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Reactivity of Allyl Monomers in Radical Polymerization

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ABSTRACT

It was shown that the difference in the polymerizability of a series of allyl monomers, e. g., vinylacetic acid, allyl acetate, dimethylvinylcarbinol, diallyl ether, allyl alcohol, dimethylallylamine, diallylamine, and allylamine is related to the polar effects of the functional groups, whose influence determines the relative stability of the C–H bond at the α-position and thus the rate of the chain transfer to the monomer (degradative chain transfer) as the result of this effect. The initial polymerization rates obey the Hammett-Taft equation, $\log(1/V_0) = \text{const} + \rho\sigma^0$, where ρ is equal to -2. The study of the effect of different acids on polymerization kinetics of allyl monomers and molecular weights of products has revealed that the increase in polymerization rate depends on the nature of monomer, molar ratio of acid and monomer, and the nature, functionality, strength, and concentration of the acid. A kinetic scheme was proposed to determine the contribution of different factors into the overall effects. From the determination of kinetic parameters, one can see that the stronger the link between proton and the group X, which ultimately depends on the basicity of monomer, the more the value of the constant of the chain transfer rate to the monomer is decreased as the result of protonation. The second factor which is responsible for the increase in polymerization rate is the conversion of degradative chain transfer into effective chain transfer. This is proved by showing that the value of probability of initiation of the chain transfer with allyl radicals $CH_2{=}CH{-}\dot{C}H{-}X$ is close to 1. Correlation was found between the polymerization rates of protonated monomers and pK values which characterize the nucleophilicity of the group X.

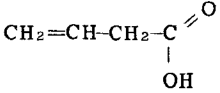
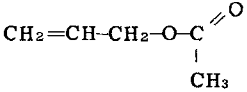
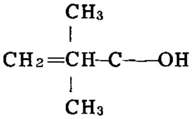
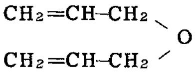
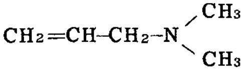
It is known that allyl compounds $CH_2{=}CH{-}CH_2X$ usually polymerize with low reaction rates and give oligomeric products because of degradative chain transfer to the monomer [1-3]. It has been shown in earlier works [4-6] that in the presence of inorganic modifying agents, i. e., complexing agents, Lewis or protic acids, the rates of polymerization and the molecular weights of the polymers were increased. The fact which needs attention here is that the rates of polymerization of the monomers, both in the presence and absence of complexing agents, depend on the nature of the functional group of the monomer. In our work we have studied quantitatively the kinetics of the radical polymerization of allyl monomers in relation to the nature of the functional group X, both in the presence and absence of the complexing agent.

The experimental technique of polymerization of allylamine (AAM), dimethylallylamine (DMAAM), and diallylamine (DAAM) were described previously [4], as were procedures for polymerization of allyl alcohol (AAl) and allyl acetate (AAc) [5, 6]. A similar technique was used for the polymerization of diallyl ether (DAEt) and of vinylacetic acid (VAcA). The physical constants of the monomers are given in the Table 1.

The absolute rates of the radiation-induced polymerization of a number of allyl monomers identically measured ($I_\gamma \cong 300$ r/sec, t = 20°C), are given in Table 1. Figure 1 represents the initial rates of polymerization as a function of pK.

One can see that the absolute rates of the polymerization depend in a definite way on the nature of the functional group in the monomer. The functional group could be characterized by pK values, where pK_a is defined [7] as the inverse logarithm of the dissociation constant of the acid derived from the corresponding conjugated base, i. e., pK_{BH^+}, where B is the base and BH^+ is its protonated form, and with the values of the Taft constant σ_0, which characterizes the polar effects of the functional groups [8]. One can see that the rate decreases with the increase in the pK values and increase with σ_0 (Table 1). In Figure 1 we can also see that the diallyl monomers,

TABLE 1. Physical Constants and Absolute Rates of Radiation-Induced Polymerization of Different Allyl Monomers[a]

Monomer	Structure	Bp (°C)		n_D^{20}		d_4^{20}	pK	σ^0[b]	$V \times 10^6$ (mole/ liter-sec)	$[H_3PO_4]/[M] = 3$ $V \times 10^6$ (mole/ liter-sec)
		Lit.	Exptl	Lit.	Exptl					
Vinylacetic acid (VAcA)	 $CH_2{=}CH{-}CH_2{-}C(=O){-}OH$	163	77-19	1.4257	1.42565	1.013	-6.1	0.36	12.5	45.4
Allyl acetate (AAc)	 $CH_2{=}CH{-}CH_2{-}O{-}C(=O){-}CH_3$	103-104	105	1.4045	1.4045	0.928	-6.5	0.36	12.0	48.2
Dimethyl vinyl carbinol (DMVC)	 $CH_2{=}CH{-}C(CH_3)_2{-}OH$	97-98	96-97	-	1.4170	0.824	-3.8	-	4.9	-
Diallyl ether (DAEt)	 $(CH_2{=}CH{-}CH_2)_2O$	94.3	93-95	1.4163	1.4170	0.826	-3.6	0.06 for O–CH₃	4.1	34.3
Allyl alcohol (AAl)	$CH_2{=}CH{-}CH_2{-}OH$	96.7	96-98	1.4134	1.4134	0.849	-2.0	0.13	4.0	72.0
Dimethylallyl-amine (DMAAM)	 $CH_2{=}CH{-}CH_2{-}N(CH_3)_2$	64/743	62-63	1.3991	1.4009	0.722	8.7	-0.15	1.0	-
Diallylamine (DAAM)	$(CH_2{=}CH{-}CH_2)_2NH$	109-111	109-110			0.788	9.3		0.8	234.0
Allylamine (AAM)	$CH_2{=}CH{-}CH_2{-}NH_2$	52.9	52-54	1.4205	1.4205	0.762	9.5	-0.14	1.3	260.0 (50%) 450.0 (87%)

[a] $t_{\gamma\text{-irr}} = 20°C$; $I_{\gamma\text{-irr}} \cong 300$ R/sec.

[b] As the values of σ^0 for the functional groups of aliphatic compounds are not given in the literature, we have used the values of σ^0 for the m-substituents in the benzene nucleus.

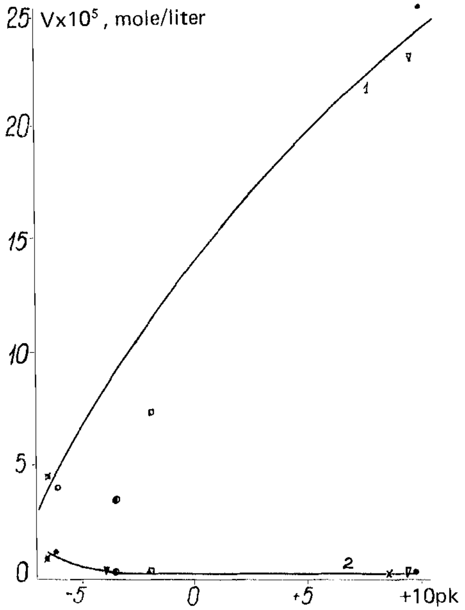


FIG. 1. Initial polymerization rates as functions of pK (1) in the presence of H_3PO_4 (87%); (2) in the absence of acid with various monomers: (⊠) AAC; (○) VAcA; (▼) DMVC; (○) DAEt; (□) AAl; (×) DMAAM; (▽) DAAM; (●) AAM. $t_{\gamma\text{-irr}} = 20°C$; $I_{\gamma\text{-irr}} \cong 300$ R/sec; $[A]/[M] = 3$.

i. e., diallylamine and diallyl ether, also behave kinetically in the same way as the monoallyl monomers.

The difference in polymerizability of the monomers can be attributed to the polar effects of the functional groups. The more powerful the electron donor group is, the greater the ease with which chain transfer to the adjacent $-CH_2$ group takes place with the formation of a more and more stable chain transfer allyl radical $CH_2{=}CH{-}CHX$. This assumption is in accord with the data obtained previously [9], where it was shown that the increase in the electronegativity value of the functional group in the molecule of N-substituted allylamine stabilized the α–C–H bond. By studying the styrene polymerization in the presence of N-acyl-substituted allylamine, it was shown that the values of chain transfer constant decreased, with the increase in the electron-accepting capacity of the functional group attached to the nitrogen atom. The quantum chemical

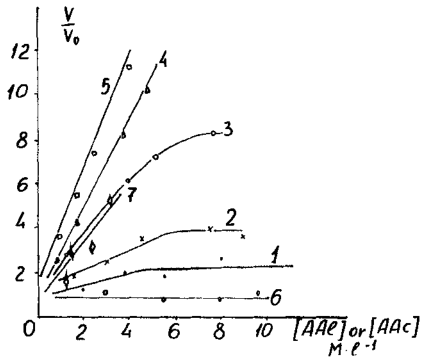


FIG. 2. Dependence of the relative polymerization rate on the concentration of AAl, $[H_3PO_4]/([AAl] + [PAl])$: (1) 0.314; (2) 0.63; (3) 0.945; (4) 1.41; (5) 2.88; (6) 0; and dependence on (7) the concentration of allyl acetate, $[H_3PO_4]/([AAc] + [EAc]) = 3$. In the presence of H_3PO_4; $t_{\gamma\text{-irr}} = 20°C$; $I_{\gamma\text{-irr}} \cong 300$ R/sec.

calculations showed that under such conditions the electron density on the nitrogen atom decreases, while on the double bond it remains unaffected.

It is known [1-4] that the rate of the polymerization of allyl monomers can be expressed by the equation:

$$V_0 = V_{in}K_p/K_{tr}$$

where V_0 is the initial rate of polymerization, V_{in} is the rate of initiation, and K_p and K_{tr} are rate constants of propagation and chain transfer, respectively. The applicability of this equation for the description of allyl polymerization was tested in this work for allyl alcohol. It was shown to be first order with respect to the dose rate and zero order with respect to the monomer concentration when propyl alcohol (PAP) was used as a diluent (see Fig. 2, curve 6).

It is assumed here that the effect of the nature of the functional group on the rate of chain transfer is linked with the polar effects of the functional groups. One can expect that for a set of allyl monomers, the dependence of the chain transfer constant on the nature of the functional group can be presented in the form of the Hammett-Taft equation,

$$\log K_{tr} = \text{const} + \rho\sigma_0$$

where σ_0 is the Taft constant and ρ is a constant for a specific reaction. If the rate of the initiation and the value of K_p do not depend on the nature of the functional group of the monomer, then the difference in the rates of the polymerization of allyl monomers can only be attributed to the difference in the values of chain transfer constant K_{tr}. Therefore it may be considered that the value of $\log 1/V_0$ will be a linear function of σ_0, and the slope will be equal to ρ; hence the equation

$$\log 1/V_0 = \log K_{tr} - \log V_{in}K_p$$

will take the form

$$\log 1/V_0 = \text{constant} + \rho\sigma_0$$

In Fig. 3 it is shown that the value of $\log 1/V_0$ depends linearly on the Taft constant, which provides additional support for the argument of the independence of the initiation and propagation rate constants on

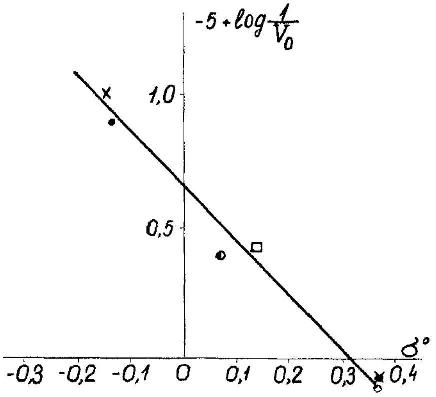


FIG. 3. Dependence of polymerization rate on Taft constant in the coordinates of the Hammett-Taft equation in the polymerization of $CH_2{=}CH{-}CH_2X$. Monomer and reaction conditions as in Fig. 1.

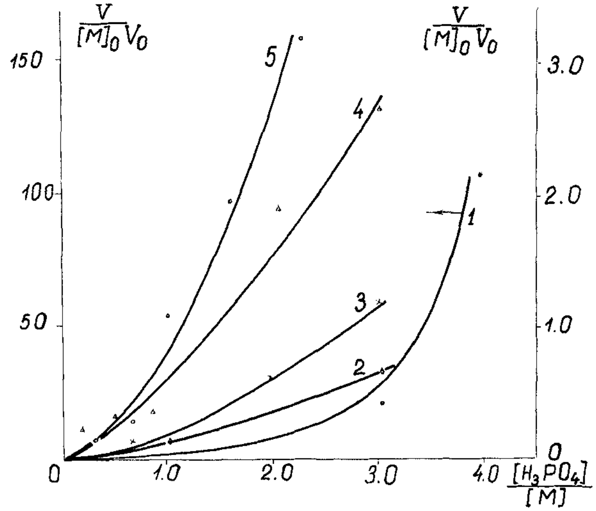


FIG. 4. Dependence of $V/V_0[M_0]$ for polymerization of different allyl monomers on molar ratio $[H_3PO_4]/[M]$: (1) DAAM, (2) VACA; (3) AAc; (4) DAEt; (5) AAl. t = 20°C; $I_{\gamma\text{-irr}} \cong 300$ R/sec.

the nature of the monomer. These results confirm that the difference in the rates of the polymerization of allyl monomers depends mainly on the rate constants of the degradation chain transfer, which in turn is determined by the nature of the functional group. A high absolute value of ρ which is almost equal to -2, shows how sensitive the chain transfer is towards the electron donor properties of the functional groups. Almost a linear dependence between log $1/V_0$ and pK is also observed (Fig. 9, curve 1).

As mentioned earlier, the rates and the molecular weights of the products of polymerization of allyl monomers can be increased in the presence of Lewis acids and protic acids. In our work we have studied the effects of the following acids: acetic, hydrochloric (37%), sulfuric (93%), phosphoric (50%, 65%, 75%, and 87%), polyphosphoric (with 74% and 76% P_2O) and methylphosphoric. The results are shown in Figs. 4-6. One can see that in the presence of acids the polymerization rates are increased in all cases. In Fig. 4 the dependence of the relative rates on the molar ratio of acid to monomer [A]/[M] for phosphoric acid (87%) with different monomers is shown. It is clear that in all cases the rate increases with the ratio [A]/[M], but the relative increase in the rates at a fixed molar

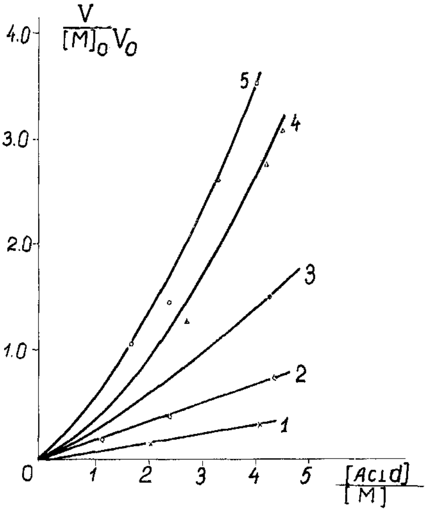


FIG. 5. $V/[M_0]V_0$ for polymerization of diallylamine in the presence of different acids: (1) CH_3COOH; (2) HCl, (3) H_3PO_4 (50%); (4) H_3PO_4 (87%); (5) H_3PO_4 (65%). $t_{\gamma\text{-irr}} = 20°C$; $I_{\gamma\text{-irr}} \cong 300$ R/sec.

ratio is higher, the more basic the functional group in the monomer (Tables 1 and 2 and Fig. 1). The dependence of the relative rates on the molar ratio [A]/[M] for the same monomer (diallylamine or allylamine) with different acids, such as the acids which differ both in functionality (HCl, H_3PO_4), strength (HCl, CH_3COOH), and in concentration is shown in Figs. 5 and 6. The relative rates rise with increasing strength and functionality of the acid. This means that in the presence of the same acid the relative rate depends on the nature of the monomers, and with the same monomer it depends on the nature, strength, functionality, and the concentration of the acids. Of all the acids, phosphoric acid increases the rate the most (Fig. 5 and Table 2). This behavior of phosphoric acid indicates that the functionality of the acids plays an important role in the activation of the polymerization of the allyl monomers. From this we conclude, that the following factors determine the increase in polymerization rates: (1) nature of the monomers; (2) molar ratio of the acid to the monomer; (3) nature, functionality, strength, and concentration of the acid.

A detailed kinetic scheme for a number of allyl monomers was drawn to explain the role of acid. In the system AAl-H_3PO_4, the experimentally determined reaction order with respect to the rate

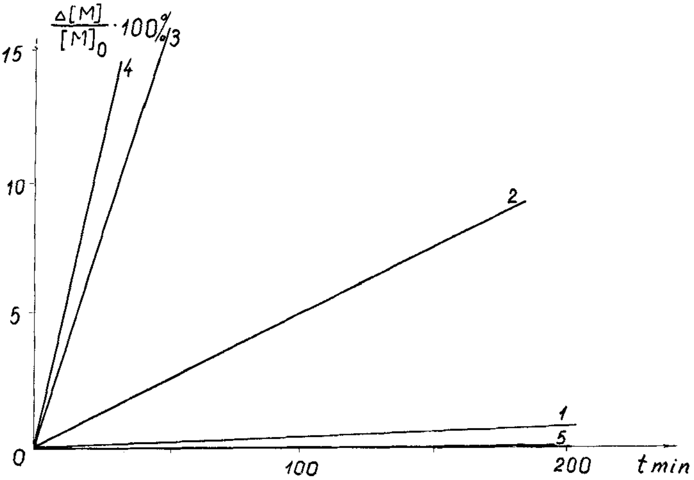


FIG. 6. Kinetics of the polymerization of allylamine in the presence of different acids: (1) $CH_3COOH/[AAM] = 2$ ($V/V_0 \cong 21.5$); (2) $[H_3PO_4]$ (50%)/[AAM] = 1.5 ($V/V_0 \cong 100$); (3) $[H_2SO_4]/[AAM] = 2.4$ ($V/V_0 \cong 550$); (4) [polyphosphoric acid]/P_2O_5 = 74% [AAM] = 2.3 ($V/V_0 \cong 1760$); (5) in the absence of acids. $t_{\gamma\text{-irr}} = 20°C$; $I_{\gamma\text{-irr}} \cong 300$ R/sec.

of the initiation decreases from 1 to 0.5 with the increase in molar ratio [A]/[M] from 0 to 0.5, but at [A]/[M] = 1 its value again increases to 1 (Fig. 7). The same behavior was observed in the case of the AAc-H_3PO_4 system (Fig. 7). In the AAM-H_3PO_4 system the polymerization was studied under the conditions of complete protonation of the monomer ([A]/[M] > 2). In this system, initiators were used as well as γ-ray initiation. The reaction order with respect to initiation rate in both cases was found to be 1.

Figure 2 shows the dependence of the polymerization rate on the concentration of the monomer in the system AAl-H_3PO_4 with propyl alcohol as diluent at different [A]/([AAl] + [P˙Al]) ratios (curves 1-6) and with mixtures of AAc with ethyl acetate (EAc) in the system [A]/([AAc] + [E Ac]) = 3. One can see that the reaction order with respect to the monomer concentration is almost zero in the absence or in the presence of lesser amounts of the acid, but with an increase in the amount of the acid the effective reaction order rises and reaches 1 at [A]/([AAl] + [PAl]) = 1.4; and this happens to be the area where the maximum value in the relative rate of the polymerization is observed. Similarly the apparent reaction order

TABLE 2. Effect of the Basicity of Acid on Absolute and Relative Polymerization Rates[a]

System[b]	$[M]_0$ (mole/liter)	[A]/[M]	$V_0 \times 10^6$ (mole/liter-sec)	V/V_0[c]
AAM	13.35	0	1.3	1
H_3PO_4 (87%)/AAM	3.7	3.2	520	~350
H_3PO_4 (50%)/AAM	3.5	1.5	130	~200
MphA/AAM	3.5	1.4	25	7.8
DAEt	8.4	0	4.1	1
H_3PO_4/DAEt	5.6	1	10.5	2.6
MphA/DAEt	4.1	1	3	~ 1

[a] $I \cong 300$ R/sec, t = 20°C.

[b] AAM = allylamine; MphA = methylphosphoric acid; CAEt = diallyl ether.

[c] V and V_0 are the initial rates of the polymerization AAM and DAEt in the presence and absence (respectively) of modifier.

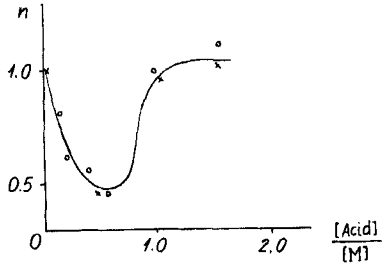


FIG. 7. Dependence of the order of polymerization rate with respect to initiation dose on phosphoric acid/monomer molar ratio: (○) for AAl; (×) for AAc. $t_{\gamma\text{-irr}}$ = 20°C.

considerably differing from zero with respect to the monomer concentration is observed in the AAM-H_3PO_4 system ($[A]/[M] > 1$) (Fig. 8), where at the higher monomer concentrations it reaches the value of 2.

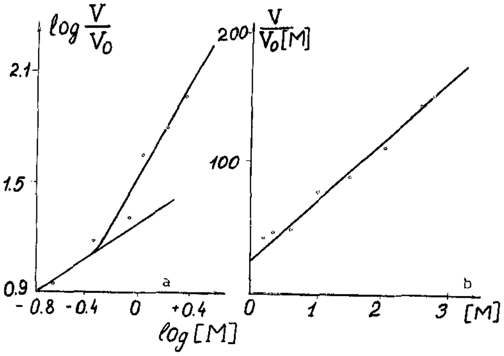


FIG. 8. Dependence of the polymerization rate on the monomer concentration: (a) in logarithmic coordinates; (b) in coordinates of Eq. (18). $[H_3PO_4]/[AAM] + [BMA] = 3.8$; $I_{\gamma\text{-irr}} \cong 750$ R/sec; $t_{\gamma\text{-irr}} = 20°C$.

Even at 20% conversion and above, solid polymers are formed in the presence of acids, similarly to that shown in the earlier works [6] where the polymerization was carried out in the presence of the nontransition metal salts. All the polymers are soluble in polar solvents. In the determination of the number-average molecular weight of the polymers it is observed that $\overline{M}_n$ of the polymers of AAl obtained in the presence of the H_3PO_4 are slightly higher than those of polymers prepared in the absence of the acid, and this value increases with the conversion; e. g., the values of $\overline{M}_n$ of the samples of poly(allyl alcohol) prepared in the presence and absence of H_3PO_4 ($[A\ Al] : [H_3PO_4] = 1{:}1$) at 18% conversion were 750 and 400, respectively. $\overline{M}_n$ of the polymer obtained in the presence of H_3PO_4 at 50% conversion was found to be ca. 1000, while the value of $\overline{M}_z$ of the same polymer was 50,000 despite the very low value of the polymer intrinsic viscosity in methanol of ~ 0.1 dl/g. These results indicate a high degree of branching and polydispersity in the polymer sample. The formation of such a highly branched macromolecule with fairly high molecular weight may be due to secondary reactions, with the participation of the oligomeric product which might have formed at the earlier stages of the reaction. A similar type of explanation was given previously in a study [6] of polymerization in the presence of nontransition metal salts.

The kinetic features of the polymerization of allyl monomers in the presence of acids and the properties of the resulting polymer indicate a considerable change in the mechanism of the polymerization. The radical mechanism of the reaction could be confirmed by the facts that the reaction does not proceed in the absence of the radical initiator, it is inhibited by radical inhibitors [4], and by the similarity of the kinetic features of the photoinitiated polymerization to that of the γ-radiation polymerization. The total effect of the acid in increasing the polymerization rate may be attributed to two factors.

First, there is a change in the polar effects of the functional group, due to the interaction of the acid with the monomer by the formation of either a hydrogen bond or protonated salt on the functional group. This effect is equivalent to the introduction of more electronegative group into the monomer. As was shown previously [8], this factor may strengthen the C–H bond in the methylene group of the monomer, which in turn decreases the probability of the degradative chain transfer.

Secondly, there is a change in the addition of the allyl radical of chain transfer to the double bond of the monomer, which is nearly equal to zero in the usual allyl polymerizations. During the polymerization of allyl monomers in the presence of salts [6], where the salts are linked with the allyl radical in the complex, the probability of such addition could be sharply increased, the degradative chain transfer being converted into an effective one. It is known [10] that the linking of the radical with the hydrogen bond usually is accompanied by a decrease in the value of the termination constant of the radicals, and the same results can be brought about by protonating the functional group of the radical. From this one can assume that in the presence of the acid, the probability of the addition of the allyl radical of chain transfer to the double bond of the monomer becomes appreciably different from zero.

The possibility of effective chain transfer by the allyl radicals is confirmed by the properties of the resulting polymers. The branching of the polymers can be easily explained by the presence of the unsaturated end groups in the polymers which originated from the initiation by the allyl radicals. Afterwards these double bonds might have been opened in the course of polymerization.

Under such conditions, the effect of the acid on the polymerization of the allyl monomers should be associated with the effects of protonation or with hydrogen bond formation, which ultimately strengthen the α-hydrogen atoms of the monomer molecule, thus raising the value of K_{tr}/K_{tr}' and raise the value of the probability of the addition of the chain-transfer allyl radical to the double bond.

By proposing the kinetic scheme shown in Eqs. (1)-(5), the contribution of the different factors during the polymerization of the allyl-monomers in the presence of the acids can be estimated.

Initiation:

$$M_0 \xrightarrow{V_i} R_0^{\cdot} \tag{1}$$

Propagation:

$$M_0 + R_0^{\cdot} \xrightarrow{K_p} R_0^{\cdot} \tag{2}$$

"Degradative" Chain Transfer:

$$M + R_0^{\cdot} \xrightarrow{K_{tr}} P + A^{\cdot} \tag{3}$$

$$M_{H^+} + R_{H^+}^{\cdot} \xrightarrow{K_{tr}'} P + A_{H^+}^{\cdot} \tag{3a}$$

$$M + R_{H^+}^{\cdot} \xrightarrow{K_{tr}'} P + A^{\cdot} \tag{3b}$$

$$M_{H^+} + R^{\cdot} \xrightarrow{K_{tr}'} P + A_{H^+}^{\cdot} \tag{3c}$$

Termination:

$$A^{\cdot} + A^{\cdot} \longrightarrow \text{products } (K_t) \tag{4}$$

$$A^{\cdot} + A_{H^+}^{\cdot} \longrightarrow \text{products } (K_t') \tag{4a}$$

$$A_{H^+}^{\cdot} = (M) \longrightarrow \text{products } (K_t'') \tag{4b}$$

Initiation by Allyl Radicals:

$$A_{H^+}^{\cdot} + M_0 \xrightarrow{K_{in}'} R_0^{\cdot} \tag{5}$$

Here M is monomer, $R^{\cdot}$ is the propagation radical, $A^{\cdot}$ is an allyl radical of chain transfer, P is a polymer, the subscript H^+ indicates a linkage with H^+, and subscript zero indicates the total concentration.

It is assumed that the rate of the initiation and propagation would be affected very little by the introduction of the acid, and the termination of the propagating radicals is due to the abstraction of the hydrogen atom from α–CH_2 group [Eqs. (3)-(3c)].

The allyl radicals of chain transfer which were linked with the acid are either added to the double bonds, thus converting into propagating radicals, or terminate. The protonated allyl radicals may decay either by the recombination with the free allyl radicals from chain transfer (second-order reaction with respect to A·) or by leaving the complex (first-order reaction with respect to A·). The latter is due to the assumption that the probability of the recombination of two acid-linked allyl radicals is very low because of electrostatic and steric factors. Such an assumption is justified in the case of allyl alcohol and allyl acetate, where the order of the reaction falls at one stage from 1 to 0.5 and again increases to 1 during the change in the proportion of the free and protonated particles. The polymerization of allylamine (due to the peculiarity of preparing a complex with phosphoric acid) was studied in the presence of an excess of H_3PO_4, where all the molecules of allyl amine are protonated. In such a case, $\alpha = 1$, and therefore the termination takes place mainly by leaving the complex (first-order reaction with respect to A·). This is confirmed by the first-order dependence with respect to the initiator during the polymerization of AAM.

The rate of the polymerization can be expressed in the form

$$V = K_p[R_0^{\cdot}]\,[M_0] \tag{λ}$$

To determine the value of $[R_0^{\cdot}]$ it is necessary to solve the following equations by using the stationary-state approximation:

$$\begin{aligned} d[R_0^{\cdot}]/dt &= V_{in} - K_{tr}(1-\alpha)^2[R_0^{\cdot}][M_0] - K_{tr}'\alpha(2-\alpha)\cdot[R_0^{\cdot}][M_0] \\ &\quad + K_{in}[A_{H^+}^{\cdot}][M_0] \\ &= 0 \end{aligned} \tag{7}$$

$$\begin{aligned} d[A_{H^+}^{\cdot}]/dt &= x\,K_{tr}'\alpha(2-\alpha)[R_0^{\cdot}][M_0] - K_{in}'[A_{H^+}^{\cdot}][M_0] \\ &\quad - K_t'[A_{H^+}^{\cdot}][A^{\cdot}] - K_t''[A_{H^+}^{\cdot}] \\ &= 0 \end{aligned} \tag{8}$$

$$d[A\cdot]/dt = K_{tr}(1-\alpha)^2[R_0^{\cdot}][M_0] + (1-x)K_{tr}'\alpha(2-\alpha)\cdot[R_0^{\cdot}][M_0] - K_t[A\cdot]^2 - K_t'[A_{H^+}^{\cdot}][A\cdot] = 0 \tag{9}$$

where α is a fraction of the acid-linked particles; the multiplying factor x, which is $0.5 < x < 1$ in the equation, takes into account the fact that not all the allyl radicals which are formed during the reactions of (3a)-(3c) may be linked with the acid. But the above system (7)-(9) is not easily solved, and it also contains a number of unknown parameters. Therefore two limiting cases are considered.

Case 1: Interval of Low α Values ($0 < \alpha < 0.5$). By summing Eqs. (7)-(9), we get

$$V_{in} - K_t''[A_{H^+}^{\cdot}] - 2K_t'[A_{H^+}^{\cdot}][A^{\cdot}] - K_t[A^{\cdot}]^2 = 0 \tag{10}$$

Without much error one can assume that

$$K_t[A\cdot]^2 \gg K_t''[A_{H^+}^{\cdot}] + 2K_t'[A_{H^+}^{\cdot}][A\cdot]$$

and

$$K_t'[A_{H^+}^{\cdot}][A\cdot] > K_t''[A_{H^+}^{\cdot}]; \text{ in the same way } [A\cdot] > [A_{H^+}^{\cdot}]$$

and $K_t > K_t'$

$$V_{in} = K_t[A\cdot]^2 \tag{11}$$

Substituting expression (11) into Eq. (8) we get

$$[A_{H^+}^{\cdot}] = \frac{x[K_{tr}']\alpha(2-\alpha)[R_0^{\cdot}][M_0]}{K_{in}'[M_0] + K_t'(V_{in}/K_t)^{1/2} + K_t''} \tag{12}$$

By substituting Eq. (12) into Eq. (7) we get the value of $[R_0\cdot]$, and the rate of the polymerization may be expressed as

$$V = \frac{K_pV_{in}}{K_{tr}(1-\alpha)^2 + K_{tr}'\alpha(2-\alpha)\left\{1 - \dfrac{xK_{in}'[M_0]}{K_{in}'[M_0] + (K_t'V_{in}/K_t^{1/2} + K_t''}\right\}} \qquad (13)$$

According to Eq. (13), the order of the polymerization rate with respect to the rate of the initiation definitely deviates from 1. It may be shown that with the increase in the value of α the value of the reaction order falls to 0.5; this was experimentally confirmed in the systems with allyl alcohol and allyl acetate with H_3PO_4. At the same time, an increase in the value of the effective order of the reaction with respect to the monomer concentration also takes place.

With further increase of α, the fraction of the nonprotonated allyl radicals falls, and the condition $K_t'[A_{H^+}^{\cdot}][A\cdot] > K_t''[A_{H^+}^{\cdot}]$ no longer holds. Under the conditions where $K_t'[A_{H^+}^{\cdot}][A\cdot] < K_t''[A_{H^+}^{\cdot}]$ transition to the other limiting case is observed.

Case 2. Interval of High α ($0.5 < \alpha < 1$). In this case one can limit consideration to Eqs. (7) and (8) and neglect the term $K_t'[A_{H^+}^{\cdot}][A]$ in Eq. (8). From here the value of $[R_0^{\cdot}]$ can be calculated, and then by substitution in Eq. (6) we get the expression for the polymerization rate:

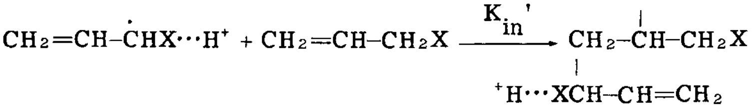
$$V = \frac{K_pV_{in}}{K_{tr}(1-\alpha)^2 + K_{tr}'\alpha(2-\alpha)\left\{1 - xK_{in}'[M_0]/(K_{in}'[M_0] + K_t''\right\}} \qquad (14)$$

According to Eq. (14), the rate of polymerization becomes directly proportional to the rate of the initiation, and the same is observed in the experiment in the presence of high amount of the acid. The order of the polymerization rate with respect to the monomer deviated from zero.

Equations (13) and (14) are identical in structure and can be expressed in the form:

$$\frac{V}{V_0} = \frac{1}{(1-\alpha)^2 + (K_{tr}'/K_{tr})\alpha(2-\alpha)(1-x\varphi)} \qquad (15)$$

where $V_0 = K_pV_{in}/K_{tr} = K_pK_{in}I/k_{tr}$ is the polymerization rate in the absence of modifier and I is the dose rate. Here φ is probability of the initiation by the allyl radicals of chain transfer by the following mechanism



$$CH_2{=}CH{-}\dot{C}HX\cdots H^+ + CH_2{=}CH{-}CH_2X \xrightarrow{K_{in}'} \underset{{}^+H\cdots XCH{-}CH{=}CH_2}{CH_2{-}\overset{|}{C}H{-}CH_2X}$$

For Case 1:

$$\varphi = \frac{K_{in}'[M_0]}{K_{in}'[M_0] + K_t'(V_{in}^{1/2}/K_t^{1/2}) + K_t''} \qquad (16)$$

and for Case 2

$$\varphi = \frac{K_{in}[M_0]}{K_{in}'[M_0] + K_t''}$$

At $\alpha = 1$, Eq. (15) can be simplified to be a linear function of $[M_0]$

$$V/V_0 = (K_{tr}/K_{tr}')\,(K_{in}'/K_t''\,[M_0] + (K_{tr}/K_{tr}') \qquad (17)$$

with the intercept equal to K_{tr}/K_{tr}'. As is shown in Fig. 2, the linear dependence of $V/V_0 = f([M_0])$ is observed in the system AAl-H_3PO_4 only at the molar ratios $[A]/[AAl] = 1.41$ and 2.88 (under these conditions $\alpha \cong 1$), and the values of K_{tr}/K_{tr}' are 1.5 and 2, respectively. This fact indicates that under such conditions the hydrogen bonding with the AAl molecule strengthens the C–H bond at the α–CH_2 group. This explains the increase of the value $\overline{M}_n$ (1.5 to 2 times) during the polymerization of AAl with H_3PO_4 at the earlier stages of the conversion, where the probability of the secondary processes of branching is very low. From the slope of the straight line in Fig. 2, we can get the value of $K_{in}/K_t'' \cong 1.7$ and $\varphi = 0.9$. The corresponding parameters for the AAc-H_3PO_4 system have been determined from the data presented on curve 7 in Fig. 2 (see Table 3).

In terms of the above mechanism the polymerization of AAM with

TABLE 3. Kinetic Parameters of Polymerization of Allyl Monomers in the Presence of H_3PO_4 ($[M]/[H_3PO_4]$) = 1/3

Monomer	K_{tr}/K_{tr}'	φ
Allylamine	~100	0.85
Allyl alcohol	~2	0.90
Allyl acetate	~1	0.80

H_3PO_4 can also be explained. Here one can see the changing reaction order with respect to the monomer concentration (diluent-butylamine (BAM) (Figs. 8a and 8b) which ultimately reaches 2 at higher concentration of the monomer and the first-order rate dependence with respect to the initiation rate. The assumptions used in deriving the corresponding equation include the linear dependence of the radiation initiation rate on the concentration of the monomer and the first-order reaction as the rate-determining step in termination of allyl radicals of chain transfer. So the expression for the relative rate of the polymerization is given as

$$V/V_0 = (K_{in}K_{tr}[M]_0/K_{in}{}^0K_{tr}) \left\{1 + (K_{in}'/K_t'')[M]_0\right\} \tag{18}$$

The plot in the coordinates of Eq. (18), $V/V_0[M_0] = f([M]_0)$, is a straight line (Fig. 8b), which ultimately confirms the validity of the above proposed equation. The intercept gives the value of $K_{in}K_{tr}/K_{in}{}^0K_{tr}'$ which is equal to 25 mole^{-1}, and the slope of this straight line gives the value $K_{in}K_{tr}K_{in}'/K_{in}{}^0K_{tr}'K_t'' = 45$ mole^{-2}. From this the value of probability of initiation of the allyl radicals of chain transfer is 0.86 (Table 3).

This value is near the value of the AAl-H_3PO_4 system and its closeness to unity shows that in the AAM-H_3PO_4 system, the probability of the addition of the chain transfer allyl radicals to the double bond is very high, which ultimately confirms the above assumption about the occurrence of effective chain transfer in these systems. The value of K_{tr}/K_{tr}' in the above system can be calculated from data of the molecular weights of the polymers. The degree of polymerization, both in the presence and absence of complexing agent, can be expressed as $\bar{P}_n = K_p/K_{tr}$. The change in the value of the probability of the abstraction of the α-hydrogen atom, as a result of the formation of a complex with the H_3PO_4 can be derived by comparing the molecular weight of the polymers, which were produced both in the presence and absence of the complexing agent. During the polymerization of pure AAM, the degree of polymerization in the initial stages is equal to $\sim 2(K_p/K_{tr} \simeq 2)$. As for the above scheme, the allyl radicals of chain transfer after addition to the monomer eventually form terminal unsaturated groups in the polymer, which may be opened in course of the further polymerization, thus giving an additional increase in the molecular weight of the polymer. Therefore the value of K_p/K_{tr} was estimated by using PAAM obtained by photopolymerization in the system AAM-H_3PO_4 at low conversions (5%). From the value of the molecular weight of such a product which is equal to ~ 10000, we get the value of $K_{tr}/K_{tr}' \simeq 10^2$. In this case, the factors responsible on the increase in the polymerization rate and molecular weights of the products in the system AAM-H_3PO_4 are the decrease in the value of constant of degradative chain transfer due to strengthening of the C–H bond in α-CH_2 group of monomer molecule, and the capability of the complexed allyl radical to initiate the reaction by opening the double bond in the monomer.

From the data in Table 3 one can see a gradual increase in the value of K_{tr}/K_{tr}' with the basicity of the monomer, i. e., the greater the degree of proton transfer to the functional group, the smaller the value of K_{tr}. The second factor responsible on the increase in the polymerization rate under the conditions of protonation is the value of φ which is close to unity, indicating transformation of the degradative chain transfer into the effective chain transfer. The effect of this second factor is particularly important in the case of monomers with high pK values, where (Table 3) in the case of the allyl acetate, the changes in K_{tr} values brought about by protonation are negligible.

Figure 9 shows the dependence of the logarithm of the reciprocal of the polymerization rate of a number of allyl monomers upon the pK values of the functional groups in presence of the acid. It can be seen that the rates correlate well with the nucleophilicity of functional groups. One can see that this dependence is contrary to that in the case of nonprotonated monomers. In the presence of acids, practically nonpolymerizable monomers (Fig. 9) like allylamine, diallylamine, and dimethylallylamine, which have highly basic functional groups, are polymerized at the rates of 10^2-10^3 times higher than those for the pure monomers. The increase in the polymerization rates of such monomers like vinylacetic acid or allyl acetate (which have more low basic functional groups) is not so high; the relative increase is 5 to 6-fold.

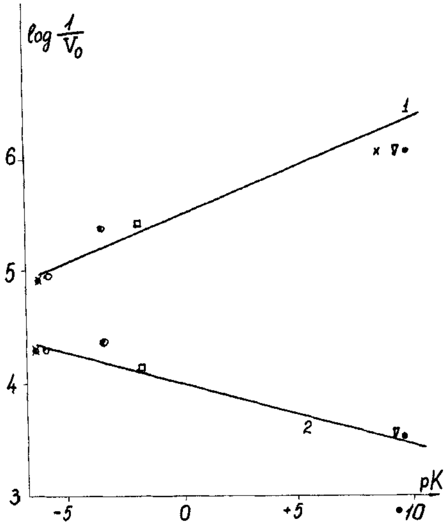


FIG. 9. Dependence of inverse polymerization rate of allyl monomers on the nature of functional groups (1) in the absence and (2) in the presence of phosphoric acid. Monomers and reaction conditions as in Fig. 1.

The rate of the polymerization of the protonated allyl monomers can be expressed by the equation

$$V_p = K_pV_{in}/[K_{tr}'(1 - \varphi)] \qquad (19)$$

from which $1/V_p \sim K_{tr}'$.

As the value of σ^0 in the series of the protonated monomers is not known, one can assume that the value of the chain transfer constant to the protonated monomer depends on the pK value, which ultimately characterizes the degree of protonation, in a way similar to Eq. (7) which is valid for nonprotonated monomers.

$$\log (1/V_p = \text{constant} + \rho''(\text{pK}) \qquad (20)$$

Agreement with this dependence (Fig. 9, curve 2) confirms the validity of the above assumption, that the values of K_p and K_{in} of different allyl monomers do not change in the presence of H_3PO_4. The constancy of φ with the same acid was verified by us for three monomers (Table 3).

Therefore the main factor which controls the rate and molecular weight of the polymer during polymerization of allyl monomers is, chain transfer to the monomer. The rate of this reaction is controlled by the inductive effect of the functional groups. In the presence of acids, the inductive effect is reversed, and the lowest rate of abstraction of the hydrogen atoms at the α-position is observed for the monomers with the highest basicity (allylamine) where the interaction of the functional group with the complexing agent is strongest. The increase in the polymerization rate in the presence of complexing agent is also connected with the high probability of addition of transfer radical to the double bond of the monomer (effective chain transfer). The probability of this reaction is determined by the nature of modifier. The combination of the above factors is ultimately responsible for the high rates of polymerization of allyl monomers and for the increase of the molecular weight of the polymers in the presence of acids.

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