

# POLYMERIZATION OF CHEMICALLY-ACTIVATED MONOMERS

V. A. KABANOV

*Chemistry Department, Moscow Lomonosov University, Moscow, U.S.S.R.*

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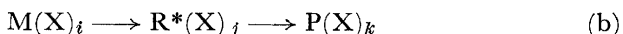
*Topchiev Institute of Petrochemical Synthesis,  
Academy of Sciences, Moscow, U.S.S.R.*

## INTRODUCTION

The conversion of monomer M into polymer P may be represented by the scheme (a) where R\* are active intermediates (propagating chains).



This scheme, however, does not take into account the interaction of M, R\* and P with the reaction medium which always takes place in the real systems. Thus, the scheme (a) could be modified for general application to scheme (b)



where X is a symbol of some medium particle interacting with monomer molecules, with active centres of propagating chains and with monomer units of polymer formed,  $i, j$  and  $k \geq 0$ .

The chemical interaction of the monomer with particles of the medium may result in an increase of absolute conversion rate or, in the case of several possible paths of polymerization, in relative acceleration of one of them. Such a phenomenon is called *chemical activation* and the corresponding monomer is said to be *chemically activated*.

The chemical activation may arise from (1) electron density redistribution on intramolecular bonds caused by interaction between M and X; let us call this *intramolecular effect*; (2) change of the character of intermolecular bonds between monomer species followed by change of their distribution and orientation (for instance formation of organized aggregates favourable for chain propagation); let us call this *intermolecular effect*.

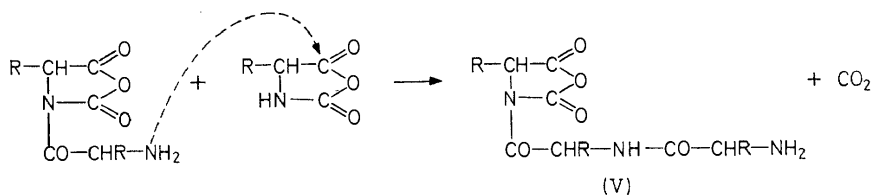
The presence of the X particles interacting with the monomer in reaction system often influences the monomer reactivity. Also the addition of the monomer molecule bonded with X (to initial active centre) may lead to the formation of a new active centre which also can attract X. Hence the possibility arises of propagating species reactivity change (for instance of their activation). In some cases it may even lead to polymerization mechanisms which are not typical for a given monomer in relatively inert media.

Finally, the interaction between X, a monomer and monomer units of a polymer may noticeably affect free energy of polymerization. Indeed if the

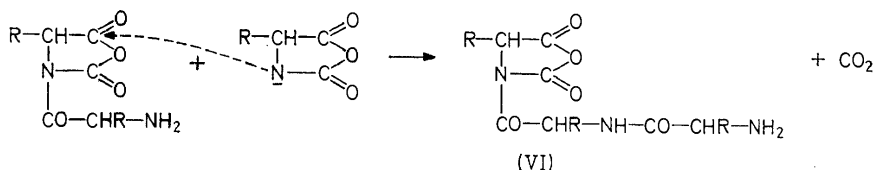


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As a result of this a bifunctional dimer is formed. The terminal amino group can attack and add a "normal" NCA molecule in the usual manner according to the scheme



In parallel with this the terminal cyclic group can be attacked by an ionized monomer molecule

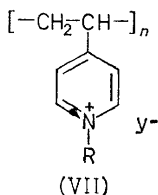


Goodman *et al.*<sup>3</sup> and Scoffone *et al.*<sup>4</sup> using initiators labelled with <sup>14</sup>C confirmed this mechanism and showed that in the presence of *tertiary* amines and strong bases (e.g. NaOCH<sub>3</sub>) chain propagation mainly proceeded according to the scheme described for the formation of (VI), viz. by addition of ionized NCA molecules, reacting much more rapidly than the initial ones. Therefore, the interaction of NCA with strong bases results in its chemical activation, i.e. sharp increase of nucleophilicity [cf. the scheme described for (III)]. The complicated mechanism of NCA polymerization with respect to the problem discussed could be treated as one of the simplest extreme cases, because the activator (base) reacts only with the monomer molecules and does not interact with growing chains [in the scheme (b)  $i = 1, j, k = 0$ ]. Alkali-initiated caprolactam polymerization proceeds in a similar way<sup>5</sup>.

In the example just considered the chemical activation accounts for the changes of separate monomer molecules but not for intermonomer bonds and according to the above accepted classification should be ascribed to intramolecular effect.

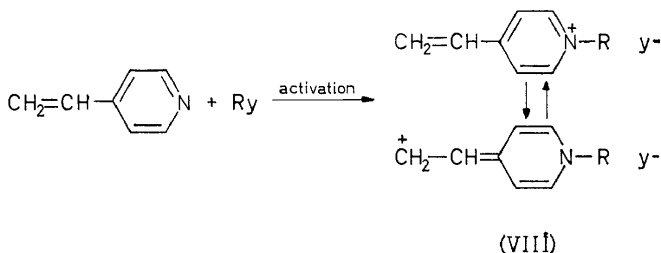
The other extreme case could be represented by the systems where initiator forms strong enough bonds with monomer molecules, with active centres of growing chains and with units of the macromolecules turning out to be the part of the polymer. Recently Kargin, Kabanov, *et al.*<sup>6</sup> have shown that at the temperatures above 5°C the reaction of 4-vinylpyridine (4-VP) with alkyl halides (Menshutkin's reaction) in organic media (benzene, nitrobenzene, acetonitrile, dimethyl sulphoxide, propylene carbonate, methanol) leads not to the expected monomer salts, but to the polymers of the general formula (VII), i.e. the spontaneous polymerization occurs. When 4-VP is in excess the polymer formation stops simultaneously with alkyl halide disappearance; unreacted 4-VP remains in the system. This indicates a close relation between salt formation and polymerization and

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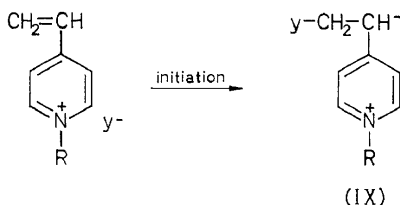


points out that only quaternized monomer molecules participate in the polymerization. Strong inhibitors of radical polymerizations (benzoquinone, diphenylpicryl-hydrazyl, *N*-oxides) do not retard the reaction and do not affect the intrinsic viscosity of the polymers. This rules out a radical mechanism of polymerization. When carrying out the reaction of 4-VP with ethyl bromide in acrylonitrile and styrene media the polymers formed do not contain nitrile or styrene units. Thus, under the reaction conditions employed styrene and acrylonitrile behave as solvents and are not copolymerized with 4-VP. Therefore the usual anionic and cationic mechanisms can be excluded. All these facts go to propose that the polymerization proceeds according to a specific mechanism; this enables selection to be made of the polymer of vinylpyridinium salt molecules formed as a result of Menshutkin's reaction. The proposed mechanism has been corroborated with detailed kinetic measurements.

The first stage limiting the rate of the whole process is Menshutkin's reaction, which can be represented as follows



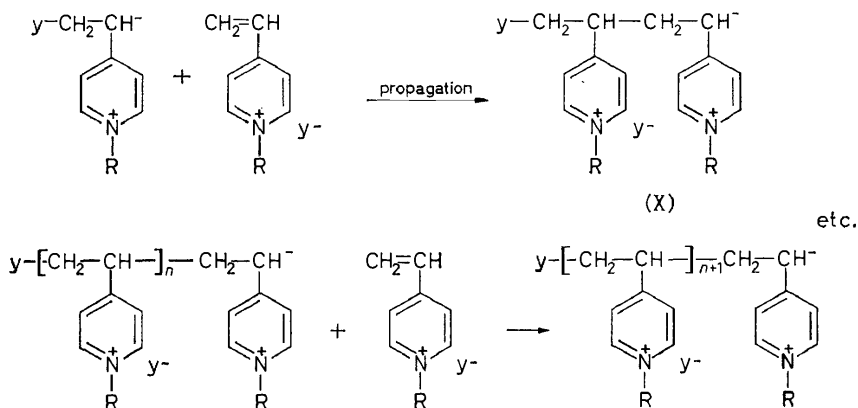
In the molecule of the monomeric salt, owing to the positive charge on nitrogen atom, the considerable shift of  $\pi$ -electrons of the double bond in the direction of pyridine ring occurs which is accompanied by sharp increase of electrophility of the double bond. Therefore, the activated monomer can easily add even weak nucleophilic agents. In the initiation reaction, the anion plays the role of such an agent



(It could be noted that this has close analogy with the well known process of pyridyl ethylation<sup>21</sup>.) The zwitter-ion formed starts chain propagation

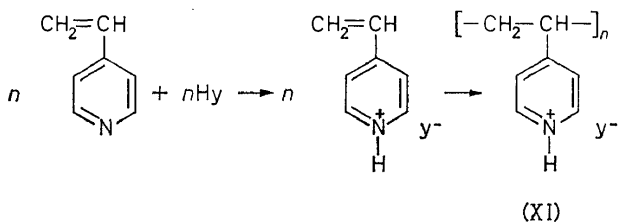
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reaction adding the next molecule of the chemically-activated monomer.



Molecules of 4-VP and other monomers cannot compete for the active centre with the molecule of vinylpyridinium salt, primarily because on the addition of any other monomer there must occur a separation of opposite charges, interacting in the initial active centre through the pyridine ring, and therefore considerable increase of energy of the system (loss of resonance energy and electrostatic effect).

In the case under reference the activator itself undergoes chemical transformation, forms strong bond with the monomer and enters polymer chain [in the scheme (b)  $i = 1, j$  and  $k$  are equal to the degree of polymerization] and cannot be removed from the polymer after the reaction. However, chemical activation of 4-VP (the same is valid for 2-VP) is also achieved by the action of strong proton acids<sup>6, 7</sup>. On mixing 4-VP with sulphuric, nitric, toluene sulphonic, and other acids in benzene, diethyl ether and other solvents at room temperature the corresponding salts of poly-4-VP are formed according to the scheme

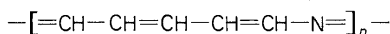


Apparently the mechanism of polymerization is in general similar to that given above but the following treatment of the reaction system with dilute alkali transforms polyvinylpyridinium into polyvinylpyridine, i.e. the activator is easily removed from the polymer. It is significant that on addition of strong acids (e.g. sulphuric) to the solution of 4-VP in styrene only 4-VP salt is polymerized. Neither excess of 4-VP nor styrene is involved in the reaction.

Therefore, conversion of 4-VP into quaternary salts brings about the generation of active centres with extremely high chemical selectivity. The

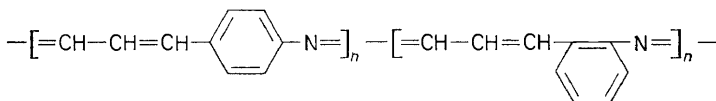
growing chains due to the peculiar nature of active centres can "select" and add only *N*-alkylated or protonized monomer molecules.

As in an essentially related case the ring opening polymerization and copolymerization of complexed aromatic heterocycles (pyridine and quinoline) could be considered<sup>9</sup>. The polymerization of stoichiometric complexes of pyridine and quinoline with zinc chloride has been studied in detail in the temperature range 250–370°C. Heating the melts of pyridine complexes above 330°C and of quinoline complexes above 250°C in the presence of proton containing initiators (HPO<sub>3</sub>, H<sub>2</sub>O, chlorohydrates of pyridine and quinoline) results in the formation of high molecular weight thermostable paramagnetic substances soluble in concentrated mineral acids. Their structures can be presented as (XIII) and (XIV).



Polypyridine

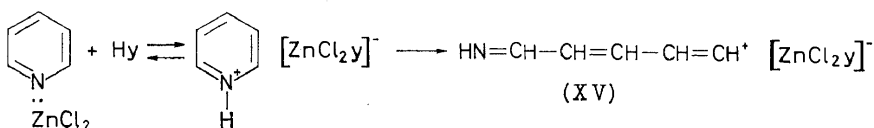
(XIII)



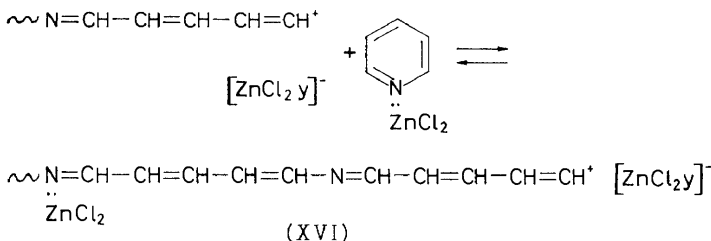
Polyquinoline

(XIV)

The kinetic role of the complexing agent does presumably consist of polarization of carbon–nitrogen bond in aromatic heterocycle which facilitates its opening at the electrophilic attack. The detailed kinetic study by Kargin, Kabanov *et al.*<sup>9</sup> enables us to propose the following reaction mechanism as the most probable one. Initiation with participation of proton donors can be represented by the scheme



(here and further for the sake of simplicity only one of two pyridine molecules bound to zinc chloride are shown). The chain propagation proceeds as the result of attack of complexed pyridine (or quinoline) by carbonium cation



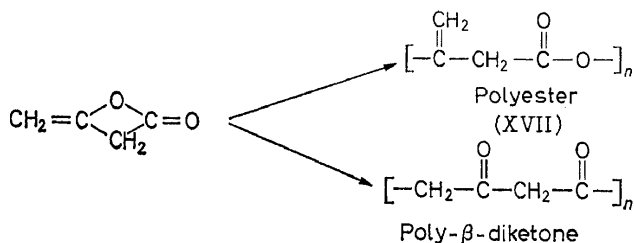
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At the end of the reaction the polymer could be separated from the complexing agent by reprecipitation from the solutions in concentrated mineral acids with water.

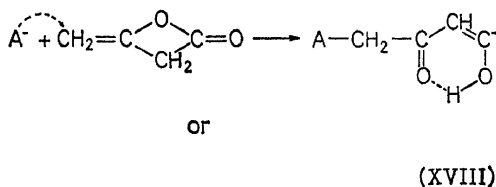
The propagation reaction at the polymerization of aromatic heterocycles is reversible. Therefore, at a given temperature an equilibrium degree of conversion is established in the system which is determined by the equilibrium monomer concentration. From the study of the temperature dependence of the equilibrium conversion it has been shown that polymerization of pyridine and quinoline complexes is characterized by floor temperature (for pyridine complex  $T_{fl} \approx 300^\circ\text{C}$ ,  $\Delta H \approx 13$  kcal/mole,  $\Delta S \approx 19$  e.u.; for quinoline complex  $T_{fl} \approx 240^\circ\text{C}$ ,  $\Delta H \approx 12$  kcal/mole,  $\Delta S \approx 19$  e.u.). The thermodynamic quantities characterizing polymerization of the complexes as has been shown above include correspondingly the difference of enthalpies and entropies of complex formation of activator with the polymer and with the monomer.

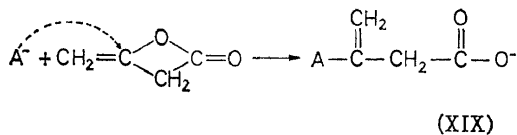
Pyridine and quinoline ring-opening polymerization is not achieved in the absence of complexing agents. Thus chemical activation of these monomers gives the opportunity to get new polymers which could not be obtained by usual synthetic ways. Some years ago by a similar method it had been possible to obtain the products of nitrile polymerization through  $\text{C}\equiv\text{N}$  bond<sup>8, 10</sup>. As starting materials complexes of nitriles with some metal halides were used.

Chemical interaction of monomers and growing chains with the particles of the medium can affect the structure of the units of the polymer formed. Such effect probably takes place at polymerization of diketene initiated with metallic magnesium<sup>11</sup>. It is known that diketene, depending on the nature of the initiator and the reaction conditions, can be polymerized to polyester<sup>12</sup> or poly- $\beta$ -diketone<sup>13</sup>

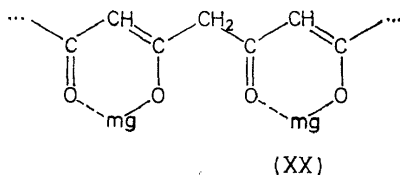


The reaction of diketene with magnesium brings about formation of substances initiating the anionic polymerization of diketene (the mechanism of initiation has been considered in ref. 11). The product obtained is a copolymer with ester and  $\beta$ -diketone units; ratio nearly equal to 1:1. The structure of each monomer unit formed is determined by the direction of nucleophilic attack of the monomer by the growing anion

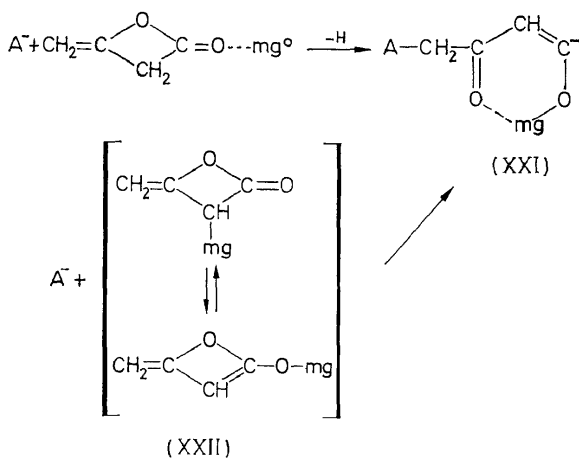




However, in the case of polymerization in the presence of excess of highly dispersed metallic magnesium suspended in the reaction system there occurs evolution of hydrogen and a polychelate (XX) is formed which does not contain ester units and which can be converted into poly- $\beta$ -diketone



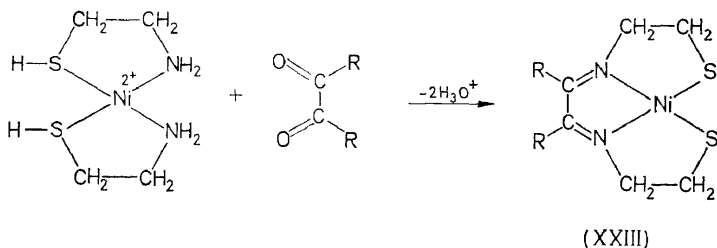
by treatment with acids (mg means equivalent of magnesium). It may be supposed that in this case the reaction proceeds with monomer molecules bound to magnesium according to one of the following schemes



The rising chelate anion is more stable than the anions (XVIII) and (XIX). Therefore, the reaction is exclusively directed to the formation of chelated  $\beta$ -diketone units. In other words the new monomer resulting from diketone and magnesium interaction is chemically activated to form poly- $\beta$ -diketone. It is to be noted that in organic chemistry there are known a number of examples when substances able to coordinate with initial and final products have decisive influence on the direction of chemical reaction (e.g. see ref. 14). As one of the numerous striking examples could be cited the synthesis of Schiff's bases (XXIII) from  $\beta$ -mercaptoethylene amine and  $\alpha$ -diketones in the presence of bivalent nickel (Thomson and Busch<sup>15</sup>).



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The resulting compound forms more stable chelate bonds than the original one. In the absence of the complexing agent instead of Schiff's base thiazolines and mercaptals are obtained. A similar principle for the synthesis of polymers might be of considerable interest.

INTERMOLECULAR EFFECT

In all systems considered above the chemical activation arises from intramolecular effect. However, the chemical interaction of a monomer with the particles of the medium does not always result in electron density redistribution affecting the reaction centres of monomer molecules responsible for the polymerization. Nevertheless such an interaction may lead to considerable acceleration of polymerization, i.e. to *activation* of the monomer in the broad sense if it causes the change of distribution of the reacting species and/or the proper orientation of the reacting centres (intermolecular effect).

The striking example is *p*-methacrylyl-oxybenzoic acid (MOBA) polymerization initiated with benzoyl peroxide in the presence of cetyl oxybenzoic acid (COBA) studied by Amerik, Konstantinov and Krentsel<sup>16</sup>. It was found that MOBA polymerizes in dimethyl formamide solution in accordance with the requirements for the conventional free radical polymerizations (the reaction order with respect to the monomer is 1.1, with respect to the initiator it is 0.5). The equimolecular mixture of MOBA and COBA exists in the form of smectic liquid crystals at the temperature range 87–133°C. The structure of the smectic layer is presented in *Figure 1*. The polymerization rate and molecular weight of the polymer obtained in liquid crystals are considerably higher than those in solution (the molecular weight changes from  $5 \times 10^4$  to  $6 \times 10^5$  at the same monomer concentration). The reaction order with respect to the monomer comes near to 0.

It is quite obvious that the hydrogen bond formation between MOBA and COBA cannot directly influence the reactivity of vinyl groups of the monomer. The polymerization rate and molecular weight increase seems to be a result of mobile organized array formation which as it was shown earlier<sup>17</sup> favours the chain propagation. It is possible that the "organized" double bonds location in smectic layers also affects the mechanism of elementary propagation step. In this respect the observed difference in temperature dependence of microtacticity of the polymers formed in liquid crystals and in solution is very important (see *Table 1*).

The percentage of iso (i), hetero (h) and syndiotactic (s) triads "normally" changes with a rise in temperature when MOBA is polymerized in solution [ $\Delta(\Delta H^\ddagger) = 1025$  cal/mole,  $\Delta(\Delta S^\ddagger) = 0.5$  e.u.]. However, when MOBA is

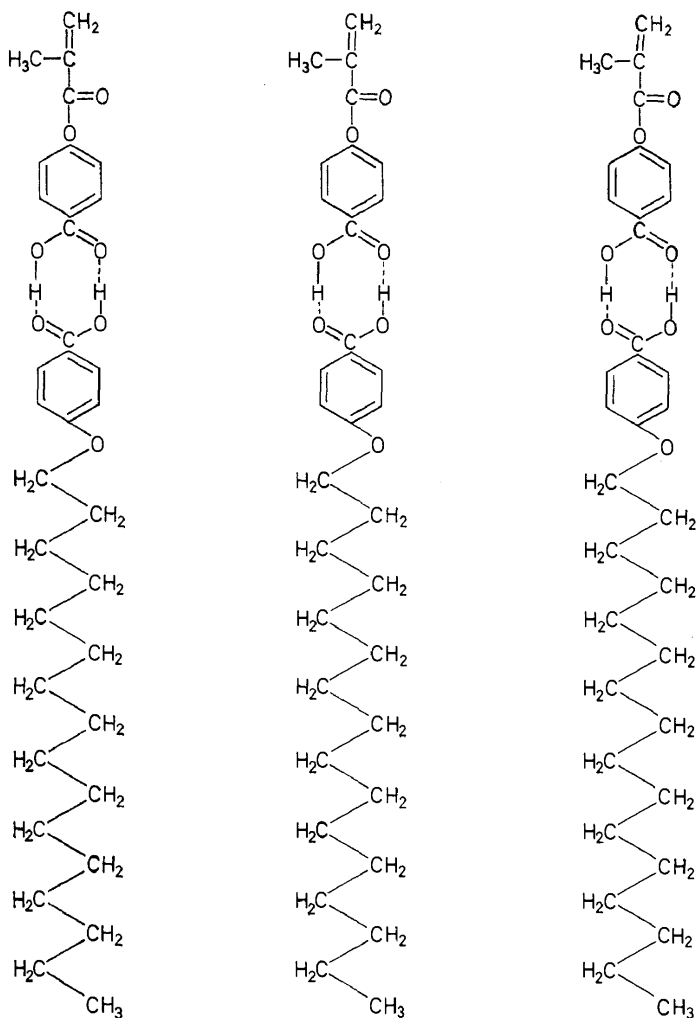


Figure 1. Structure of the liquid crystal smectic layer of the *p*-methacrylyl-oxybenzoic acid-*p*-cetyl-oxybenzoic acid complex

Table 1. Temperature dependence of microtacticity of polymethacrylil oxybenzoic acid<sup>16†</sup>

Polymerization temperature (°C)	In solution			In liquid crystals		
	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	47.0
110	8.7	30.1	61.2	8.0	45.0	47.0
130				8.0	45.0	47.0

† Measured by n.m.r. after converting poly-MOBA into polymethyl methacrylate.

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polymerized in the liquid crystals state the isomer composition of the polymer is rather different and is not dependent upon the temperature at all [ $\Delta(\Delta H^\ddagger) \simeq 0$ ,  $\Delta(\Delta S^\ddagger) = 0.8$  e.u.]. These data at least indicate the difference of energetics of transition states in solution and in liquid crystal.

It should also be stressed that poly-MOBA depolymerization rate at 100°C and higher in the absence of COBA is commensurate with the rate of propagation. Therefore, when MOBA is polymerized in solution a polymerization-depolymerization equilibrium is established and consequently a polymer yield of 100 per cent is not achieved. At the same time the polymerization in liquid crystals leads to complete conversion of MOBA into polymer up to the melting point of the liquid crystals. Thus in the example considered the activator affects not only the kinetics but the thermodynamics of polymerization as well.

The "pure" intermolecular effect becomes apparent in the case of polymerization in channel complexes. It is known that urea and thiourea in the presence of some organic compounds form tetragonal crystals with tubular channels, of molecular diameter filled up with molecules of the organic substance. Some vinyl compounds and dienes being situated in such channels form linear sequences and can be rapidly polymerized under accelerated electrons,  $\gamma$ - or x-ray irradiation. The fast electron irradiation of the channel complexes of 1,3-butadiene with urea and of 2,3-dimethylbutadiene with thiourea leads to the formation of corresponding 1,4-*trans*-polydienes (Brown and White<sup>18</sup>). It is well known that radiation polymerization of these monomers in bulk or in solution is always followed with irregular polymers of mixed structure. The weak van der Waals interaction of diene molecules with the wall of the channel cannot practically induce any electron density redistribution in individual monomer molecules. Therefore, the chemical specificity developed in this type of polymerization, namely the strong increase of relative rate of 1,4-*trans* addition should be mainly ascribed to favourable double bonds orientation, i.e. to intermolecular effect. Strictly speaking the term "chemical activation" can be applied to this phenomenon with the same reserve as the term "chemical compound" to channel complex.

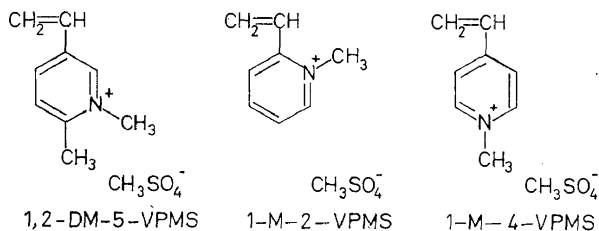
Continuing this line of consideration one may mention the significant increase of polymerization rate in the course of liquid and glassy monomers crystallization<sup>17, 19</sup>. It was shown that such an increase closely connected with mobile organized monomer layers becomes intense on the moving crystal liquid interface, i.e. with intermolecular effect. However, in this case the mobile organized monomer array is caused not by chemical but physical factors. So the "chemical activation" concept degenerates.

## COMBINATION OF INTRA- AND INTER-MOLECULAR EFFECTS: POLYMERIZATION IN MACROMOLECULAR "MATRICES"

In a number of cases the combination of intra- and inter-molecular effects becomes apparent. As has been mentioned above, the quaternary salts of 4-VP and alkyl halides spontaneously polymerize *statu nascendi* in organic solvents. In accordance with the mechanism discussed above one should expect that quaternary VP-salts in which the double bonds are in 5 or 3

position and hence are less polarized should have less tendency to spontaneous polymerization. Indeed the quaternization of 2-methyl-5-vinylpyridine (MVP) by ethyl bromide, methyl iodide, dimethyl sulphate, etc. in organic media is not followed by polymerization: the crystalline monomer salts precipitate. The 4-VP and 2-VP monomer salts with anions of reduced nucleophilicity can also be prepared using some cooled organic solvents (acetone, ethyl acetate, etc.). However, all these monomers spontaneously polymerize in concentrated aqueous solutions.

The author together with Kargin, Patrikeeva, *et al.*<sup>6, 20</sup> studied the spontaneous polymerization 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



It was found that  $\text{CO}_2$ ,  $\text{NaHCO}_3$  (being in equilibrium with  $\text{CO}_2$ ) and  $\text{SO}_2$  were strong inhibitors of spontaneous polymerization. This fact apparently excludes the assumption by Shyluk<sup>21</sup> about radical mechanism and is in a good agreement with specific anionic mechanism of 4-VP salts polymerization in organic media. In the latter case the inhibition may be considered as a result of  $\text{CO}_2$  or  $\text{SO}_2$  addition to carbanion of the active centre.

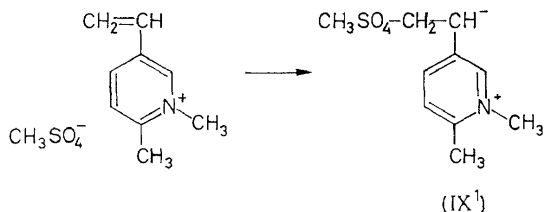
The presence or addition of the inhibitors leads to induction periods on the kinetic curves. In the case of 1,2-DM-5-VPMS it was shown that the induction period related to the rate of generation of active centres according to the simple equation (2) usually applied in the case of strong inhibitors.

$$V_a = [\text{inhibitor}]/\tau \quad (2)$$

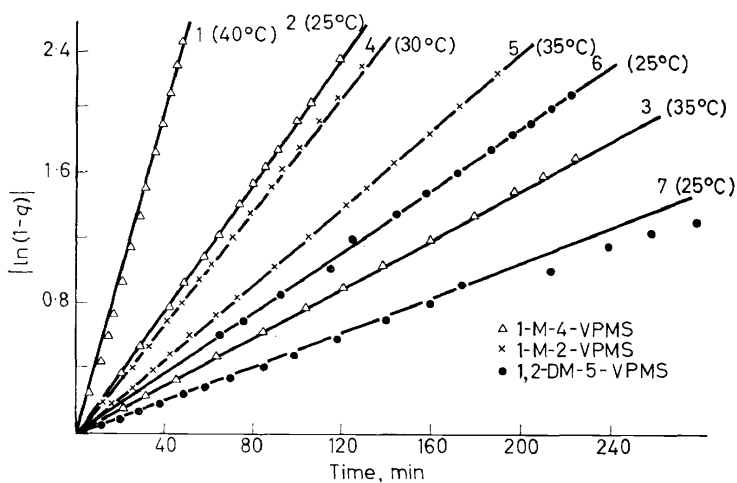
Thus the possibility of direct measurement of  $V_a$  appears.

One may expect that the rate of active centres formation according to the reaction of the type involved in the formation of (IX) would be higher the stronger the polarization of the double bond of quaternary salt molecule. Indeed the  $V_a$  values determined from the experimental data are 3.5–4 orders higher for 1-M-2-VPMS and 1-M-4-VPMS than for 1,2-DM-5-VPMS (for 1,2-DM-5-VPMS,  $k_a$  at 25°C is  $0.4 \times 10^{-6} \text{ min}^{-1}$ ,  $E_a \approx 7 \text{ kcal/mole}$ ). In the case of 1,2-DM-5-VPMS it was shown that initiation reaction was characterized by the first order with respect to the monomer, in good agreement with a scheme of the following type

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At the same time the kinetic curves of polymerization in concentrated aqueous solutions (2.5 mole/l. and higher) were linearized in the first order coordinates (*Figure 2*) up to degrees of conversion  $q$  close to 1. It means that the total reaction was also of the first order with respect to the



*Figure 2.* Typical kinetic curves of the spontaneous polymerization of vinyl pyridinium salts plotted in the first order coordinates. [ $\Delta$ ] 1-methyl-4-vinylpyridinium methyl sulphate; ( $\times$ ) 1-methyl-2-vinylpyridinium methyl sulphate; ( $\bullet$ ) 1,2-dimethyl-5-vinylpyridinium methyl sulphate]. Concentration of the monomers: (1), (2) and (3) and 3.5 moles/l.; (4) and (5), 4 moles/l.; (6), 3 moles/litre; (7), 2.5 moles/l. Temperatures of polymerization are indicated in the figure

monomer. However, the initial rate of conversion  $(dq/dt)_0$  dropped sharply when the initial monomer concentration  $M_0$  was decreased (*Figure 3*) though this characteristic should not at all be a function of  $M_0$  for the usual first order reactions. The intrinsic viscosity (molecular weight) of the polymers formed also markedly decreased with dilution (*Figure 3*). The temperature dependences of the polymerization rate and molecular weight were quite unusual too. When the temperature increased the polymerization rate and intrinsic viscosity went through the maximum (*Figures 4 and 5*).

All attempts to explain the experimental results based on ordinary considerations of homogeneous kinetics have failed. However, the observed regularities could be explained if one assumed that some ordered aggre-

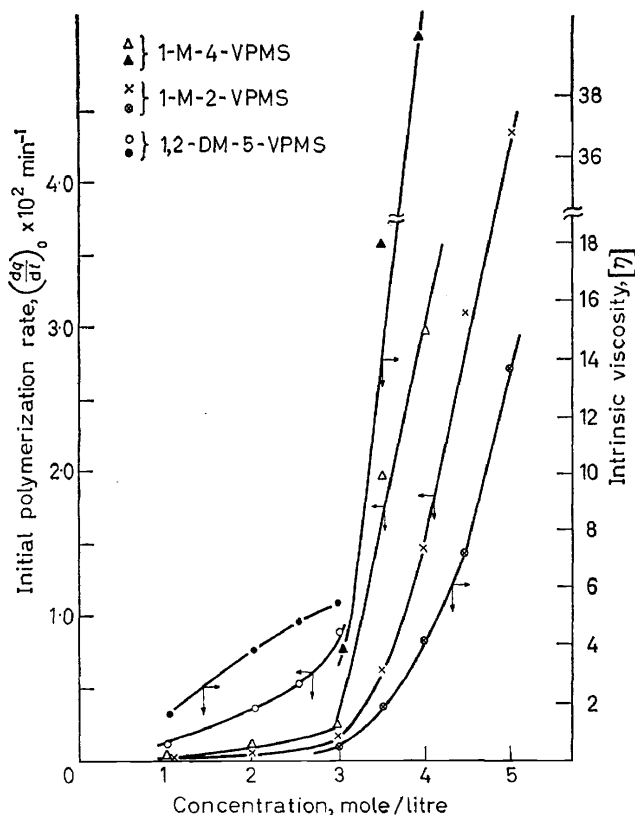


Figure 3. Dependence of the initial polymerization rate of vinyl pyridinium salts and intrinsic viscosity of the polymers on monomer concentration. Temperature 25°C. The viscosity was measured at 25°C in 0.05 N aqueous solution of KBr

gates of monomer molecules (similar to those in liquid crystals present in concentrated solutions) have lifetimes which are at least commensurable with the time of propagation. The hypothetical structure of the ordered aggregate is presented in Figure 6. In this structure the double bonds form the layers stabilized by hydrophobic interaction. One assumes that "organized" monomer molecules reserving enough mobility are easily polymerized if the active centre rises in the ordered aggregate.

Based on independence of the molecular weight upon degree of conversion (it is shown experimentally and proves the stationarity of the process) one may write Eq. (3) for the polymerization rate, where  $M$  is current monomer

$$-\frac{dM}{dt} = V_1 \bar{v} \quad (3)$$

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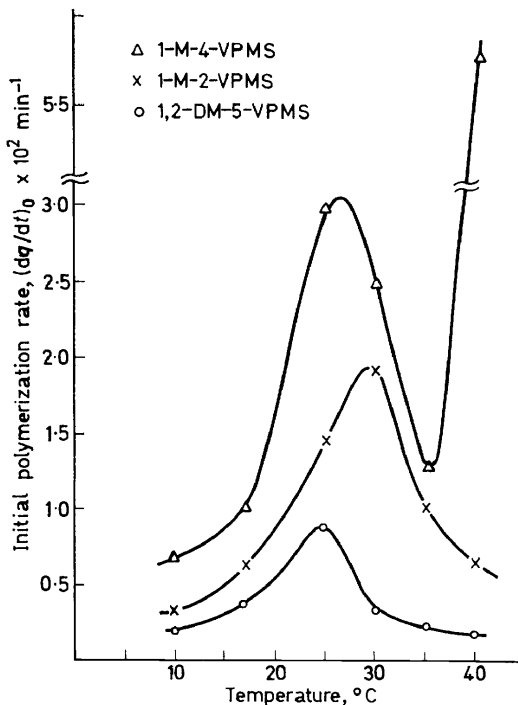


Figure 4. Dependence of the initial polymerization rate of vinyl pyridinium salts on temperature. [( $\Delta$ ) 1-methyl-4-vinylpyridinium methylsulphate,  $M_0 = 4$  moles/l.; ( $\times$ ) 1-methyl-2-vinylpyridinium methyl sulphate,  $M_0 = 4.0$  moles/l.; ( $\circ$ ) 1,2-dimethyl-5-vinyl pyridinium methyl sulphate,  $M_0 = 3$  moles/l.]

concentration,  $\bar{\nu}$  is average length of kinetic chain, and  $V_i$  is the rate of initiation. The experimentally observed first order of initiation with respect

$$V_i = \phi V_a = \phi k_a M \tag{4}$$

to the monomer is expressed in Eq. (4) where  $k_a$  is the rate constant of active centres generation, and  $\phi$  is efficiency of initiation. Noticing that  $q = (M_0 - M)/M_0$  and substituting Eq. (4) into Eq. (3) one obtains:

$$\frac{dq}{dt} = \bar{\nu} \phi k_a (1 - q) \tag{5}$$

At high  $M_0$  the experimental time dependence of  $q$  is described by the following equation:

$$-\ln(1 - q) = \bar{\nu} \phi k_a t \tag{6}$$

which is the result of integration of Eq. (3). If one assumes that some active centre reaching the border of the ordered aggregate is instantly terminated by proton or water molecule addition it should be considered that  $\bar{\nu}$  value

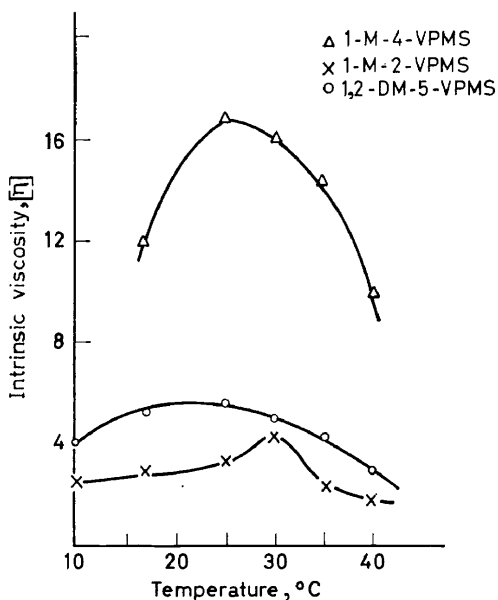


Figure 5. Dependence of the intrinsic viscosity of the polyvinyl pyridinium salts on temperature. Reaction conditions and symbols are the same as in Figure 4

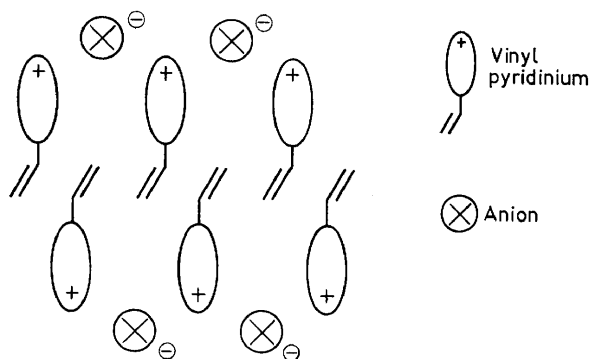


Figure 6. Hypothetical structure of organized aggregate in concentrated aqueous solution of vinylpyridinium salt

is connected with the dimensions of ordered aggregates. In highly concentrated systems the formation of macromolecules does not result in disturbance of neighbouring ordered regions. Therefore,  $\bar{v}$  is not dependent on degree of conversion ( $\bar{v} = \text{const.}$ ) and polymerization kinetics can be described by usual first order equation. However, the dilution of the initial system or sufficient temperature increase leads to decrease of the dimensions ("melting") of ordered aggregates and reduces the rate of polymerization and molecular weight. This consideration is supported by a sharp fall of the viscosity of 1,2-DM-5-PVMS solutions when diluting (Figure 7) and



POLYMERIZATION OF CHEMICALLY-ACTIVATED MONOMERS

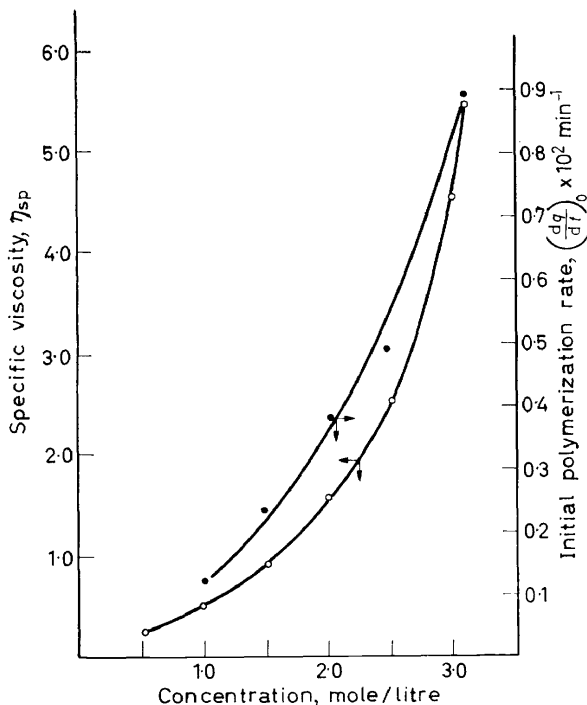


Figure 7. Dependence of specific viscosity and polymerization rate of 1,2-dimethyl-5-vinylpyridinium methyl sulphate in aqueous solution on monomer concentration. Viscosimetric and kinetic measurements were done at 25°C

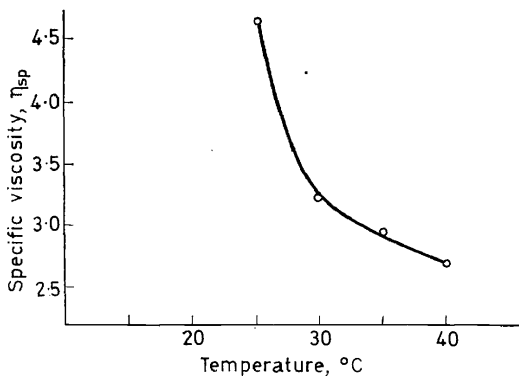


Figure 8. Dependence of specific viscosity of aqueous solution of 1,2-dimethyl-5-vinylpyridinium methyl sulphate on temperature. Concentration 3 moles/l.

heating (Figure 8) which is observed in the same concentration and temperature range as the fall of the polymerization rate and molecular weight.

One of the reasons of polymerization rate increase with temperature at lower temperatures should be ascribed to a positive temperature coefficient of initiation (in case of 1,2-DM-5-VPMS  $E_a = 7 \text{ kcal/mole}$ ). Thus, the maxima

on the rate-temperature curves may be explained by superposition of two opposite factors: increase of the rate of initiation and disturbance of the ordered aggregates. However, this is not enough for interpretation of extremal molecular weight dependences. Nevertheless if one assumes that chain termination occurs not only on the borders of ordered aggregates but also with some probability inside them (i.e. by addition of water molecules penetrated into hydrophobic regions) the extremal temperature dependence of the molecular weight can be satisfactorily explained too. Indeed the maximum average length of the chains which can be formed at given reaction conditions ( $\bar{v}_{\max}$ ) is determined by the average length of ordered aggregates. In general case the number average degree of polymerization DP is expressed as

$$DP = (1 - \lambda) \bar{v}_{\max} + \lambda \frac{k_p}{k_t} \quad (7)$$

where  $k_p$  is a rate constant of propagation,  $k_t$  is a rate constant of termination inside the aggregates,  $\lambda$  is a fraction of the chains being terminated inside. If the activation energy of chain propagation is higher than that of inside termination, at low temperatures the most part of the chains terminates inside ( $\lambda \simeq 1$ ). Then DP is determined by the ratio  $k_p/k_t$  as well as its change with temperature by the difference of activation energies of propagation and termination. In such a temperature range DP increases with temperature rise. At higher temperatures when the ordered aggregates melt and diminish,  $\bar{v}_{\max}$  falls and becomes less than  $k_p/k_t$ . Thus the most part of the chains terminates on the borders ( $\lambda \simeq 0$ ) and DP is determined by considerably decreased  $\bar{v}_{\max}$  value. In the absence of chain transfer reaction the rate of polymerization may be represented by Eq. (8). This expression explains the

$$-\frac{dM}{dt} = V_1 \left[ (1 - \lambda) \bar{v}_{\max} + \lambda \frac{k_p}{k_t} \right] \quad (8)$$

similarity in the dependences of the polymerization rate and molecular weight on reaction conditions observed in the experiment†.

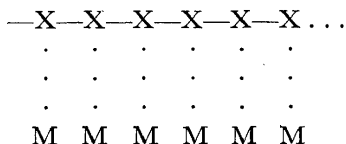
Thus, for the explanation of the regularities of spontaneous polymerization of VP-salts in concentrated aqueous solutions the idea of monomer activation due to intramolecular effect (polarization of the double bond in quaternized monomer molecules) appears to be insufficient. The kinetic data draw the additional assumption about mobile organized monomer aggregates, raised as the result of intermolecular interaction in the reaction medium, i.e. intermolecular effect.

The superposition of intra and intermolecular effects of chemical activation is very closely connected with the problem of "matrix" or "replica"

† The behaviour of 1-M-4-VPMS in the temperature range 35–40°C (Figure 5) is an exception. After the normal maximum the polymerization rate suddenly increases near to six times in spite of continuing decrease of the molecular weight. The activation energy of this increase is about 70 kcal/mole. However, the kinetic curves at 40°C are still linearized in the first order coordinates (Figure 2, curve 1). The observed effect may be the result of sudden rearrangement of ordered aggregates in narrow temperature range.

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polymerization. Let us assume that the particles of activator X are chemically linked and form some long sequences. Then after the monomer addition the following system is to be formed:



Monomer and matrix can be chosen so that chemical reactivity of M bound to X would be much higher than that of free M. Then on each sequence of  $X_n$  the chain  $M_n$  grows from activated monomer molecules.

As an interesting example may be cited the reaction recently described by Furukawa *et al.*<sup>22</sup> Studying the interaction of acetaldehyde with active aluminium oxide the Japanese researchers have found that the adsorbed monomer polymerizes with high yields at  $-70^\circ\text{C}$  to the amorphous rubber-like polyacetal. In i.r. spectrum of acetaldehyde adsorbed on aluminium oxide there is strong shift of carbonyl bond into long-wave region comparatively to the liquid monomer ( $6.4\text{ m}\mu$  instead of  $5.8\text{ m}\mu$ ) that indicates considerable polarization of  $\text{C}=\text{O}$  bond (intramolecular effect). The authors suppose that the monomer adsorption is accompanied by ordering of acetaldehyde molecules in adsorption layer as is shown in Figure 9 (intermolecular effect). Both factors favour fast growth of polymer chains, i.e. chemically activate the monomer.

The above described chemical activation of the double bonds of 4-VP when converting into quarternary salts permits one to carry out the polymerization of this monomer on polyacid "matrices"<sup>6, 23</sup>. Polystyrene sulphonic acid (PSSA), polyethylene sulphonic acid (PESA), polyacrylic acid (PAA),

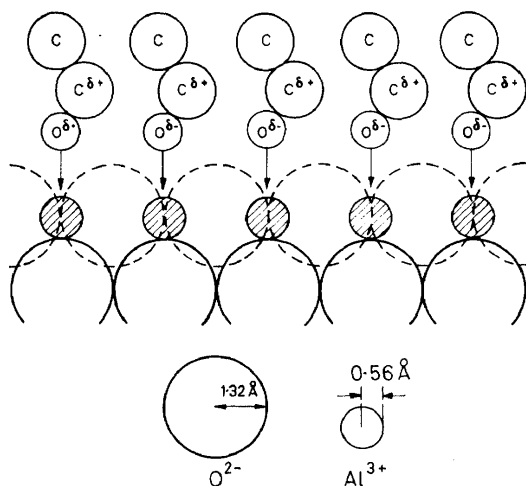
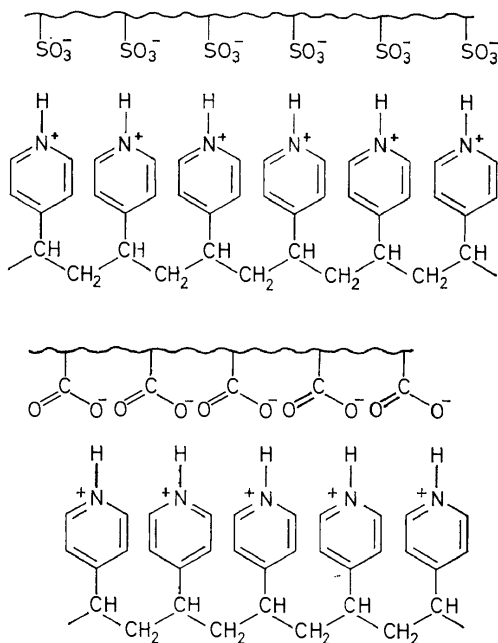


Figure 9. Acetaldehyde adsorbed on  $\gamma\text{-Al}_2\text{O}_3$  surface (Furukawa and Saegusa<sup>22</sup>)

etc. can be used as macromolecular activators in solution. 4-VP being chemisorbed on polyacids in equivalent quantities activates and polymerizes by the mechanism considered above. The reaction leads to poly-salts, i.e. the coupled macromolecules of polyacid and polybase (*Figure 10*).



*Figure 10.* The structure of the product of "matrix" polymerization

4-VP molecules which are short of space on "matrices" remain inactive and do not take part in the reaction.

Polymerization of 4-VP on polyacids proceeds quickly at room temperature even in very dilute aqueous solutions if the degree of polyacid neutralization (i.e. degree of filling of the matrix) is close to 1 because independently on the average concentration the activated monomer molecules are clustered along the chains of the polymer activator. However, the rate of polymerization very strongly depends on the degree of filling, sharply increasing at its approach to 1. The question about the effect of degree of filling of the "matrix" on the polymerization rate is of the primary importance because it is directly related to the study of the character of interaction of the substrate with the activator.

Strong dependence of the polymerization rate on the degree of filling  $\alpha$  can be explained coming from two different suppositions. The first assumes that vinyl pyridinium cations formed at polyacid neutralization are rigidly bound to its units and cannot migrate along the matrix. Then the probability of formation of continuous sequence of activated 4-VP molecules is given by Eq. (9). The average length of the continuous sequences

$$\omega_{\rho} = \alpha^{\rho-1} (1 - \alpha) \quad (9)$$

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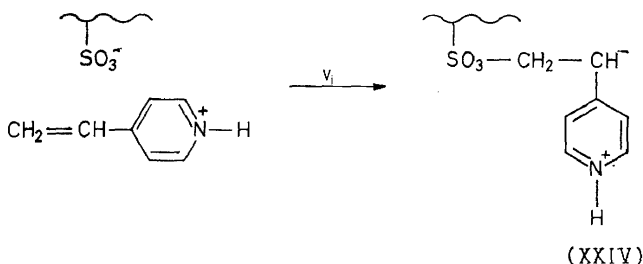
can then be expressed by Eq. (10). If one assumes that the length of the

$$\bar{\nu} = \sum_1^{\infty} \rho \omega_{\rho} = \sum_1^{\infty} \rho \alpha^{\rho-1} (1 - \alpha) = \frac{1}{1 - \alpha} \quad (10)$$

kinetic chain is determined by the length of the continuous sequence of the activated molecules on the matrix, the rate of polymerization can be expressed as in Eq. (11), where  $V_1$  is the rate of initiation. Assuming that

$$V_p = \frac{1}{2} V_1 \bar{\nu} \quad (11)$$

initiation proceeds as the first order reaction (see above) according to the scheme



one may write Eq. (12), where  $k_1$  is initiation constant,  $M$  is monomer

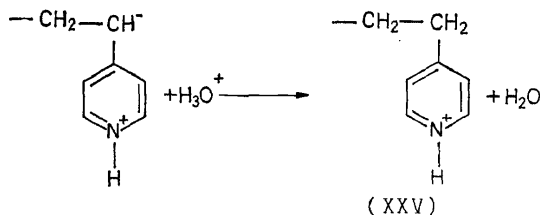
$$V_1 = k_1 M = k_1 \alpha C \quad (12)$$

concentration,  $C$  is concentration of polyacid. Substituting Eq. (12) into Eq. (11) one obtains Eq. (13). The Eq. (13) predicts very strong increase

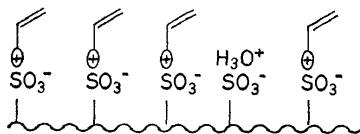
$$V_p = \frac{1}{2} k_1 C \frac{\alpha}{1 - \alpha} \quad (13)$$

of initial polymerization rate at  $\alpha$  approaching 1 (conversion of  $V_p$  into infinity at  $\alpha = 1$  is conditioned by simplification assumed at the derivation that "matrices" are of infinite length).

The second possible explanation is based on the more realistic assumption that activated 4-VP molecules can move in some volume along the "matrix" and the length of the kinetic chain at  $\alpha < 1$  is related to probability of termination of the active centres with unneutralized hydroxonium ions



In fact the construction of the reaction system formed at titration of the polyacid by 4-VP in difference with that accepted for polymerization of vinylpyridinium salts in concentrated solutions cannot provide electrostatic defence of the active centres from protons. The construction can be represented as follows



(XXVI)

In the regions where the "matrix" is not filled with the monomer the probability of collision of the active centre with hydroxonium ion which is attracted there, due to electrostatic interaction with polyanion is high. Thus the termination rate  $V_t$  is expressed by Eq. (14), where  $k_t$  is termination

$$V_t = k_t n [\text{H}_3\text{O}^\oplus] \quad (14)$$

constant and  $n$  is concentration of active centres. The average length of kinetic chain at low conversions when the change of the concentration of the activated monomer can be neglected is given by Eq. (15) and the initial rate of polymerization by Eq. (16), where  $k_p$  is propagation constant.

$$\bar{\nu} = \frac{k_p n M}{k_t n [\text{H}_3\text{O}^\oplus]} = \frac{k_p \alpha C}{k_t [\text{H}_3\text{O}^\oplus]} \quad (15)$$

$$V_p = V_i \bar{\nu} = \frac{k_i k_p}{k_t} C^2 \frac{\alpha^2}{[\text{H}_3\text{O}^\oplus]} \quad (16)$$

Remembering that for a strong acid:

$$\alpha = \frac{[\text{H}_3\text{O}^\oplus]_0 - [\text{H}_3\text{O}^\oplus]}{[\text{H}_3\text{O}^\oplus]_0} \quad \text{and} \quad [\text{H}_3\text{O}^\oplus]_0 = C$$

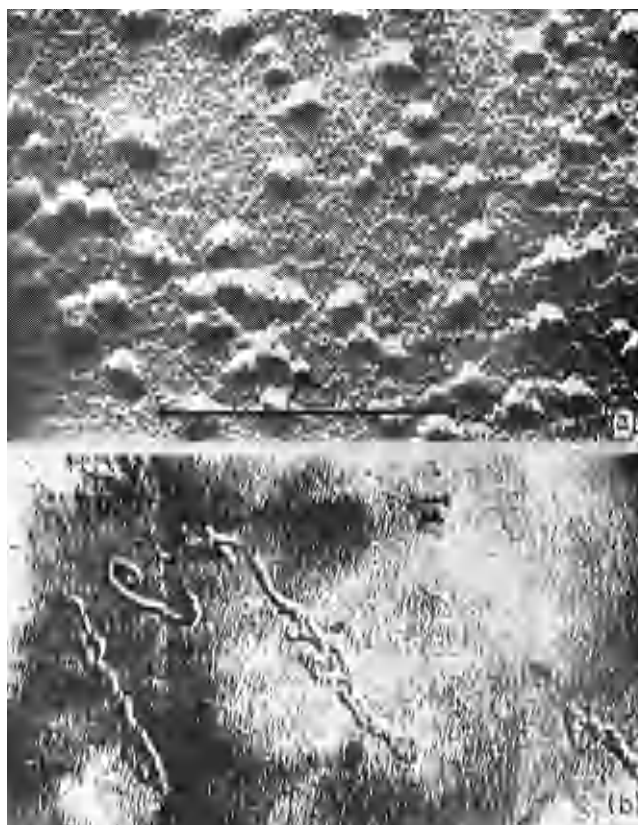
where  $[\text{H}_3\text{O}^\oplus]_0$  is the initial concentration of hydroxonium ions in untitrated

$$V_p = \frac{k_i k_p C}{k_t} \frac{\alpha^2}{1 - \alpha} \quad (17)$$

acid one finally gets Eq. (17). Both Eqs. (17) and (13) predict very sharp increase of the initial polymerization rate at  $\alpha \rightarrow 1$ .

In order to ascertain which of the two assumptions is valid it would be necessary to "spoil the matrices" before the addition of 4-VP by titration with some unpolymerizable base such as an alkali. Then if  $\beta$  is the degree of prior neutralization and the total degree of neutralization is again  $\alpha$ , the Eq. (13) is to be rewritten as Eq. (13'), and Eq. (17) as Eq. (17'):

$$V_p = k_i C \frac{\alpha - \beta}{1 - (\alpha - \beta)} \quad (13')$$



*Figure 11.* Electron photomicrographs of the product of “matrix” polymerization of 4-vinylpyridine on polystyrene sulphonic acid (a) in methanol; (b) in water.

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

As follows from Eqs. (13') and (17') the assumption of rigid fastening of vinylpyridinium ions on the macromolecules of polyacid predicts much higher sensitivity of the conversion rate to prior neutralization at  $\alpha \rightarrow 1$ , than the assumption of termination on hydroxonium ions.

In order to elucidate which of the kinetic equations describes the real process, two sets of experiments were done. In the first one 0.0119 N aqueous solution of PESA was titrated with 0.076 N aqueous solution of 4-VP to pH = 5.6 that corresponds to  $\alpha \simeq 0.999$ . In the second one the solution of PESA was half neutralized with NaOH and then pH was also made up to 5.6 by adding 4-VP solution. Thus in the first set  $\beta = 0$ ,  $\alpha = 0.999$ ; in the second one  $\beta = 0.5$ ,  $\alpha = 0.999$ . The polymerization rate was controlled spectrophotometrically. It turned out that in solutions where  $\beta$  was equal to 0 the conversion rate was 3.6–3.9 times higher than in those where  $\beta$  had a value of 0.5.

Let us now compare the experimental results with predictions of the theory. The relative rate decrease  $\gamma'$ , assuming that there is a rigid fastening of the activated monomers, can be found by dividing Eq. (13) by Eq. (13'). In the resulting Eq. (19), substituting  $\alpha$  and  $\beta$  values from the experimental

$$\gamma' = \frac{\alpha(1 - \alpha + \beta)}{(1 - \alpha)(\alpha - \beta)} \quad (19)$$

data one gets  $\gamma' \simeq 1000$ . So the expected rate of polymerization on "spoiled" matrices should be about 1000 times slower than that on matrices titrated only with 4-VP. The relative rate decrease  $\gamma''$  (Eq. 20) assuming that (i) migration of vinylpyridinium ions takes place along the polyacid molecules, and (ii) there is a termination of active centres on non-neutralized protons, is obtained by dividing Eq. (17) by Eq. (17'). For given values

$$\gamma'' = \frac{\alpha^2}{(\alpha - \beta)^2} \quad (20)$$

of  $\alpha$  and  $\beta$ , Eq. (20) gives  $\gamma'' \simeq 4$ ; this value agrees with the experimental value.

It is significant that the morphology of the products of 4-VP polymerization on polyacids is closely related to the shape of the "matrix" in solution. Electron microscopic study has shown that in the case of polymerization in methanol, where macromolecules of polyacid are coiled, the polysalt is formed as disordered globular aggregates. However, polymerization in water, where "matrices" are ionized and straightened, produces the distinctive fibrillous structures (*Figure 11*).

Thus the chemical activation of 4-VP with polyacids is really attributed to combination of intra- and intermolecular effects. It should be emphasized that the conversion of 4-VP into vinyl pyridinium ion only is not enough for



realization of the process with sufficient rates in aqueous media. In diluted aqueous solutions of 4-VP salts of monomeric acids spontaneous polymerization is much slower or practically does not proceed. In equimolar mixtures of 4-VP and glacial acetic acid during several days some traces of polymer are formed. At the same time a 50 per cent conversion of 4-VP and PAA salt into polysalt in 0.092 N aqueous solutions at 20°C is achieved in 35 min. It is difficult to explain the observed acceleration coming from low molecular to high molecular weight activators with trivial concentration effect.

Polymerization on macromolecular activators may be considered as a simplest model of synthesis of macromolecules in living cells. It is well known that prior chemical activation of the substrate is one of the fundamental principles of biochemical processes.

### CHEMICAL ACTIVATION AT RADICAL POLYMERIZATION

It is known that the properties of free radicals and the rates of radical reactions in solution are comparatively small depending on the properties of reaction medium (in particular on its polarity). But it is valid in cases where particles of the medium are not able to enter into specific chemical or semi-chemical interaction with the reacting particles. Even a relatively weak chemical interaction of the functional groups of radical or monomer with the medium can affect propagation constants at radical processes.

A systematic study of the role of some organic complexing agents in radical copolymerization was recently carried out by Ryabov, Semchikov *et al.*<sup>24</sup> They specially showed that the introduction of proton donors into the system: styrene (St)-2-VP appreciably changes the composition of copolymers at radical initiation and also (this is of particular importance) the character of composition curves. In *Table 2* are given the copolymerization constants

*Table 2.* The effect of organic complexing agents on copolymerization constants for styrene ( $M_1$ ) and 2-vinylpyridine ( $M_2$ )<sup>24</sup>

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

obtained in the copolymerization of styrene and 2-VP in the presence of different proton donors (complexing agents); pK values of the complexing agents are also given.

At bulk polymerization styrene and 2-VP do not have the tendency to alternate. In all monomer ratios the copolymer is somewhat enriched with 2-VP.

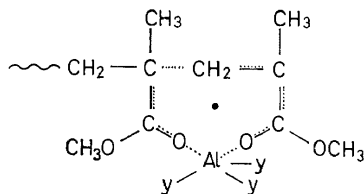
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In the presence of proton donors there appears to be a tendency to alternate; this tendency increases with an increase in acidity of the donor. This may be due to the positive polarization of double bond in 2-VP molecule as a result of the formation of hydrogen bond between nitrogen atom of pyridine ring and the complexing agent. This inference is to some extent confirmed by treatment of the data by means of Hummett's equation and Q-e scheme. Even more pronounced effect on radical polymerization is caused by strong inorganic complexing agents.

In 1958 Bamford, Genkins and Johnston<sup>25</sup> had shown that the rate of acrylonitrile (AN) polymerization initiated by radical initiators in dimethylformamide was appreciably increased by the addition of LiCl which complexed with C≡N groups. The effect was hypothetically explained with the idea of the higher reactivity of complexed propagating radicals. Two years later Kargin, Kabanov and Zubov<sup>26</sup> had shown that the rate of photo-initiated polymerization of methylmethacrylate (MMA) saturated with zinc chloride was sharply increased at the crystal-liquid interface. At the same time Parrot and Monteiro<sup>27</sup> confirmed Bamford's results by discovering the acceleration of the radical polymerization of AN on the addition of LiCl, MgCl<sub>2</sub> and AlCl<sub>3</sub>. The data on the effect of ZnCl<sub>2</sub> on kinetics of polymerization and copolymerization constants had been obtained by Imoto *et al.*<sup>28</sup>. The kinetic measurements by Bamford *et al.*<sup>29</sup> proved that during photopolymerization in the system MMA-ZnCl<sub>2</sub> the rate increase was caused by the increase of chain propagation constant. Termination constant was practically unchanged.

The question about the mechanism of the increase of rate of radical chain propagation in the presence of inorganic complexing agents is now a subject of detailed study. The first attempt at theoretical interpretation of the phenomenon was made by Tazuke *et al.*<sup>30</sup> on the basis of molecular orbital calculations. Using the simple LCAO approximation these workers calculated the values of super delocalizability  $S_r^B$  (regarded as a measure of the monomer reactivity) and stabilization energy of the transition state  $\Delta E_{rs}$  in the case of complexes of differently substituted VP, AN and MMA with zinc chloride and obtained results which were in qualitative agreement with the experiment. Such calculations in fact are expected to explain intramolecular effects of complexing agents. However, in some cases chemical activation apparently could not be explained by intramolecular effect alone especially at polymerization in bulk or in concentrated solution in the presence of stoichiometric or close to stoichiometric quantities of complexing agents.

Some light on the problem was shed by the results of Zubov *et al.*<sup>31</sup> studying MMA photopolymerization in bulk in the presence of aluminium chloride and aluminium bromide. The kinetic data, study of i.r. spectra of complexed monomer and e.s.r. spectra of complexed radicals enabled the authors to put forward some considerations about the mechanism of the polymerization acceleration. It is supposed that at a low content of inorganic activators (i.e. at the ratios of monomer: activator considerably higher than stoichiometric) the observed acceleration is mainly attributed to intramolecular effect. The hypothetical structure of the transition complex can be expressed by the structure (XXVII).



(XXVII)

The unpaired electron of complexed radical which according to e.s.r. data spends part of the time on Al atom (spin density on Al is about 1 per cent) is transferred in the transition state to monomer molecule. This elementary step is supposed to proceed with higher probability than the usual radical addition. Thus the propagation constant in the presence of the complexing agent turns out to be higher. However, such an explanation is not enough to account for the kinetic data at monomer complexing agent ratios close to stoichiometric. Probably in this case the important role belongs to rising of mobile organized array of complexed MMA molecules facilitating chain propagation as it occurs, e.g. in some liquid crystals (intermolecular effect).

Quite recently Nechaev, Zubov and Kabanov<sup>32</sup> have observed acceleration of photoinitiated MMA polymerization in the presence of anhydrous sulphuric acid. The rate of polymerization and molecular weight of the polymer formed increase with concentration of sulphuric acid in the system approaching a maxima (Figure 12). The viscosity of the initial reaction

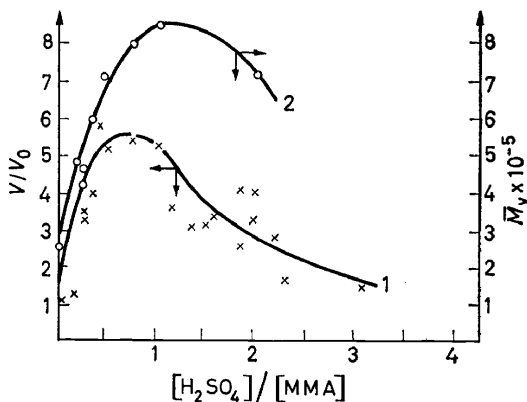


Figure 12. Dependence of the rate of polymerization of methyl methacrylate in bulk (curve 2), and of molecular weight of the polymer (curve 1) formed on methyl methacrylate-H<sub>2</sub>SO<sub>4</sub> molar ratio. Temperature 20°C.

mixture also attains maximum value at H<sub>2</sub>SO<sub>4</sub>: MMA ratio near to 1; this indicates some strong association of MMA molecules complexed with sulphuric acid. It may be supposed that the rising of these associates, i.e. intermolecular effect is one of the reasons of chemical activation of MMA.

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An understanding of the intramolecular effect is not enough to explain the sharp increase in the rate of radiation and photo-induced polymerization of allylic monomers in the presence of zinc chloride<sup>31, 33</sup> when equimolar quantities of  $ZnCl_2$  are used; allylacetate (AA) is polymerized 5.5–6 times faster than pure AA. The rate of allyl alcohol (AAl) polymerization at molar ratio  $AAl:ZnCl_2 = 2$  increases 24 times. As long as the double bond in allylic monomers and the unpaired electron in the corresponding propagating radicals are not conjugated with functional groups participating in complex formation it is hard to expect that introduction of zinc chloride considerably changes their reactivity. One of the possibilities consists in the activation of complexed allyl radicals of chain transfer. But accounting for only this possibility does not permit one to explain completely the observed kinetic dependences. Obviously the explanation is to be looked for in a combination of intra- and inter-molecular effects.

Radical polymerization in the presence of complexing agents is one of the recently originated fields of investigation which development may lead to principally new trends in polymer chemistry and probably to the establishment of principally new ways to control the rates and stereochemistry of radical processes. Especial perspectives seem to have started in some laboratories by studying monomer chemical activation by charge transfer complex formation.

### CONCLUSION

The polymerization of chemically-activated monomers can be considered as an element of the general problem of influence of interaction between the substrate and the medium on the substrate ability to further reaction. On an average the introduction of the usual concept "medium" is to some extent the result of not sufficient information of the researcher about the nature and distribution of specific interactions on molecular level in the reaction system. This averaging creates big conveniences at analysis and probably is justified in the case of weak interactions. However, it bears the fundamental limitations on the way of studying detail mechanism of chemical transformation. In this paper are described the systems for which the necessity to establish the term "interaction with the medium" is quite obvious. Somewhat more wide consideration of the problem of monomer-activator enables us to come to the more general conclusion. Let us consider the system where the number of monomer molecules somewhat exceeds the number of activator molecules. If activator is bound with units of forming polymer as strong or stronger than with monomer molecules the concentration of activated molecules is permanently decreased in the course of the reaction. Actually this means that in the initial system part of the less active monomer is replaced by the more active one. The examples of such systems are given above. If the bonds between activator and units of polymer chain are much weaker than those between activator and monomer one activator molecule can act many times and facilitate the conversion of a number of monomer molecules into polymer. The concept of "activator" is linked with the classical concept of "catalyst"; the polymerization of chemically activated *N*-carboxyanhydrides described above can be considered as an example. And finally the activator molecule interacts with

the end of the growing chain considerably strongly than with monomer molecules and monomer units of the polymer. During chain propagation the activator should be kept on the growing end. In terms of the accepted interpretation of catalytic polymerizations the activator is regarded as the essential part of the catalytic complex carrying the chain process; in this way it proceeds (e.g. at lithium polymerization of MMA, dienes, etc.) in the presence of organic donors (tetrahydrofuran, amines, etc.).

Between the three extreme cases it might be a great number of intermediate variations. It is known to have a number of deviations from the usual catalyst behaviour. It is not excluded that these "deviations" are to be regarded as the results of the general rules pertinent to the systems of intermediate type. This consideration is applicable to a wide variety of other chemical processes besides polymerization. Further progress in this field may probably lead to generalized treatment of the problems of catalysts, active solvents, modifying agents, etc.

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\* Thermodynamic consideration in this paper is not correct.

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