations constitute the basis of the approach formulated and developed in recent years by Kargin and his school.

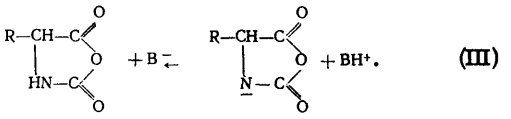
Certain examples, adduced to demonstrate a number of important aspects of the polymerisation of chemically activated monomers, are discussed below.

2. INTRAMOLECULAR EFFECT

A classical example is the polymerisation of *N*-carboxy-anhydrides (NCA) to polypeptides. The mechanism of this reaction has been examined in detail in Szwarc's review[2]. NCA are known to polymerise easily in the presence of bases (amines, alkalis, alkali metal alkoxides, and others). When primary amines are used as initiators, the initiation takes place as a result of the nucleophilic attack by the amino-group on the carbon atom of the carbonyl group of the monomer in position 5:

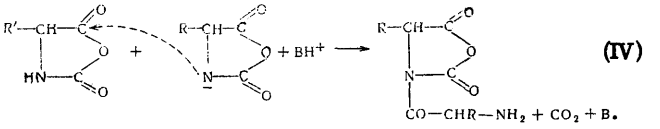


Chain growth takes place similarly, but with participation of the terminal amino-group of the chain being formed. However, this mechanism does not account for the experimental data when polymerisation is initiated by secondary amines or strong bases. Some years ago Bamford and Block[3] proposed another mechanism for the polymerisation of NCA, based on the hypothesis that in the presence of a sufficiently strong base the monomer exists in two forms described by the equilibrium:



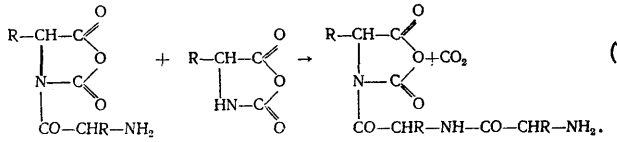
(III)

Initiation takes place as a result of the interaction between the "normal" and ionised monomer molecules:



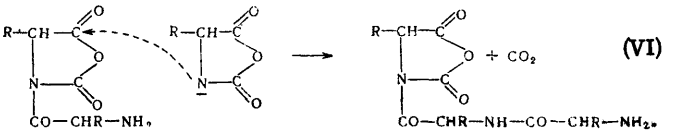
(IV)

This results in the formation of a bifunctional dimer, whose terminal amino-group can attack and add to the "usual" NCA molecule by the mechanism



(V)

At the same time the terminal cyclic group can be attacked by an ionised monomer molecule:

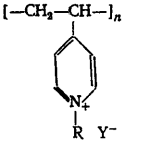


(VI)

Using ^{14}C-labelled initiators, Goodman and coworkers[4] and Scoffone and coworkers[4] confirmed this mechanism and showed that in the presence of tertiary amines and strong bases (in particular sodium methoxide) chain growth takes place mainly by mechanism (VI), i.e. by the addition of ionised NCA molecules, which react significantly faster than the initial molecules. Thus the interaction of NCA with strong bases results in its chemical activation (greatly enhanced nucleophilic character) by mechanism (III). Within the framework of the problem under discussion, the complex mechanism of the polymerisation of NCA must be assigned to one of the simplest limiting cases, since the activator (base) reacts only with monomer molecules and not with the growing chains [in mechanism (II) $i = 1$ and j, $k = 0$]. The alkali-catalysed polymerisation of caprolactam, studied in detail by Wichterle and coworkers[5], takes place similarly.

In the example just considered the activation is due to the chemical modification of the individual monomer molecules and not to the intermolecular bond between them, i.e. according to the classification adopted above the activation must be attributed to the intramolecular effect.

Systems in which the activator forms fairly strong bonds with monomer molecules, the active centres of the growing chains, and the units of the macromolecular molecules, i.e. constitutes a component of the polymer, can be assigned to the second limiting case. It has been shown recently[6-10] that in the interaction of 4-vinylpyridine (4-VP) with alkyl halides (Menshutkin reaction) in organic media (benzene, nitrobenzene, acetonitrile, dimethyl sulphoxide, propylene carbonate, and methanol) at -5° and above, instead of monomeric quaternary salts, the products isolated are high-molecular amorphous substances with the general formula

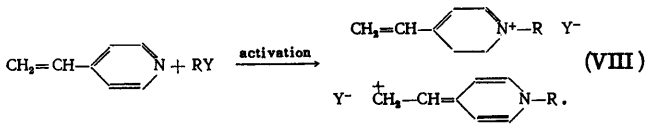


(VII)

which do not contain free pyridine base groups, i.e. spontaneous polarisation takes place. In the presence of an excess of 4-VP the formation of the polymer ceases as soon as the alkyl halide has been used up, and unreacted 4-VP remains in the system. This indicates a close relation between salt formation and polymerisation and that only 4-VP molecules which have undergone the Menshutkin reaction participate in the polymerisation. Strong inhibitors of radical polymerisation (benzoquinone, diphenylpicrylhydrazyl, and *N*-oxides) do not retard the reaction and do not affect the characteristic viscosity of polymers. This means that a radical mechanism of polymerisation can be excluded. When the reaction between 4-VP and ethyl bromide is carried out in acrylonitrile and in styrene, the resulting polymers do not contain nitrile and styrene units respectively, i.e. under the reaction conditions both styrene and acrylonitrile behave as solvents and do not copolymerise with 4-VP. This makes it possible to eliminate the

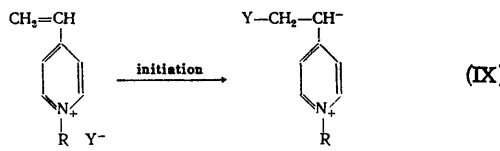
usual anionic and cationic mechanisms. The findings enumerated above necessitated the hypothesis that the polymerisation has a specific mechanism whereby only the molecules of the vinylpyridinium salts formed in the Menshutkin reaction are selectively polymerised. This mechanism was confirmed by detailed kinetic measurements (Aliev, Kabanov, Kargin)[8-10].

The first stage, which is rate-limiting for the process as a whole, is the Menshutkin reaction:



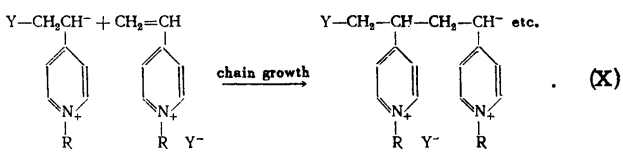
(VIII)

As a result of the appearance of a positive charge on the nitrogen atom in the monomeric salt, the π-electrons of the double bonds are appreciably displaced towards the pyridine ring, this being accompanied by a sharp increase in the electrophilicity of the double bond. The activated monomer now readily combines even with weak nucleophilic agents. The role of such an agent in the initiation reaction is fulfilled by the anion Y^-:



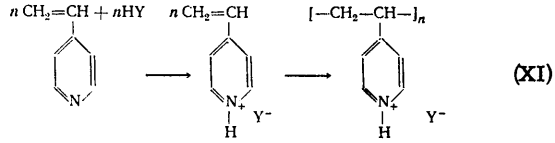
(IX)

[It should be noted that Eqn. (IX) bears a profound analogy to the well known pyridylethylation processes][11,12]. The zwitter-ion produced begins chain growth, by combining with the next molecule of the chemically activated monomer:



(X)

The molecules of 4-VP and other monomers cannot compete with those of the vinylpyridinium salt, in the first place because on addition of any other monomer to the active centre charges of opposite sign, which in the initial active centre interact via the π-bond system of the pyridine ring, would have to be separated, i.e. the energy of the system would increase significantly (loss of conjugation in the zwitter-ion and electrostatic effect). In the example examined the activator itself undergoes chemical reaction, forming a strong bond with the monomer and entering into the composition of the polymeric chain [in mechanism (II) i = 1 and j and k are equal to the degree of polymerisation], and cannot be removed from the polymer after the reaction. However, chemical activation of 4-VP (as well as that of 2-vinylpyridine) occurs also under the action of strong proton acids[6,10,13]. When 4-VP is mixed with sulphuric, nitric, toluenesulphonic, and other acids in benzene, ethyl ether, and other solvents at room temperature, the corresponding salts of poly-4-VP are formed:



(XI)

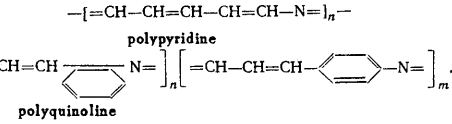
The mechanism of the polymerisation is probably largely similar to the one just described, but the subsequent treatment of the system with dilute alkali converts polyvinylpyridinium ions into polyvinylpyridine, i.e. the activator is readily removed from the polymer. It is striking that on addition of strong acids (in particular sulphuric acid) to 4-VP solutions in styrene the 4-VP salt produced immediately polymerises. Neither the excess 4-VP nor styrene are involved in the reaction. Thus the conversion of 4-VP into quaternary salts results in the generation of active centres with exceptional chemical selectivity. By virtue of the unusual nature of the active centres, the growing chains are capable of "selection" from the reaction system and can combine with N-alkylated or protonated monomer molecules.

The polymerisation and copolymerisation of complexed aromatic heterocycles (pyridine and quinoline) with ring opening may be regarded, in principle, as a closely related case[14-19]. The polymerisation of the stoichiometric complexes of pyridine and quinoline with zinc chloride has been investigated in detail between 250° and 370°:



(XII)

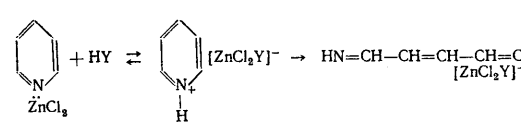
When melts of the pyridine complexes are heated above 330° and those of quinoline complexes above 250° in the presence of proton-donating initiators (HPO_3, H_2O, and pyridinium or quinolinium chlorides), high-molecular thermostable paramagnetic substances soluble in concentrated mineral acids are produced; their structure may be described by the formulae



(XIII)

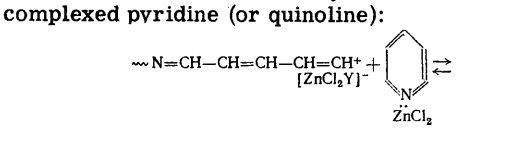
(XIV)

The kinetic role of the complex-forming agent probably consists in the polarisation of the nitrogen–carbon bond in the aromatic heterocycle which facilitates its heterolytic splitting when attacked by an electrophilic agent. Detailed kinetic studies[10,15-17] suggest that the following polymerisation mechanism is the most likely. Initiation in the presence of proton donors can be represented by the mechanism



(XV)

(for simplicity, only one of the pyridine molecules bound to each zinc chloride molecule is shown here). Chain growth occurs as a result of the attack by the carbonium cation on the complexed pyridine (or quinoline):



(XVI)

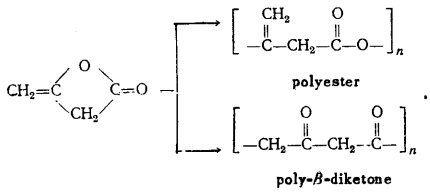
At the end of the reaction the polymer can be separated from the complex-forming agent by reprecipitation with water from concentrated mineral acids.

Chain growth in the polymerisation of aromatic heterocycles is reversible. For this reason, at a given temperature a limiting degree of conversion, determined by the equilibrium concentration of the monomer complex, is established in the system. The study of the temperature

variation of the limiting conversion showed that the polymerisation of pyridine and quinoline complexes is characterised by a lower limiting temperature (for the pyridine complex $T_{1.lim} \simeq 300°$, $\Delta H \simeq 13$ kcal mole^{-1}, and $\Delta S \simeq 19$ e.u., and for the quinoline complex $T_{1.lim} \simeq 240°$, $\Delta H \simeq 12$ kcal mole^{-1}, and $\Delta S \simeq 19$ e.u.). As shown above, these thermodynamic quantities include respectively the differences between the enthalpies and entropies of formation of the complex of the activator with the polymer and with the monomer.

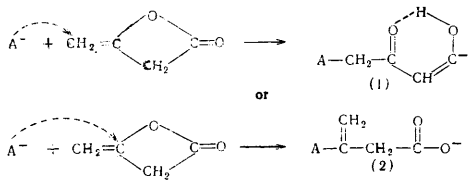
In the absence of complex-forming agents, polymerisation of pyridine and quinoline with ring opening cannot be achieved. Thus chemical activation of these monomers yields new polymers, which cannot be obtained by the usual methods of synthesis. Some years ago polymeric products were obtained by a similar procedure from nitriles by polymerisation at the C≡N bond[10,14,20-26]‡. The starting materials were complexes of nitriles with coordination-unsaturated metal halides.

Chemical reactions of monomers and growing chains with the species derived from the medium can influence the structure of the polymer units. Possibly this effect actually takes place in the polymerisation of diketen initiated by metallic magnesium[27]. It is known that, depending on the nature of the initiating agents and the reaction conditions, diketen can polymerise to a polyester[28] or a poly-β-diketone[29]:



(XVII)

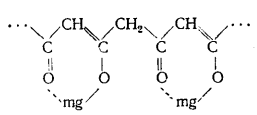
The reaction of diketen with magnesium results in the formation of substances which initiate the anionic polymerisation of diketen (the initiation mechanism has been examined by Shul'gina et al.[27]). A copolymer is then formed, in which the ratio of polyester and poly-β-diketone units is approximately 1 : 1. The structure of each successive unit is determined by the mode of the nucleophilic attack on the vinyl group of the monomer by the growing anion:



(XVIII)

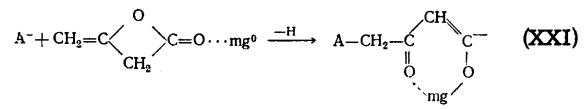
(XIX)

However, when the polymerisation is carried out in the presence of an excess of highly dispersed metallic magnesium (dispersed in the reaction system) hydrogen is evolved during the reaction and a polychelate, not containing ester units, is formed:



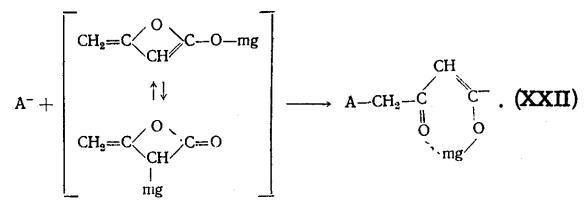
(XX)

After treatment with acid, the polychelate is converted into poly-β-diketone (mg represents one equivalent of magnesium). It may be supposed that in this case the polymerisation involves monomer molecules combined with magnesium and the reaction proceeds by one of the following mechanisms:



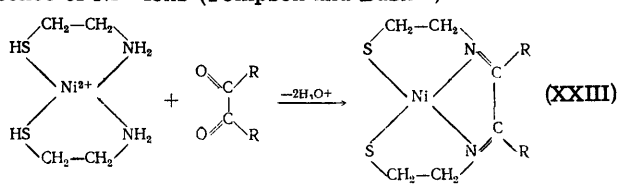
(XXI)

or



(XXII)

The chelate anion formed is more stable than anion (1) in mechanism (XVIII) and anion (2) in mechanism (XIX). For this reason, the reaction results exclusively in the formation of β-diketone units. In other words, the new monomer obtained in the reaction between diketen and magnesium is chemically activated for the formation of poly-β-diketone. It is noteworthy that in the chemistry of low-molecular compounds there are a number of cases where substances capable of coordinating the starting materials and the final products have a decisive influence on the mode of the chemical reaction (see, for example, Ref. 30). Of the numerous examples available, one may quote the synthesis of Schiff bases from β-mercaptoethylamine and α-diketones in the presence of Ni^{2+} ions (Tompson and Bush[31]):



(XXIII)

The reaction yields a compound with a significantly more stable chelate unit than the initial substance. In the absence of a complex-forming agent, thiazolines and mercaptals are formed instead of the Schiff base. The use of a similar principle in the synthesis of polymers may be of considerable interest.

3. INTERMOLECULAR EFFECT

In all the systems examined so far chemical activation must be regarded as due to an intramolecular effect. Although chemical interaction between the monomer and the species derived from the medium by no means always leads to a redistribution of electron density involving the reaction centres of the monomeric molecules responsible for polymerisation, such interaction can nevertheless lead to a considerable acceleration of polymerisation, i.e. to the activation of the monomer in the broad sense of the word, if it results in a change of the distribution of the reacting species, and (or) orientation of the reaction centres favouring chain growth (intermolecular effect).

An outstanding example is the initiation by benzoyl peroxide of the polymerisation of *p*-methacryloyloxybenzoic acid (MOBA) in the presence of *p*-cetyloxybenzoic acid

‡ The thermodynamic considerations concerning the polymerisation of complexed nitriles presented by Kargin et al.[20] are erroneous.

(COBA), investigated recently by Amerik et al.[32] In dimethylformamide solution MOBA polymerises in accordance with laws characteristic of the usual radical processes (reaction order with respect to the initiator 0.5 and with respect to the monomer 1.1). An equimolar mixture of MOBA and COBA forms smectic liquid crystals in the temperature range 87–133°. The structure of the smectic layer of such a crystal is shown in Fig. 1.

The rate of polymerisation and the molecular weight of the polymer formed in liquid crystals are significantly higher than in solution (at the same monomer concentrations the molecular weight changes from 5×10^4 to 6×10^5). The order of the reaction with respect to the monomer is close to zero. It is quite evident that the formation of hydrogen bonds between MOBA and COBA cannot influence directly the reactivity of the vinyl groups of the monomer. The acceleration of polymerisation and the increase of molecular weight are probably due to the existence in the system of labile monomeric "seeds", which, as shown earlier[33-35], favour the growth of polymeric chains. One cannot exclude the possibility that the "organised" disposition of double bonds in smectic layers can also influence the mechanism of the fundamental chain growth step. In view of this, the observed differences in the temperature variation of the microtacticity of polymers formed in solution and in liquid crystals are of considerable interest (Table 1).

In the polymerisation of MOBA in solution the percentage content of isotactic (i), heterotactic (h), and syndiotactic (s) triads in the polymer varies in the "normal" way [$\Delta(\Delta H^{+}) = 1025$ cal mole^{-1}; $\Delta(\Delta S^{+}) = 0.5$ e.u.]. In the liquid-crystal polymerisation the isomeric composition of the polymer differs significantly and is altogether independent of temperature [$\Delta(\Delta H^{+}) \simeq 0$; $\Delta(\Delta S^{+}) = 0.8$ e.u.]. The above data show at least a difference in the energy relations of the transition states in solution and in the liquid crystal. It

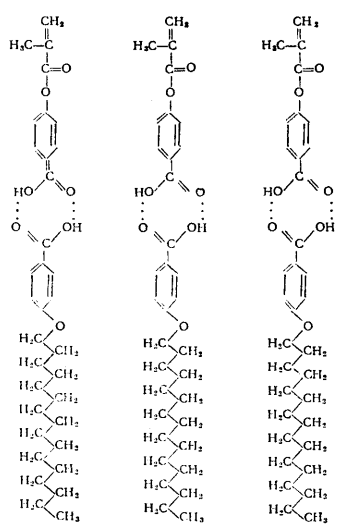


Fig. 1. The structure of the smectic layer of a liquid crystal complex of *p*-methacryloyloxybenzoic and *p*-cetyloxybenzoic acids[32].

TABLE 1. Temperature variation of the microtacticity of poly-*p*-methoxybenzoic acid (poly-MOBA)[32] measured by the NMR method after the conversion of poly-MOBA into poly(methyl methacrylate).

Polymerisation temperature, °C	In solution			In the liquid crystal		
	i	*h*	*s*	*i*	*h*	*s*
0	6.2	18.8	75.0			
40	7.0	23.3	69.7			
90	8.2	28.8	63.0	8.0	44.0	48.0
110	8.7	30.1	61.2	8.0	45.0	47.0
130				8.0	45.0	47.0

should also be noted that in the absence of COBA at temperatures above 100° the rate of depolymerisation of poly-MOBA is comparable with the rate of its formation. Therefore, when the reaction is carried out in solution, a polymerisation–depolymerisation equilibrium is established, and the yield of polymers does not reach 100%. Polymerisation in the liquid-crystal state at temperatures up to the melting point of the liquid crystals results in complete conversion of the monomer into the polymer. Thus in this case the activator not only influences the kinetics but also the thermodynamics of the polymerisation.

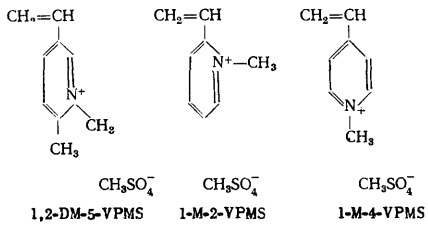
The intermolecular effect is shown "in a pure form" in polymerisation in canal compounds[36,37]. It is known that in the presence of certain organic substances urea and thiourea form tetragonal crystals with tubular channels of molecular diameter, which become filled with molecules of the organic substances. Certain vinyl compounds and dienes become arranged into linear sequences of molecules in such channels and can be rapidly polymerised under the action of accelerated electrons and γ- or X-radiation. When canal compounds of buta-1,3-diene with urea and dimethylbuta-2,3-diene with thiourea are irradiated with electrons, the corresponding crystalline *trans*-poly-1,4-dienes are formed[36,37], although the radiation-induced polymerisation of these monomers in the solid state or in solution always results in irregular polymers of mixed structure. The weak van der Waals interaction with the walls of the channels cannot lead to appreciable redistribution of electron density in the individual monomer molecule. Therefore the chemical effects shown in polymerisation in canal compounds, in particular the sharp increase in the relative rate of 1,4-*trans*-addition of dienes, must be attributed in the first place to the favourable mutual orientation of the double bonds of the initial monomeric sequences, i.e. to an intermolecular effect. Strictly speaking, even if the term "chemical activation" is applicable to the above phenomenon the same stipulations must be made as in the application of the term "chemical compound" to canal compounds.

Pursuing further this approach, one can cite the familiar phenomenon of the sharp increase in the rate of polymerisation in the crystallisation of liquid and vitreous monomers[33-35,38]. It has been shown that the acceleration is closely related to the formation at the interface between the crystalline and amorphous phases of mobile ordered aggregates of monomeric molecules — "labile seeds"[38] — i.e. is also due to an intermolecular effect. However, in this case the factors which lead to the formation of "labile seeds" are physical and not chemical in nature: the concept of "chemical activation" degenerates.

4. SIMULTANEOUS OCCURRENCE OF INTRA- AND INTER-MOLECULAR EFFECTS. MACROMOLECULAR "MATRICES"

In many cases the intramolecular and intermolecular effects occur simultaneously in chemical activation. It was noted above that the quaternary salts of 4-VP and alkyl halides polymerise spontaneously in organic media in statu nascendi. In accordance with the polarisation mechanism examined above, it is to be expected that quaternary salts of vinylpyridines with the double bond in position 5 or 3 and hence polarised to a lesser extent should show a smaller tendency towards spontaneous polymerisation. Indeed in the reaction between 2-methyl-5-vinylpyridine (MVP) and ethyl bromide, methyl iodide, dimethyl sulphate, and others in organic solvents (acetone, ethyl acetate, etc.) polymerisation does not occur: crystalline monomeric salts are precipitated. The salts of 4-VP and 2-VP whose anions exhibit relatively weak nucleophilic properties can also be obtained in a monomeric form in organic solvents at low temperatures. However, all these monomers polymerise spontaneously in concentrated aqueous solutions.

Kargin et al.[7,8,10,39-41] studied this spontaneous polymerisation of 1,2-dimethyl-5-vinylpyridinium methyl sulphate (1,2-DM-5-VPMS), 1-methyl-2-vinylpyridinium methyl sulphate (1-M-2-VPMS), and 1-methyl-4-vinylpyridinium methyl sulphate (1-M-4-VPMS) in water:



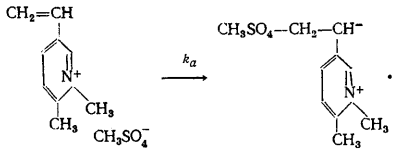
1,2-DM-5-VPMS 1-M-2-VPMS 1-M-4-VPMS

It has been established that carbon dioxide, sodium bicarbonate (which is in equilibrium with carbon dioxide), and sulphur dioxide are powerful inhibitors of spontaneous polymerisation. This finding eliminates Shyluk's hypothesis[42] of radical initiation and is in good agreement with the specific anionic mechanism of the polymerisation of 4-VP salts in organic media proposed above. Inhibition can then be regarded as a result of the addition of carbon dioxide or sulphur dioxide to the active centre carbanion.

When these inhibitors are present or specially added, induction periods appear on the kinetic curves. Using 1,2-DM-5-VPMS as an example, it has been shown that the duration of the induction period τ is related to the rate of generation of active centres v_a by the following simple expression characteristic of strong inhibitors:

$$\tau = [\text{inhibitor}]/v_a . \qquad (2)$$

Hence there is a possibility of a direct measurement of v_a. It may be expected that the rate of formation of active centres by reactions of the type of reaction (IX) (see p. 77) will be higher the greater is the polarisation of the double bond in the quaternary salt molecule. Indeed the rates v_a determined from the experimental values of τ and calculated by Eqn. (2) proved to be higher by a factor of 3.5–4 for 1-M-2-VPMS and 1-M-4-VPMS than for 1,2-DM-5-VPMS (in the range 10–35°, k_a for 1,2-DM-5-VPMS varies from 2.8×10^{-7} to 4×10^{-7} min^{-1}). Using 1,2-DM-5-VPMS as an example, the initiation reaction has been shown to be of first order with respect to the monomer, which is in complete agreement with the type (IX) mechanism, i.e.



(IX')

At the same time the kinetic curves for polymerisation in concentrated aqueous solutions (2.5 M and higher) yield satisfactory straight lines when plotted in terms of the equation for first-order reactions (Fig. 2) up to conversions (q) close to one. This means that the overall reaction is also of first order with respect to the monomer. However, the initial rate of reaction $(dg/dt)_0$ falls sharply when the initial concentration of the monomer $[M]_0$ is reduced (Fig. 3), although for a usual first-order reaction this quantity should not be a function of $[M]_0$ at all. At the same time the characteristic viscosities (molecular weights) of the polymers formed were found to decrease appreciably (Fig. 3). The temperature variation of the rate of polymerisation and the molecular weight is also quite unusual. When the temperature is increased, the rate of polymerisation and the characteristic viscosity pass through a maximum (Figs. 4 and 5).

All the attempts to account for all the experimental data using the normal concepts of homogeneous kinetics were unsuccessful. However, the observed relations can be readily explained if it is assumed that in concentrated solutions of monomeric salts ordered aggregates ("labile seeds") are present, whose lifetimes are greater or at least comparable with the time required for chain formation, as happens in liquid crystals. A hypothetical structure of an ordered aggregate is shown in Fig. 6. With this arrangement of the species in the aggregate, the double bonds form "layers" stabilised by hydrophobic interaction. It is suggested that "organised" monomer molecules, which retain sufficient mobility, are readily polymerised when an active centre enters an ordered layer. The electrical

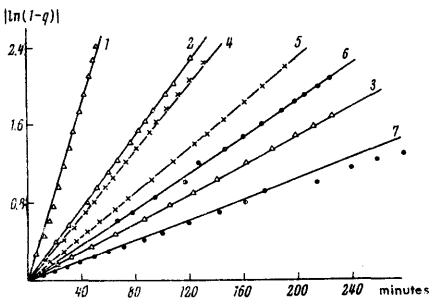


Fig. 2. Kinetic curves for the spontaneous polymerisation of vinylpyridinium salts plotted in terms of the equation for a first-order reaction:
1)–3) 1-methyl-4-vinylpyridinium methyl sulphate;
4) and 5) 1-methyl-2-vinylpyridinium methyl sulphate;
6) and 7) 1,2-dimethyl-5-vinylpyridinium methyl sulphate;
monomer concentrations (M): 1)–3) 3.5; 4) and 5) 4; 6) 3; 7) 2.5;
polymerisation temperatures: 1) 40°; 2), 6), and 7) 25°; 3) and 5) 35°; 4) 30°.

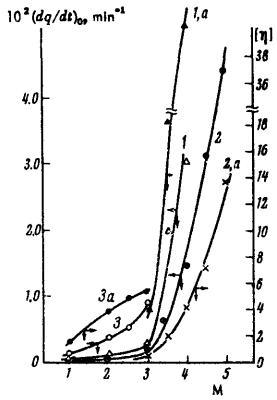


Fig. 3. Variation of the initial rate of polymerisation of vinylpyridinium salts and of the characteristic viscosity of the resulting polymers with monomer concentration: 1) and 1*a*) 1-methyl-4-vinylpyridinium methyl sulphate; 2) and 2*a*) 1-methyl-2-vinylpyridinium methyl sulphate; 3) and 3*a*) 1,2-dimethyl-5-vinylpyridinium methyl sulphate: temperature 25°; the viscosities were measured in 0.05 *N* aqueous solutions of potassium bromide.

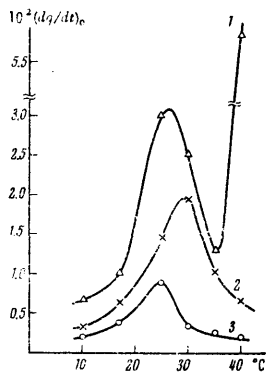


Fig. 4. Temperature variation of the initial rate of polymerisation of vinylpyridinium salts: 1) 4 M 1-methyl-4-vinylpyridinium methyl sulphate; 2) 4 M 1-methyl-2-vinylpyridinium methyl sulphate; 3) 3 M 1,2-dimethyl-5-vinylpyridinium methyl sulphate.

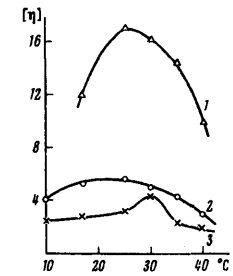


Fig. 5. Variation of the characteristic viscosity of polyvinylpyridinium salts with polymerisation temperature; the reaction conditions and the legend are the same as for Fig. 4.

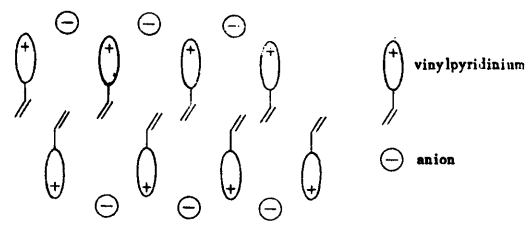


Fig. 6. The hypothetical structure of an organised aggregate in concentrated aqueous solutions of a vinylpyridinium salt.

double layer prevents the access of charged species, in particular H_3O^+ ions, to the growing chain and hence the destruction of carbanions by the addition of protons. Therefore the rate of polymerisation is independent of the pH of the medium between 2 and 9. In contrast to protons, the uncharged carbon dioxide and sulphur dioxide molecules easily reach the active centres and inhibit the process.

On the basis of the independence of the molecular weight of the degree of conversion (which has been shown experimentally and is evidence of the attainment of a steady state), the expression for the rate of polymerisation can be written in the form

$$-\frac{d[M]}{dt} = v_i\bar{\nu}, \qquad (3)$$

where [M] is the concentration of the monomer at any instant, $\bar{\nu}$ the average length of the kinetic chain, and v_i the rate of initiation. The first order of the initiation reaction with respect to the monomer, found experimentally, implies that

$$v_i = \varphi v_a = \varphi k_a[M], \qquad (4)$$

where k_a is the rate constant for the generation of active centres by a reaction of type (IX′) and φ is the initiation efficiency.

Noting that $q = (M_0 - M)/M_0$ and substituting Eqn. (4) in Eqn. (3), we obtain

$$\frac{dq}{dt} = \bar{\nu}\varphi k_a(1-q). \qquad (5)$$

At high values of $[M]_0$ the experimental variation of q with time is described by the equation

$$-\ln(1-q) = \bar{\nu}\varphi k_a t, \qquad (6)$$

which is obtained by integrating Eqn. (5). If it is assumed that, having attained the boundary of the ordered aggregate the active centre is immediately destroyed by combining with a proton or a water molecule, $\bar{\nu}$ should of course be related to the size of the ordered aggregates. In highly concentrated systems the formation of a macromolecule does not result in the breakdown of adjacent ordered regions.

Therefore $\bar{\nu}$ is independent of the degree of conversion ($\bar{\nu}$ = = const) and the polymerisation kinetics are described by the usual first-order equation. However, dilution of the initial system or a fairly appreciable temperature rise result in a decrease of the size of the ordered regions ("fusion") and the experimentally observed fall of the rate and the molecular weight. The validity of these considerations is confirmed by the sharp decrease of the viscosity of 1,2-DM--5-VPMS solutions on dilution (Fig. 7) and on raising the temperature, which is observed in the same range of concentrations and temperatures as the decrease of the rate and the molecular weight.

One of the causes of the increase of the rate with temperature in the region of lower temperatures must be attributed to the positive temperature coefficient of the initiation reaction ($E_a \simeq 7$ kcal mole^{-1} for 1,2-DM-5-VPMS). Thus the maxima on the rate–temperature curves can be explained by the superposition of two opposed factors — the increase of the rate of initiation and the breakdown of "labile seeds". However, this explanation cannot account for the extremal temperature variation of the molecular weight. Nevertheless, if it is assumed that chain termination occurs not only at the boundaries of the ordered aggregates but also, with a certain probability, within them (for example at water molecules which sometimes penetrate into the hydrophobic regions), then the extremal temperature variation of the molecular weight can also be satisfactorily accounted for. Indeed the maximum average length of the chains which can form under the given conditions ($\bar{\nu}_{max}$) is determined by the average length of the seeds. In the absence of chain transfer, the number-average degree of polymerisation $\overline{DP}$ can be expressed by the formula

$$\overline{DP} = (1-\lambda)\,\bar{\nu}_{max} + \lambda\,\frac{k_p}{k_t}, \qquad (7)$$

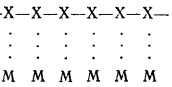
where k_p is the chain growth rate constant, k_t the chain termination rate constant within the seed, and λ the fraction of chains which are destroyed before reaching the end of the seed. If the activation energy for chain growth is higher than for chain termination within the seed, then at low temperatures most of the chains are terminated within the seeds ($\lambda \simeq 1$) and $\overline{DP}$ is determined by the ratio k_p/k_t and its temperature variation by the difference between the activation energies for chain growth and termination. In this temperature range $\overline{DP}$ increases with temperature. At high temperatures, where "fusion" takes place and the size of the ordered aggregates decreases, $\bar{\nu}_{max}$ falls and becomes smaller than k_p/k_t. Then most of the chains are destroyed at the edges of the seeds ($\lambda \simeq 0$) and $\overline{DP}$ is determined by the greatly reduced value of $\bar{\nu}_{max}$. In the absence of chain transfer, the rate of polymerisation can be written

$$-\frac{d[M]}{dt} = v_i\left[(1-\lambda)\,\bar{\nu}_{max} + \lambda\,\frac{k_p}{k_t}\right]. \qquad (8)$$

This expression explains the experimentally observed similarity of the variation of the rate of polymerisation and the molecular weight with the reaction conditions§.

Thus the concept of chemical activation of the monomer as a result of an intramolecular effect (polarisation of the double bond in the quaternary salt molecule) proved to be inadequate to account for the relations observed in the spontaneous polymerisation of vinylpyridinium salts in concentrated aqueous solutions. The kinetic data require the additional hypothesis of "labile seeds" which arise as a result of intermolecular interaction in the reaction system, i.e. of an intermolecular effect.

The combination of intra- and inter-molecular effects in chemical activation is closely related to the problem of "matrix" polymerisation. Suppose that the activator species X are chemically bound into long sequences. Then on addition of the monomer, the following system forms:



The monomer and the "matrix" can be chosen so that the reactivity of the monomer M bound to X should be significantly higher than that of free M. Then a chain M_n is formed from activated monomer molecules on each X_n sequence.

The reaction described recently by Furukawa and coworkers[43] may be quoted as an interesting example. In their study of the interaction between acetaldehyde and activated alumina the Japanese investigators observed that the adsorbed monomer polymerises with high yields at -70° to amorphous rubberlike polyacetal. The infrared spectrum of acetaldehyde adsorbed on alumina shows a pronounced bathochromic shift of the absorption band due to the carbonyl group, compared with the liquid monomer (6.4 instead of 5.8 μm), which indicates appreciable polarisation of the C=O bond (intramolecular effect). The authors[43] suggest that on adsorption the acetaldehyde molecules assume an ordered arrangement in the adsorption layer, as shown in Fig. 8 (intermolecular effect). Both factors favour rapid growth of polymeric chains, i.e. lead to the activation of the molecule.

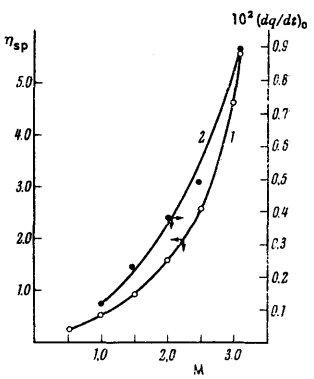


Fig. 7. Variation of the specific viscosity of an aqueous solution (curve 1) and the rate of polymerisation (curve 2) of 1,2-dimethyl--5-vinylpyridinium methyl sulphate with monomer concentration; the viscometric and kinetic measurements were made at 25°.

§ The behaviour of 1-M-4-VPMS in the temperature range 35–40° is exceptional (Fig. 4). Despite the continuing fall of the molecular weight, the rate of polymerisation increases suddenly after passing through a maximum by a factor of nearly six, which corresponds to an effective activation energy of about 70 kcal × × mole^{-1}. As before, the kinetic curves for polymerisation at 40° yield straight lines when plotted in terms of the equation for a first-order reaction (Fig. 2, curve 1). This effect can be attributed to a sudden rearrangement of the aggregates over a narrow temperature range.

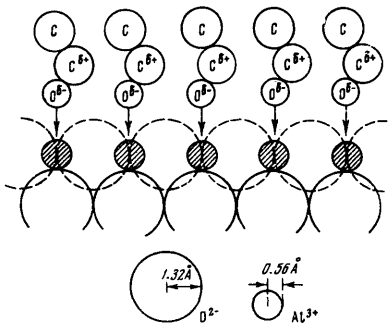


Fig. 8. Acetaldehyde adsorbed on the surface of γ-alumina [43].

The phenomenon of chemical activation of the double bonds of 4-VP in its conversion to the quaternary salt, described above, recently enabled Kargin et al. to achieve polymerisation on macromolecular "matrices" [7,8,10,13,44]. Polystyrenesulphonic acid (PSSA), polyethylenesulphonic acid (PESA), and polyacrylic acid (PAA) were used as the matrices. In all cases an equivalent amount of 4-VP was chemisorbed on the polymeric acids, activated, and polymerised by the mechanism described above. The products were polymeric salts, paired macromolecules of the polymeric acid and polymeric base (Fig. 9). The 4-VP molecules for which there is no room on the "matrices" remain inactive and are not involved in the reaction.

If the degree of neutralisation of the polymeric acid (i.e. the degree of saturation of the "matrix") is close to unity, the polymerisation of 4-VP on the polymeric acids is rapid at room temperature even in dilute aqueous solutions, since the activated monomer species are grouped along the polymeric activator chains regardless of the average concentration. However, the rate of polymerisation greatly depends on the degree of saturation, increasing sharply when the latter approaches unity. The problem of the effect of the degree of saturation of the "matrix" on the rate of the process is cardinal, since it is directly related

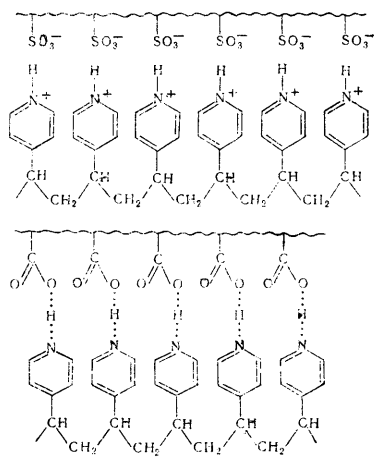


Fig. 9. The structure of the "matrix" polymerisation product.

to the problem of the elucidation of the nature of the interaction between the substrate and activator.

The marked dependence of the rate of polymerisation on the degree of saturation α can be explained on two different hypotheses. The first of these reduces to the following. Suppose that the vinylpyridinium cations formed on neutralisation of the polymeric acid are firmly bound to its units and cannot migrate along the "matrix". The probability of the formation of a continuous sequence of p-activated 4-VP molecules is

$$\omega_p = \alpha^{p-1}(1-\alpha). \qquad (9)$$

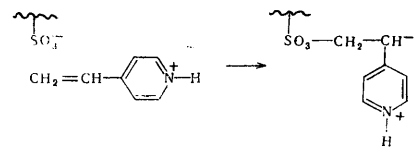
The average length of continuous sequences at a given value of α is

$$\bar{\nu} = \sum_1^\infty p\omega_p = \sum_1^\infty p\alpha^{p-1}(1-\alpha) = \frac{1}{1-\alpha}. \qquad (10)$$

If it is assumed that the length of the kinetic chain is determined by the length of the continuous sequence of activated molecules on the matrix, then, provided that initiation is possible in any unit of this sequence, the initial rate of polymerisation is

$$v_p = v_i\frac{\bar{\nu}}{2} = \frac{v_i}{2(1-\alpha)}, \qquad (11)$$

where v_i is the rate of initiation. Assuming further that the initiation reaction is of first order with respect to the monomer (see above), i.e. takes place by the mechanism



(XXIV)

one can write

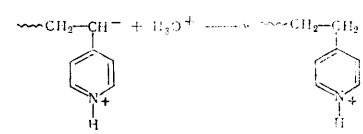
$$v_i = k_i[M] = k_i\alpha[C], \qquad (12)$$

where k_i is the initiation rate constant, [M] the concentration of the monomer, and [C] the concentration of the polymeric acid. On substituting Eqn. (12) in Eqn. (11), we obtain

$$v_p = {}^1/_2 k_i[C]\frac{\alpha}{1-\alpha}. \qquad (13)$$

Eqn. (13) predicts a rapid increase of the initial rate of polymerisation as α approaches unity (v_p tends to infinity when α = 1 because of the simplifying assumption made in the derivation that the "matrices" are of infinite length).

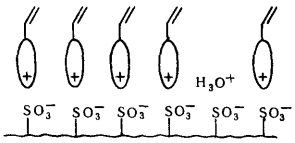
The second possible explanation is based on the assumption that activated 4-VP molecules can migrate within a certain space along the "matrix" and that the length of the kinetic chain for $\alpha < 1$ is related to the probability of the destruction of the active centre by the non-titrated hydronium ions, by the mechanism



(XXV)

In fact the "structure" of the reaction system formed on titration of the polymeric acid with 4-VP cannot ensure

electrostatic protection of the active centre from the non-titrated protons, in contrast to the mechanism adopted for the polymerisation of vinylpyridinium salts in concentrated aqueous solutions (see p. 81). This structure can be represented as follows:



(XXVI)

In the regions where the matrix is not saturated by the monomer, the probability of an encounter between an active centre and hydronium ions, which are held in the vicinity of such regions by the electrostatic interaction with the polymeric anion, is very high. Then the rate of chain termination v_t is given by the equation

$$v_t = k_t n [H_3O^+], \quad (14)$$

where k_t is the termination rate constant and n the concentration of active centres.

The average length of the kinetic chain at low conversions, when the change in the concentration of the activated monomer may be neglected, is given by the expression

$$\bar{\nu} = \frac{k_p n [M]}{k_t n [H_3O^+]} = \frac{k_p \alpha [C]}{k_t [H_3O^+]}. \quad (15)$$

The initial rate of polymerisation is

$$v_p = v_i \bar{\nu} = \frac{k_i k_p}{k_t} C^2 \frac{\alpha^2}{[H_3O^+]}, \quad (16)$$

where k_p is the chain propagation rate constant. Noting that for a strong acid

$$\alpha = \frac{[H_3O^+]_0 - [H_3O^+]}{[H_3O^+]_0},$$

where $[H_3O^+]_0$ is the concentration of hydronium ions in the non-titrated acid, we have finally

$$v_p = \frac{k_i k_p \alpha^2 [C]}{k_t (1 - \alpha)}. \quad (17)$$

Eqn. (17), like Eqn. (13), predicts a very rapid increase in the initial rate of polymerisation when α tends to unity.

In order to decide which of the two hypotheses is correct, it is necessary to "spoil" the "matrices" by titrating them before the addition of 4-VP with any non-polymerisable base, for example alkali. Then if we denote the degree of preliminary neutralisation by β and the overall degree of neutralisation by α as before, Eqn. (13) becomes

$$v_p = {}^1/_2 k_i [C] \frac{\alpha - \beta}{1 - (\alpha - \beta)}, \quad (13')$$

and Eqn. (17) becomes

$$v_p = \frac{k_i k_p (\alpha - \beta)^2 [C]}{k_t (1 - \alpha)}. \quad (17')$$

It follows from Eqns. (13') and (17') that the hypothesis of the rigid fixation of vinylpyridinium ions on the polymeric acid macromolecules leads to the theoretical prediction of a higher sensitivity of the rate of reaction to preliminary neutralisation in the range of α values close to unity than the hypothesis of chain termination by hydronium ions.

To decide which of the two kinetic equations describes the real process, two series of experiments were made. In the first series a 0.0119 N aqueous solution of PESA was titrated with 0.076 N aqueous solution of 4-VP to pH 5.6, which corresponds to $\alpha \simeq 0.999$. In the second series the same PESA solution was 50% titrated with the sodium hydroxide solution and then the pH was again brought to 5.6 by the addition of a solution of 4-VP. Thus in the first series of experiments we have $\beta = 0$ and $\alpha = 0.999$ and in the second series $\beta = 0.5$ and $\alpha = 0.999$. The rate of polymerisation was measured spectrophotometrically. It was found that in the solutions where $\beta = 0$ the rate of reaction was 3.6–3.9 times higher than in the solutions where $\beta = 0.5$.

It is now necessary to compare the result with the theoretical predictions. The relative decrease of the rate of polymerisation γ' on the assumption of rigid fixation of the activated monomers can be found by dividing Eqn. (13) by Eqn. (13'):

$$\gamma' = \frac{\alpha (1 - \alpha + \beta)}{(1 - \alpha)(\alpha - \beta)}. \quad (18)$$

On substituting the values of α and β specified in the experiments, we obtain $\gamma' \simeq 1000$, i.e. the rate of polymerisation on the "spoiled matrix" should be lower by a factor of one thousand than on the matrix titrated with 4-VP only. The relative decrease of the rate of polymerisation γ'' on the assumption of migration of vinylpyridinium ions along the polymeric acid molecules and the destruction of active centres by non-titrated protons is obtained by dividing Eqn. (17) by Eqn. (17'):

$$\gamma'' = \frac{\alpha^2}{(\alpha - \beta)^2}. \quad (19)$$

For the values of α and β used, $\gamma'' \simeq 4$, which is in good agreement with experiment.

It is striking that the morphology of the polymerisation products of 4-VP on polymeric acids is closely related to the form of the "matrix" in solution. Electron microscope studies have shown that in the polymerisation in methanol, where the macromolecules are rolled into globules, the polymeric salts form as disordered globular aggregates. In the polymerisation in water, where the matrices are ionised and extended, distinctly fibrillar structures are produced[7,8,10,13]. Thus chemical activation of 4-VP by polymeric acids is indeed due to a combination of intramolecular and intermolecular effects. It must be emphasised that the conversion of 4-VP into vinylpyridinium ions is by itself insufficient to ensure appreciable reaction rates in aqueous media. In dilute aqueous solutions of 4-VP salts and low-molecular acids there is virtually no spontaneous polymerisation. In equimolar mixtures of 4-VP and glacial acetic acid only traces of a polymer are formed in several days. At the same time 50% conversion of the 4-VP salt and PAA into a polymeric salt in 0.092 N solution at 20–50° is attained in 35–3 min (overall activation energy 26.4 kcal mole^{-1}). It may be supposed that in this case too the formation of "labile seeds" from activated monomeric molecules plays a very significant role, since it is difficult to account for the observed acceleration on going from low-molecular to high-molecular activators by the concentration effect alone.

Polymerisation on macromolecular activators still constitutes only a very rough approximation to the synthesis of polymeric chains in living cells. However, it is well known that preliminary chemical activation of the substrate is one of the fundamental principles of biochemical processes.

5. CHEMICAL ACTIVATION IN RADICAL POLYMERISATION

It is known that the properties of free radicals and the rates of radical reactions depend relatively little on the properties of the medium (in particular its polarity). However, this is true only in those cases where the species of the medium are incapable of specific chemical or semichemical interaction with the reacting species. Even relatively weak chemical interaction of the functional groups of the radical or monomer with the medium influences the chain growth rate constants in radical processes.

A systematic study of the role of organic complex-forming agents in radical copolymerisation was recently undertaken by Ryabov, Semchikov, and coworkers[45]. They showed, in particular, that introduction of proton donors into the system styrene (St)–2-VP alters markedly the composition of the copolymers formed on radical initiation, and, what is particularly important, the nature of the composition curves. Table 2 presents the relative activities and their products for the copolymerisation of styrene and 2-VP in the presence of various proton donors taken in ratios of approximately 1 : 1.5 relative to 2-VP. The table also gives the pK values of the complex-forming agents investigated.

In their solid-phase copolymerisation styrene and 2-VP do not exhibit a tendency towards alternation. Over the entire range of relative concentrations the copolymer is slightly enriched in 2-VP. In the presence of proton donors a tendency towards alternation appears, and increases with the acidity of the donor. The authors attribute the observed effect to the positive polarisation of the double bond in the 2-VP molecule, as a result of the formation of a hydrogen bond between the nitrogen atom of the pyridine ring and the complex-forming agent. This conclusion is confirmed to some extent by the application of the Hammett equation and the Q–e scheme to the data obtained.

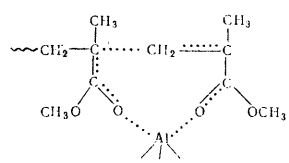
Strong inorganic complex-forming agents have an even more significant influence on radical polymerisation. In 1958 Bamford et al.[46] showed that the rate of polymerisation of acrylonitrile (AN) in dimethylformamide, initiated by free radicals, increases appreciably on addition to the system of lithium chloride which forms complexes with C≡N groups. A preliminary explanation of this effect was based on the postulated higher reactivity of the complexed chain propagation radicals. Two years later Kargin et al.[47] noted that the rate of the photo-initiated polymerisation of methyl methacrylate (MMA) saturated with zinc chloride increases sharply near the interface between the crystals and the liquid. At the same time Parrot and Monteiro[48] confirmed the results of Bamford and coworkers[46] by their observation of the acceleration of the radical polymerisation of acrylonitrile on addition of lithium chloride, magnesium chloride, and aluminium chloride. Data on the effect of zinc chloride on the polymerisation kinetics and the copolymerisation rate constants for a number of monomers were obtained by Imoto and coworkers[49]. The kinetic measurements of Bamford and coworkers[50] showed that the acceleration of photopolymerisation in the system MMA–$ZnCl_2$ is due to an increase of the chain propagation rate constant: the chain termination rate constant remains virtually unchanged.

TABLE 2. Effect of organic complex-forming agents on the copolymerisation constant of styrene (M_1) and 2-vinylpyridine (M_2).[45]

Complex-forming agent	pK	r_1	r_2	$r_1 \times r_2$
—	—	0.57 ±0.05	1.33 ±0.08	0.758
Ethanol	18	0.486±0.07	0.862±0.08	0.418
Methanol	16	0.426±0.05	0.607±0.06	0.258
Phenol	9.95	0.253±0.06	0.549±0.07	0.139
Acetic acid	4.75	0.16 ±0.04	0.36 ±0.07	0.058

The problem of the mechanisms leading to an increase of the rate of the radical-initiated chain propagation in the presence of inorganic complex-forming agents is at present the subject of detailed studies. The first attempt at a theoretical interpretation of this phenomenon was undertaken by Tazuke et al.[51] by the molecular orbital method. Using the simple LCAO approximation, they calculated the values for the extent of delocalisation S_r^R, regarded as a measure of the reactivity of the monomer, and of the stabilisation energy of the transition state ΔE_{rs} for complexes of various substituted derivatives of vinylpyridine, acrylonitrile, and methyl methacrylate with zinc chloride, and obtained a qualitative agreement between the theory and the kinetic experiments. Such calculations are made essentially to take into account the intramolecular effect of the complex-forming agents. However, in many cases chemical activation probably cannot be explained solely by the intramolecular effect, particularly in solid-phase polymerisation or in polymerisation in concentrated solutions in the presence of stoichiometric or nearly stoichiometric amounts of complex-forming agents.

Some light has been thrown on this problem by the results of Zubov et al.[52], who investigated the solid-phase photopolymerisation of methyl methacrylate in the presence of aluminium chloride and bromide. The kinetic data, the study of the infrared spectra of the complexed monomer, and the ESR spectra of the complexed radicals enabled the authors to put forward certain ideas concerning the mechanism of the acceleration of the polymerisation. It is suggested that, in the presence of low concentrations of inorganic activators (i.e. for monomer : activator ratios significantly lower than the stoichiometric values), the observed acceleration is mainly caused by the intramolecular effect. The hypothetical structure of the activated complex may be represented as follows:



(XXVII)

The unpaired electron of the complex radical, which according to the ESR data spends some time on the aluminium atom (spin density on aluminium about 1%), is transferred to the monomer molecule in the transition state. It is suggested that this fundamental step has a higher probability than the usual radical addition. For this reason, the chain propagation rate constant is higher in the presence of the complex-forming agent. However, the above hypothesis cannot account for the kinetic data obtained when the monomer : complex-forming agent ratios are close to the stoichiometric value. In this case the formation of organised aggregates of complexed methyl methacrylate molecules ("labile seeds"), favouring chain growth, probably

begins to play a significant role, as happens, for example, in certain liquid crystals (intermolecular effect).

Quite recently Nechaev et al. [53] observed the acceleration of the photo-initiated polymerisation of methyl methacrylate in the presence of 4% oleum. It was found that the rate of polymerisation increases with the concentration of sulphuric acid and passes through a maximum. At the molar ratio H_2SO_4 : MMA = 1 the molecular weight is also a maximum (Fig. 10). It may be supposed that in this case the intermolecular effect is one of the causes of the chemical activation of methyl methacrylate.

The intramolecular effect postulates cannot account for the sharp increase in the rate of the radiation-induced photopolymerisation of allyl monomers in the presence of zinc chloride [52]. Allyl acetate (AA) to which an equimolar amount of zinc chloride has been added polymerises 5.5–6 times faster. The rate of polymerisation of allyl alcohol (AAlc) increases by a factor of 24 in the presence of zinc chloride at an allyl alcohol : zinc chloride ratio of 2. Since the double bond in allyl monomers and the unpaired electrons in the corresponding chain propagation radicals are not conjugated with the functional groups participating in the formation of complexes, it is difficult to expect an appreciable change in their reactivity as a result of the addition of zinc chloride. One of the possibilities consists in the activation of the complexed allyl chain transfer radicals. Nevertheless this alone does not fully explain the observed kinetic features. The explanation should probably also be sought in a combination of intramolecular and intermolecular effects.

Radical polymerisation in the presence of complex-forming agents has been recently introduced in polymer chemistry and its further development will probably lead to fundamentally new methods for the control of the rates and the stereochemistry of radical processes. The studies of the chemical activation of monomers in the formation of charge-transfer complexes which have been begun in a number of laboratories are particularly promising.

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The problems of the polymerisation of chemically activated monomers may be regarded as part of the general problem of the effect of the interaction between the substrate and the species derived from the medium on the capacity of the substrate to undergo a particular reaction. The

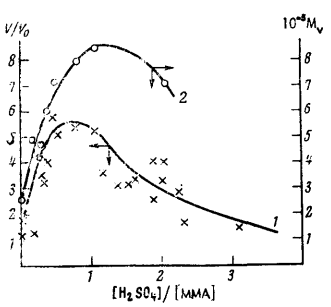


Fig. 10. Variation of the relative rate of polymerisation of methyl methacrylate (curve 1) and the molecular weight of the resulting polymer (curve 2) with the monomer : activator molar ratio at 20°.

averaging simplification associated with the introduction of the macroscopic concept (medium) is always to some extent a consequence of the insufficient knowledge of the investigator of the nature and distribution of the concrete interactions in the reaction system at a molecular level. This averaging simplification is very convenient in analysis and is probably justified in the case of weak interactions, but it involves fundamental limitations in the elucidation of the detailed mechanisms of chemical reactions. The present review deals with systems for which the necessity to formulate the term "interaction with the medium" in a more concrete form is quite evident. The examination of the monomer–activator problem on a somewhat wider scale leads to an important generalisation. Imagine a system in which the number of monomer molecules is somewhat higher than the number of activated molecules. If the activator combines with the units of the polymer being formed as strongly or more strongly than with the monomer molecules, then during the reaction the fraction of the activated monomer decreases continuously. Actually this means that in the initial system part of the less active monomer is replaced by a more active variety. Examples of such systems are quoted above. If the bond between the activator and the polymer chain units is much weaker than that with the monomer, then one activator molecule can be used repeatedly and can facilitate the polymerisation of a large number of monomer molecules: the concept of the "activator" merges with the classical concept of the "catalyst". An example is the polymerisation of *N*-carboxy-anhydrides examined above. Finally, if the activator molecules interact with the growing ends of the chain more strongly than with the average monomer molecules and with the macromolecular units, they will be retained at the end of the chain during its growth and, within the framework of the generally adopted interpretation of catalytic polymerisation processes, the activator may be regarded as a component of the catalytic complex responsible for the chain process. This is precisely what happens in the lithium-induced polymerisation of methyl methacrylate, dienes, etc. in the presence of organic donors (tetrahydrofuran, amines, etc.).

Between these three limiting cases enumerated above, there should be a multiplicity of intermediate situations. A number of deviations from the normal behaviour of catalysts are known. It cannot be excluded that such "deviations" should in fact be regarded as an effect of the general laws governing the characteristics of systems of an intermediate type.

The above discussion is applicable to a wide range of other chemical processes as well as polymerisation. Further progress in this field will probably lead to a general examination of the problem of catalysts, active solvents, modifiers, etc.

1. V.A. Kargin and V.A. Kabanov, Dokl. Akad. Nauk SSSR, 167, 124 (1966).
2. M. Szwarc, Adv. Polymer Sci., 4, 1 (1965).
3. C.H. Bamford and H. Block, "Polyaminoacids, Polypeptides and Proteins", University of Wisconsin Press, 1965, p. 65.
4. M. Goodman and E. Peggion, Vysokomol. Soed., 9, in the press.
5. O. Wichterle, J. Šebenda, and J. Kraličeк, Khim. i. Tekhnol. Polim., No. 7, 39 (1961).
6. V.A. Kargin, V.A. Kabanov, K.V. Aliev, and E.F. Razvodovskii, Dokl. Akad. Nauk SSSR, 160, 604 (1965).
7. V.A. Kabanov, K.V. Aliev, O.V. Kargina, and T.I. Patrikeeva, "International Symposium on Macromolecular Chemistry", Prague, 1965, Preprints of Scientific Paper, P129.

8. V.A.Kabanov, K.V.Aliev, O.V.Kargina, and T.I.Patrikeeva, J.Polymer Sci., C, in the press.
9. K.V.Aliev, Candidate's Thesis, Topchiev Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1966.
10. V.A.Kabanov, Doctoral Thesis, Topchiev Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1966.
11. "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods for the Investigation of Organic Compounds), Izd.Khimiya, Moscow, 1964, Vol.14.
12. W.Doering and R.Weil, J.Amer.Chem.Soc., 69, 2461 (1966).
13. V.A.Kargin, V.A.Kabanov, and O.V.Kargina, Dokl.Akad. Nauk SSSR, 161, 1131 (1965).
14. V.A.Kabanov, V.P.Zubov, V.P.Kovaleva, and V.A.Kargin, J.Polymer Sci., C1, 1009 (1964).
15. V.P.Kovalenko, E.D.Kukina, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., 6, 1676 (1964).
16. D.A.Topchiev, V.A.Kabanov, and V.A.Kargin, Vysokomol. Soed., 6, 1814 (1964).
17. V.A.Kabanov, V.A.Kargin, V.P.Kovaleva, and D.A.Topchiev, Vysokomol.Soed., 6, 1852 (1964).
18. V.A.Kabanov, D.A.Topchiev, V.G.Popov, and V.A.Kargin, Vysokomol.Soed., 8, 1760 (1966).
19. D.A.Topchiev, V.G.Popov, M.V.Shishkina, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., 8, 1767 (1966).
20. V.A.Kargin, V.A.Kabanov, V.P.Zubov, and A.B.Zezin, Dokl.Akad.Nauk SSSR, 139, 605 (1961).
21. V.P.Zubov, I.P.Terekhina, V.A.Kabanov, and V.A.Kargin, Symposium, "Geterotsepnye Vysokomolekulyarnye Soedineniya" (Hetero-Chain High-Molecular Compounds), Izd. Nauka, Moscow, 1963, p.147.
22. V.P.Zubov, E.T.Zakharenko, V.A.Kabanov, and V.A.Kargin, *ibid.*, p.186.
23. E.Oikawa and S.Kambara, J.Polymer Sci., 2B, 651 (1964).
24. E.Oikawa and S.Kambara, Bull.Chem.Soc.Japan, 37, 1849 (1964).
25. V.P.Zubov, N.Ya.Rechenskaya, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., 8, 795 (1966).
26. O.P.Komarova, V.P.Zubov, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., A9, 336 (1967).
27. E.S.Shul'gina, V.P.Zubov, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., 8, No.11 (1966).
28. J.Furukawa, S.Saigusa, N.Mise, and A.Kawasaki, Makromol.Chem., 39, 243 (1960).
29. R.Oda and S.Munemiya, Makromol.Chem., 43, 149 (1961).
30. "Reactions of Coordinated Ligands", Advances in Chemistry Series, American Chemical Society, Washington, 1963.
31. M.S.Tompson and D.H.Bush, J.Amer.Chem.Soc., 84, 1782 (1962).
32. Yu.B.Amerik, I.I.Konstantinov, and B.A.Krentsel, "International Symposium on Macromolecular Chemistry", Tokyo-Kyoto, 1966, p.30.
33. V.A.Kargin, V.A.Kabanov, and I.M.Papisov, Dokl.Akad. Nauk SSSR, 141, 389 (1961).
34. V.A.Kargin, V.A.Kabanov, and I.M.Papisov, J.Polymer Sci., C1, 767 (1964).
35. V.A.Kabanov, I.M.Papisov, A.N.Gvozdetskii, and V.A.Kargin, Vysokomol.Soed., 7, 1787 (1965).
36. J.F.Brown and D.M.White, J.Amer.Chem.Soc., 82, 5671 (1960).
37. D.M.White, J.Amer.Chem.Soc., 82, 5678 (1960).
38. M.Letort and A.J.Richard, Compt.rend., 240, 86 (1955).
39. V.A.Kabanov, T.I.Patrikeeva, and V.A.Kargin, Dokl.Akad. Nauk SSSR, 168, 1350 (1966).
40. T.I.Patrikeeva, T.V.Nechaeva, M.I.Mustafaev, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., A9, 332 (1967).
41. V.A.Kabanov, T.I.Patrikeeva, O.V.Kargina, and V.A.Kargin, see Ref.32, 1966, Vol.II, p.60
42. W.P.Shyluk, J.Polymer Sci., A2, 2191 (1964).
43. J.Furukawa and S.Saigusa, "Polymerisation of Aldehydes and Epoxides" (Translated into Russian), Izd.Mir, 1965, p.118.
44. O.V.Kargina, M.V.Ul'yanova, L.Mishustina, V.A.Kabanov, and V.A.Kargin, Vysokomol.Soed., A9, 340 (1967).
45. A.V.Ryabov, Yu.D.Semchikov, N.N.Slavnitskaya, and V.N.Vakhrusheva, Dokl.Akad.Nauk SSSR, 154, 1135 (1960).
46. C.H.Bamford, A.D.Jenkins, and R.Johnston, J.Polymer Sci., 120, 355 (1958).
47. V.A.Kargin, V.A.Kabanov, and V.P.Zubov, Vysokomol. Soed., 2, 765 (1960).
48. J.Parrot and H.Monteiro, Compt.rend., 251, 2026 (1960).
49. M.Imoto, T.Otsu, and S.Shimizu, Makromol.Chem., 65, 174 (1963).
50. C.H.Bamford, S.Brumby, and R.P.Wayene, Nature, 209, 292 (1966).
51. S.Tazuke, K.Tsuji, and T.Yunezawa, see Ref.32, 1966, Vol.II, p.52.
52. V.P.Zubov, M.B.Lachinov, V.F.Kulikova, V.B.Golubev, V.A.Kabanov, and V.A.Kargin, *ibid.*, p.56.
53. P.P.Nechaev, V.P.Zubov, and V.A.Kabanov, Vysokomol. Soed., 8, No.12 (1966).

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THE STRAINED DOUBLE BOND

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