

interactions which set the size and number of the elements of structure and also the strength of contacts between them, which determines the mechanical properties of the materials.

In our case the introduction of EA raises the strength of the interstructural bonds and the number of elements of structure which ultimately during the formation of the coating leads to increase in the crystallization seeds and hence to fall in the size of the spherulites in the film for the same duration of formation of the coats. Change in the phase state of the system also affects the morphology of the films.

Translated by A. CROZY

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MECHANISM OF COMPLEX-RADICAL COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH MONOALLYL- AND TRI-n-BUTYLSTANNYLALLYL MALEATES*

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The kinetics and mechanism of radical copolymerization of maleic anhydride with monoallylmaleate and tri-n-butylstannylallylmaleate have been studied. IR and PMR spectroscopy established the formation of complexes between the monomer pairs studied and helped to

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determine their complexation constants. The kinetic parameters of copolymerization and the quantitative contribution of the monomer complexes to the radical chain growth reactions have been calculated.

EARLIER it was shown that the monoallyl ester of maleic acid and its organotin derivative readily enter radical alternating copolymerization with styrene and form macromolecules with the allyl group in the side chain [1]. The patterns of complex radical copolymerization of some allyl monomers with the anhydride of maleic acid have also been reported [2].

The present paper discusses some kinetic aspects and the mechanism of radical copolymerization of monoallylmaleate (MAM) and tri-*n*-butylstannylallyl maleate (TBSAM) with an electron acceptor monomer—maleic anhydride (MA).

MA was purified by recrystallization from benzene solution and by two-fold sublimation *in vacuo*, M.P. 52.8°C.

MAM, TBSAM, the monoallyl ester of succinic acid (AESA) and the monopropyl ester of maleic acid (PEMA) were synthesized by known techniques [1, 3]. MAM: n_D^{20} 1.4708 and d_4^{20} 1.1517; TBSAM: n_D^{20} 1.4988 and d_4^{20} 1.2114; AESA: n_D^{20} 1.4502 and d_4^{20} 1.1268; PEMA n_D^{20} 1.4563 and d_4^{20} 1.1370.

The monomers studied were polymerized and copolymerized in glass dilatometers or reactors in a medium of methylethylketone (MEK) at 60–70°C in presence of an initiator—benzoyl peroxide (BP).

After purification by two-fold reprecipitation from MEK and washing with several portions of benzene and ether the polymers obtained had the following specifications:

PMAM: softening point 60–62°C (after Cramer-Sornov), η_{sp} in MEK at 20°C 0.13 dl/g, acid number (by potentiometric titration) 350 mg KOH/g, degree of unsaturation (according to iodometry) 29.4%, IR spectrum (film): $\nu_{C=C}$ (—CH=CH—)=1650; $\nu_{C=C}$ (—CH=CH₂)=1625; $\nu_{C=O}$ (COOCH₂—CH=CH₂)=1735; $\nu_{C=O}$ (COOH)=1710; $\nu_{C=O}$ (lactone)=1772; δ_{CH_2} =930, 990, ν_{CH} =3080 cm⁻¹.

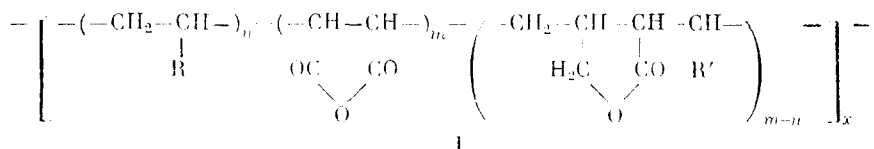
PTBSAM: softening point 54–56°C, η_{sp} in MEK 0.09 dl/g, IR spectrum (film): ν_{Sn-C}^s =535; ν_{Sn-C}^{as} =650; $\nu_{C=C}$ (—CH=CH—)=1650; $\nu_{C=O}$ (C—C=O...SnR₃)=1575; $\nu_{C=O}$ (—CH=CH₂)=1625; $\nu_{C=O}$ (COOCH₂—CH=CH₂)=1735; $\nu_{C=O}$ (lactone)=1775; δ_{CH_2} =930, 995; $\nu_{C=O}$ =1780, 1845; ν_{CH} =3080 cm⁻¹.

MA—MAM copolymer: softening point 305–308°C, η_{sp} in MEK 0.07 dl/g, acid number 670 mg KOH/g, degree of unsaturation 31.5 mole %. IR spectrum (film) $\nu_{C=C}$ (—CH=CH—)=1650; $\nu_{C=O}$ × (COOCH₂—CH=CH₂)=1735; $\nu_{C=O}$ =1780, 1845; $\nu_{C=O}$ (COOH)=1710; δ_{CH_2} =930, 990; ν_{C-O-C} =1180, 1225; ν_{CH_2} =2960; ν_{CH} =3080 cm⁻¹.

MA—TBSAM copolymer: softening point 100–102°C, η_{sp} =0.06 dl/g, degree of unsaturation 40.4 mole %. IR spectrum (film): ν_{Sn-C}^s =535; ν_{Sn-C}^{as} =650; $\nu_{C=C}$ (—CH=CH—)=1650; $\nu_{C=O}$ (C—C=O...SnR₃)=1575; $\nu_{C=O}$ (COOCH₂CH=CH₂)=1735; δ_{CH_2} =930, 995; $\nu_{C=O}$ =1780, 1845; ν_{C-O-C} =1180, 1230; ν_{CH} =3080 cm⁻¹.

In the IR spectra of the homopolymers (Fig. 1) together with the main band 1735 ($\nu_{C=O}$ —COOCH₂CH=CH₂), 1710 ($\nu_{C=O}$ —COOH) and 1650 ($\nu_{C=C}$ —CH=CH—) cm⁻¹ a new absorption band at 1772 cm⁻¹ ($\nu_{C=O}$) appears characteristic of the cyclic lactone structure [4]. The spectra of the MA—MAM and MA—TBSAM copolymers contain the characteristic absorption bands 1845 and 1775 ($\nu_{C=O}$ anhydride), 1735 ($\nu_{C=O}$ complex ester), 1715 ($\nu_{C=O}$ —COOH), 1575 ($\nu_{C=O}$ R₃SnOOC⁻) and 1650 ($\nu_{C=C}$ —CH

$=\text{CH}-$) cm^{-1} . As is clear from the spectra the band of the $\text{C}=\text{O}$ group of the lactone overlaps with the anhydride band, which complicates the demonstration of the formation of analogous cyclic structures in the macromolecules of the copolymers studied. However, the observed considerable deviation of the total degree of unsaturation (31.5 and 40.4 mole% for the MA-MAM and MA-TBSAM copolymers respectively) from the theoretical value for the copolymers of equimolar composition (unsaturation 50 mole%) may serve as confirmation of the presence of intramolecular cyclic fragments in the chain of the macromolecules



where $\text{R} = \text{CH}_2\text{COOCCH}=\text{CHCOOH}$, $\text{CH}_2\text{OOCCH}=\text{CHCOOSn}(\text{n-C}_4\text{H}_9)_3$;
 $\text{R}' = \text{COOH}$, $\text{COOSn}(\text{n-C}_4\text{H}_9)_3$; $n = 31.5$ and 40.4 ; $m = 50$.

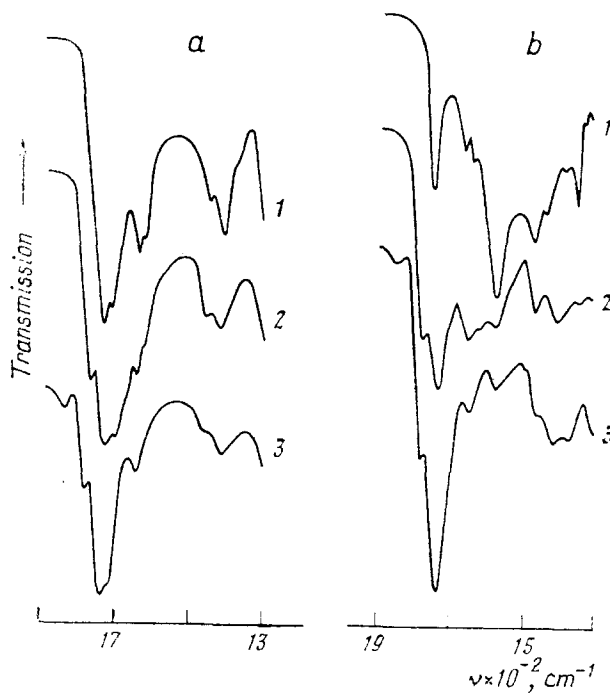


FIG. 1. IR spectra: *a*—MAM (1), PMAM (2), MA-MAM copolymer (3), *b*—TBSAM (1), PTBSAM (2), MA-TBSAM copolymer (3).

To elucidate the mechanism of the formation of these copolymers the first need was to investigate the process of complexing between the initial monomers. For the sake of clarity we designate MA as A (acceptor). MAM as D_1 (donor) and TBSAM as D_2 (donor).

The formation from the monomer pairs $A...D_1$ and $A...D_2$ of complexes with charge transfer is confirmed by the data of PMR spectroscopy presented in Figs. 2 and 3. In the PMR spectrum of MAM (Fig. 2) signals of the protons of the $-CH=CH-$ and $-COOH$ groups appear in the form of singlets 6.3 and 11.05 ppm. The assignment of the singlet 11.05 ppm to the $-COOH$ group is confirmed by the observed shift in it to the strong field with increase in the content of MAM in the monomer mixture studied (spectra 4 and 6).

On introducing the R_3Sn group into the MAM molecule the protons of the $-CH=CH-$ bond become non-equivalent and their signals are transformed to the spectrum of the AB type ($J_{cis}=9.0$ Hz) with displacement of the chemical shifts of these protons to the strong field (Fig. 3, spectrum 1).

The observed displacements of the chemical shifts of the protons of A in a mixture with the donor monomers D_1 and D_2 for a heavy excess of the latter allow one to calculate the equilibrium constants of the formation of the complexes $A...D_1$ and $A...D_2$. Using the Ketelaar equation [5] from the graphic function $1/\Delta \rightarrow 1/[D]$ (Fig. 4) we found the values of $K_1=0.101 \pm 0.01$ and $K_2=0.214 \pm 0.015$ l./mole.

The comparatively high value of K_2 may be explained by the influence of the pentacoordination tin increasing the proneness of D_2 to complexing with A.

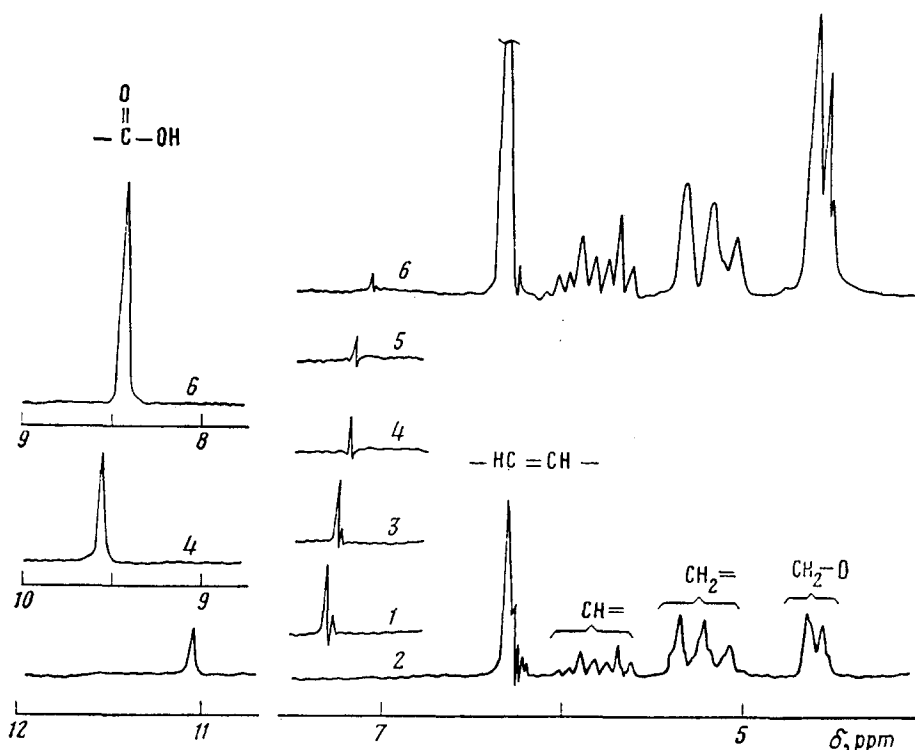


FIG. 2. PMR spectra of MA (1), MAM (2) and their mixtures in MEK for a molar ratio 1 : 10 (3), 1 : 20 (4), 1 : 30 (5) and 1 : 40 (6).

From the donor-acceptor properties of the multiple bonds of the monomers (allyl—donor and olefine —CO—CH=CH—CO— acceptor) one may assume the formation and participation in chain growth also of the intramolecular charge transfer complexes of the type

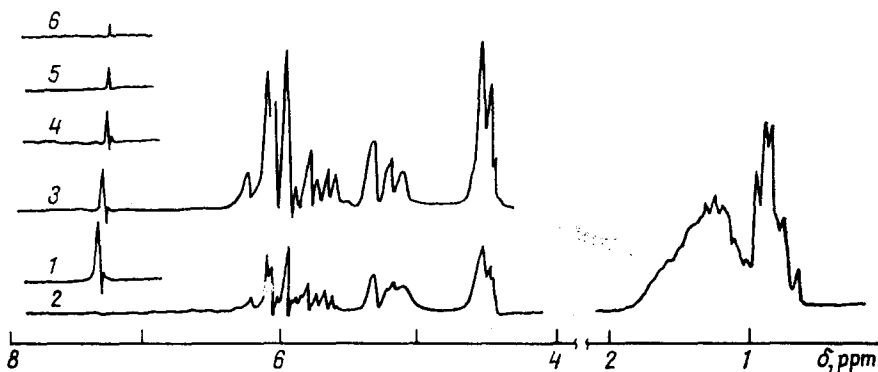
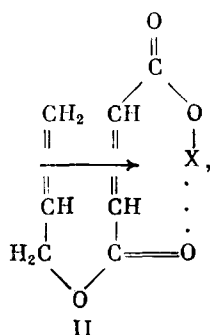


FIG. 3. PMR spectra of MA (1), TBSAM (2) and their mixtures in MEK for the molar ratio 1 : 5 (3), 1 : 10 (4), 1 : 15 (5) and 1 : 20 (6).

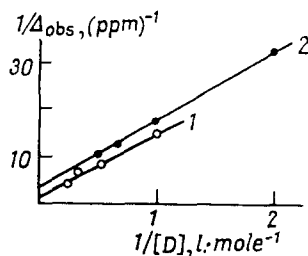


FIG. 4. Graphic method of determining the complexing constants K for the MA...MAM (1) and MA...TBSAM (2) complexes. $1/\Delta_K$ is the segment cut off on the ordinate; $\tan \alpha = 1/(\Delta_K K)$; $[D]$ concentration of donor (MAM or TBSAM); Δ_{obs} difference in chemical shifts of protons of free MA and in mixtures of it with the donor ($[MAM] \gg [MA]$ and $[TBSAM] \gg [MA]$).

TABLE 1. DATA OF PMR SPECTRA TO DETERMINE THE EQUILIBRIUM CONSTANTS BETWEEN AESA AND PEMA

[AESA]	[PEMA]	$\Delta \times 10^2$, ppm	[AESA]	[PEMA]	$\Delta \times 10^2$, ppm
mole/l.			mole/l.		
0.1	1.0	2.0	0.1	3.0	4.5
0.1	2.0	3.4	0.1	4.0	5.7

TABLE 2. COPOLYMERIZATION OF MA (A) WITH MAM (D₁) AND TBSAM (D₂) (Solvent MEK; initiator [BP]=0.5%; [M]=1.5 mole/l.; 70°C; degree of conversion $\leq 10\%$)

[D ₁] in initial mixture, mole %	Content in copolymer, mole %		[Sn]*	Acid number,* mg KOH/g for copolymer A-D ₁	$F/f(f-1)^{\dagger}$		F^2/f	
	[D ₁]	[D ₂]			A-D ₁	A-D ₂	A-D ₁	A-D ₂
25	47.05	44.30	20.35	695	0.086	0.045	0.13	0.12
35	47.56	46.10	20.25	680	0.093	0.023	0.33	0.30
50	50.48	50.36	21.22	670	0.0099	0.020	0.99	0.98
65	51.56	52.96	21.62	630	0.198	0.104	3.05	3.20
75	52.81	54.85	22.10	620	0.520	0.272	7.43	8.18

* Calculated values for copolymers of equimolar composition [Sn]=21.85%; acid number 662 mg KOH/g.

 \dagger F and f are the ratios of the monomers in initial mixture and copolymers respectively.

(X=H, Sn(n-C₄H₉)₃) promoting the formation of cyclic structures in the macromolecular chain I.

To confirm the possible formation of the structure II we studied the model system AESA-PEMA. From the PMR spectra of these compounds in the free state and mixtures for different ratios (Table 1) we estimated the values of the complexing constant: $K=0.06 \pm 0.01$ l./mole. Consequently, it may be assumed that the formation of the lactone fragments is connected with the possible realization of the intramolecular chain growth reaction through the stage of complexing.

To demonstrate the role of the monomer complexes found on radical copolymerization and quantitative evaluation of their contributions to the radical chain growth reactions it was necessary to study the kinetic patterns of the copolymerization of the monomer pairs A-D₁ and A-D₂ for different ratios and concentrations of the reacting components.

From Table 2 using the Fineman-Ross equation we calculated the values of the copolymerization constants: $r_1=0.04 \pm 0.006$ and $r_2=0.05 \pm 0.005$ for the pair A-D₁ and $r_1=0.083 \pm 0.005$ and $r_2=0.01 \pm 0.002$ for the pair A-D₂. However these values do not allow for the contribution of the complexes to the radical reactivity of the monomers. Therefore the experimental findings obtained were treated according to the Seiner-Litt equation [6] which together with attachment to the growing macroradicals of the free monomers takes into account the attachment of the complex-bound monomers (C) giving the following values of the copolymerization constants: $r_{21}=0.05$, $r_{2C}=0.022$,

$r_{2C_1}=0.027$, $r_{2C_2}=0.11$ and $r_{12}=0.04$ for the system A-D₁; $r_{21}=0.099$, $r_{2C}=0.008$, $r_{2C_1}=0.023$, $r_{2C_2}=0.09$ and $r_{12}=0.083$ for the system A-D₂.

From the dependence of the copolymerization rate on the concentration of BP and monomers (Fig. 5) it follows that the reaction orders for the initiator and monomers are 0.53 and 1.25 for the system A-D₁ and 0.52 and 1.55 for the system A-D₂.

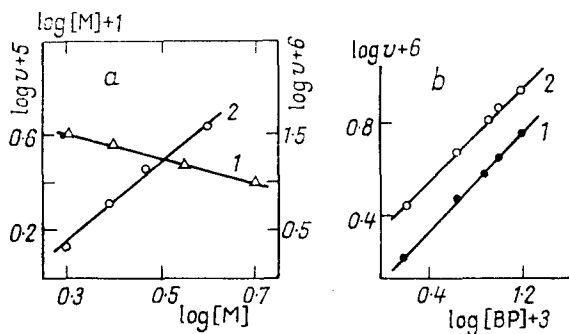


FIG. 5

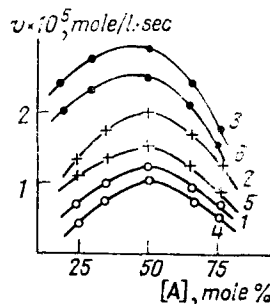


FIG. 6

FIG. 5. Logarithmic dependence of the rate of copolymerization on the total concentration of monomers (a) and concentration of initiator (b): 1—MA-MAM, 2—MA-TBSAM.

FIG. 6. Copolymerization rate v as a function of the composition of monomer mixture for total concentration of monomers 2.0 (1), 2.5 (2) and 3.0 (3) mole/l. for A-D₁ and 1.0 (4), 1.5 (5) and 2.0 (6) mole/l. for A-D₂.

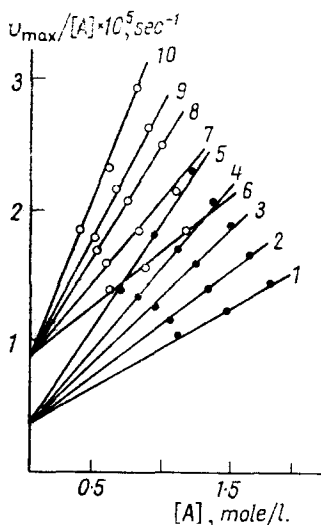


FIG. 7

FIG. 7. Graphic dependence of $v_{\max}/[A]$ on $[A]$ for the ratios of initial monomers $F=0.67$; 0.82; 1.0; 1.22 and 1.5. 1–5—MA-MAM; 6–10—MA-TBSAM.

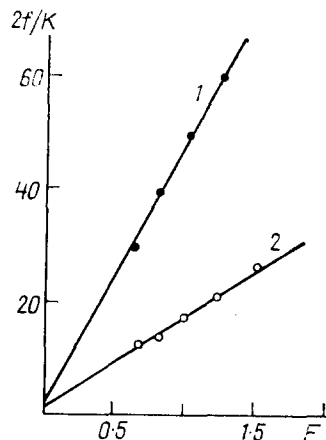


FIG. 8

FIG. 8. Ratio $2f/K$ as a function of F for determining the values of the contribution of the charge transfer complexes MA...MAM (1) and MA...TBSAM (2).

The values of the global activation energy E_a calculated from the temperature dependence of the initial copolymerization rate are 28.1 for the system A-D₁ and 17.7 for the system A-D₂ (kcal/mole).

The high value of the order for the monomers and the low value of E_a for the system A-D₂ as compared with the system A-D₁ may be explained by the participation of the coordination-bound complexes II in the reactions of initiation; a similar phenomenon was earlier found for the monomer TBSAM-styrene system [1].

For both pairs of monomers studied A-D₁ and A-D₂ the dependence of the copolymerization rate v on the ratio and global concentration of the initial monomers (Fig. 6) is of an extremal character; v_{\max} corresponds to 50 mole% A in the initial mixture.

As follows from Fig. 6 at a constant concentration of monomers A copolymerizes with D₂ at a faster rate than A with D₁, which may be explained by the high polarizability and reactivity of the monomers and complex A...D₂.

Considering that the monomers studied separately polymerize with difficulty in conditions of alternating copolymerization one may ignore the chain growth reactions leading to formation of the structures $\sim A-A'$, $\sim D_1-D'_1$ or $D_2-D'_2$. In addition, from the character of the curves in Fig. 6 it may be assumed that the chain growth reactions come about by a "free monomer" or "complex" mechanism.

For the quantitative characterization of the participation of the complex-bound monomers in the radical chain growth reaction, we used the kinetic method [7] based on determination of the ratios of the rate constants of chain growth through the complexes (k_{1c} and k_{2c}) and free monomers (k_{12} and k_{21}). For each system of monomers we constructed the function $v/[A] \rightarrow [A]$ (Fig. 7) from which we found the values of f corresponding to the different ratios of the monomers F and v_{\max} . Next, from the dependence of $2f/K$ on F (Fig. 8) we find the values $k_{1c}/k_{12} = 1.75$ and 1.25 (segments on the ordinate axis) and $k_{2c}/k_{21} = 46.6$ and 16.4 (slope of straight lines) for the systems A-D₁ and A-D₂ respectively.

The high values of these ratios for both systems favour the complex mechanism of chain growth. The complex-bound monomers make a considerable contribution to the reactions with the participation of the macroradicals containing the terminal D₁ and D₂ units. Despite the high value of K for the coordination-bound complex A...D₂ its contribution to radical chain growth is less than that of the complex A...D₁ which may be explained by spatial factors due to the organotin fragments.

It may be concluded that in the radical copolymerization of the monomer pairs studied a considerable role is played by the reactions of the complexes with growing macroradicals $\sim A'$ and $\sim D$ and also $\sim A'$ with electron-donor monomers in the intramolecular-complex state and responsible for the process of formation of cyclic structures in the macromolecular chain.

Translated by A. CROZY

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SYNTHESIS, STUDY AND CHEMICAL MODIFICATION OF VINYL-TETRAZOLE POLYMERS*

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The authors have studied the radical polymerization of 5-vinyltetrazole and 1-vinyl-5-aminotetrazole. The monomers are readily polymerized by the radical mechanism in presence of AIBN and redox systems. The phenomenon of association and ionization of the monomer and polymer molecules has been found. It has been established that poly-5-vinyltetrazole possesses polarographic activity due to the presence of an acid proton. The thermogravimetric method has established that vinyltetrazole polymers are thermally stable up to 250–260°C after which their heavy degradation is observed. Chemical modification of poly-5-vinyltetrazole has been carried out and some physicochemical properties of the solutions of the initial and modified polymer studied.

TETRAZOLE derivatives have found application in medical practice and in photography as anti-corrosive coats [1]. Yet vinyltetrazole derivatives remain a poorly studied class of compounds. Only a few sources of a patents character [2–4] exist on the polymerization of vinyltetrazoles.

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