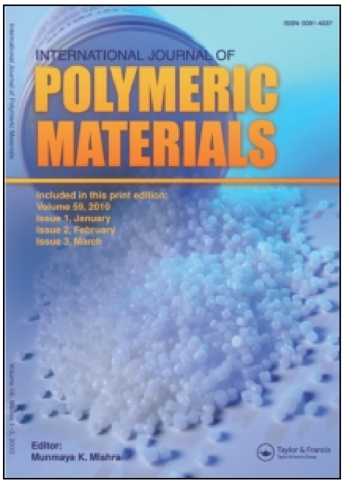

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Synthesis and Investigation of Properties of Vinylcontaining Silyllactams and Their Copolymers

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The interactions of vinylorganochlorsilanes with lactams (ε-caprolactam, γ-pyrolidon) have been studied. New vinylcontaining N-silyllactams and aminosilanes have been synthesized and characterized, and the copolymerization reactions of N-vinyl-silyllactams with organic vinyl monomers (styrol, methyl- and butylmethacrylate, fluorine and silicium-containing methacrylate) have been carried out.

The obtained copolymers were investigated by element analysis, IR- and NMR spectroscopic analyses, MMD. The results of these investigations have shown that the introduction of silicium-containing monomers into the main chain of polystyrols and polyacrylates causes their chemical modifications with improving thermostability, processability, etc.

KEY WORDS Vinyl, lactames, silyllactames, copolymers.

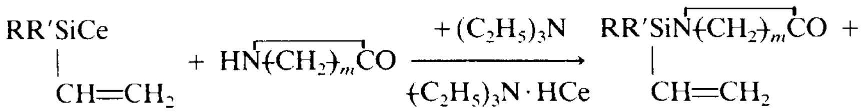
INTRODUCTION

Polymers on the base of vinylcontaining monomers (acrylates, methacrylates, styrol) are widely employed in applied optics and optoelectronics. But these polymers have not a sufficient thermal and IR-radiation resistance, which restricted the possibilities of their applications.

One of the ways for the improvement of operational properties of the polymers for optical usage on the base of these monomers can be their chemical modification by introducing the nitrite-containing silylorganic monomers in the backbone chains of their macromolecules via the radical block interpolymerization of the vinylcontaining silicoorganic compound with the organic vinyl monomers.[1]

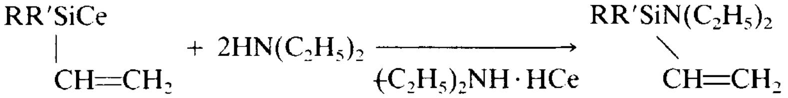
RESULTS AND DISCUSSION

As initial silylorganic monomers, we used vinylcontaining silyllactames, which were prepared by the heterofunctional condensation of the suitable monochlorsilanes with ε-caprolactames and γ-pyrolidon. For comparison, methylisopropylvinyldiethyl-aminosilane (MP_2VAS) was prepared. The reaction of condensation of chlorsilanes with lactames (1) and diethylamin (2) proceed according to the schemes (see Table I).

1. 

$$\underset{\displaystyle CH{=}CH_2}{\overset{\displaystyle RR'SiCe}{|}} + H\overline{N(CH_2)_mCO} \xrightarrow[-(C_2H_5)_3N\cdot HCe]{+(C_2H_5)_3N} \underset{\displaystyle CH{=}CH_2}{\overset{\displaystyle RR'Si\overline{N(CH_2)_mCO}}{|}} +$$

where $m = 3$, $R = R' = CH_3(I)$, $R = CH_3$, $R' = C_2H_5(II)^{+\text{polymer}}$, $R = CH_3$, $R' = C_6H_5(III)$.
$m = 5$, $R = CH_3$, $R' = C_2H_5(IV)$, $R = CH_3$, $R' = i - C_3H_7(V)$, $R = CH_3$, $R' = C_6H_5(VI)$.

2. 

$$\underset{\displaystyle CH{=}CH_2}{\overset{\displaystyle RR'SiCe}{|}} + 2HN(C_2H_5)_2 \xrightarrow[-(C_2H_5)_2NH\cdot HCe]{} \underset{\displaystyle CH{=}CH_2}{\overset{\displaystyle RR'SiN(C_2H_5)_2}{\diagdown}}$$

Reactions proceeded in dry solvents (benzene, diethyl ether) in the presence of $(C_2H_5)_3N$ at the temperature of 40°C and equimolar contents of the parent compounds. The process of condensation was controlled by the production of hydrochloric acidiferous triethylamine.

Above-mentioned organosilylated lactames are produced with the reaction yield up to −4% which decreases in the series of $(CH_3)_2(CH_2{=}CH)SiCe > CH_3(C_2H_5)(CH_2{=}CH)SiCe > CH_3(C_6H_5)(CH_2{=}CH)SiCe$.

All synthesized compounds after vacuum distillation represent colourless transparent liquids, which are readily soluble in several organic solvents. Their hydrolytic stability depends mainly on the nature of the organic radical of Si atom and is the highest for methylvinylphenylsilyllactames.

The physico-chemical constants, yields and the elemental composition of vinylsilyllactames and aminosilanes are listed in Table I.

The structure of the synthesized compounds is confirmed by IR and NMR spectra data. In all IR spectra of vinylsilyllactames, there are absorption bands in the regions of 835–860 cm^{-1}, 920–970 cm^{-1} and 1600 cm^{-1}, which characterize the oscillations of $\rightarrow Si{-}N$ and $\rangle C{=}C\langle$ valent bonds, respectively, and an absorption band at 1650–1700 cm^{-1}, which is specific for $\rangle C{=}O$ groups in lactames.

In the NMR spectra of the compounds V and VI (see Table I) signals are observed from $CH_3{-}Si$ groups (δ^* 0.43 for V and 0.30 for VI), $CH_2{=}CH{-}Si$ ($\delta 5.7 \div 6.6$ for V and $\delta\ 5.6 \div 5.9$ for VI), multiplets of ABC type, $CH_3(CH_2)_2$ ($\delta 1.06$ CH_3, 1.4 $(CH_2)_2$ for V, $C_6H_5(\delta 7.2 \div 7.8)$ for VI, and also specific ones for ε-caprolactam cycle $-CH_2{-}C{=}O$ ($\delta 2.6 \div 3.0$), $-CH_2{-}CH-$ ($\delta 2.0 \div 2.4$) and $(CH_2)_3$ ($\delta 1.4$).

The noticed effects were obtained at the investigation of these compounds by the method of NMR-^{13}C spectroscopy. The chemical shifts of the carbon nucleus in the lactame cycle are sensitive to the silicium nucleus substitution, especially for CH_2 group connected with the nitrogen nuclei ($\delta 42.3$ for VI and $\delta 44.8$ for V) and the carbonyl group ($\delta 36.7$ for VI and 37.7 for V), the resonance line of the latter

TABLE I

Physico-chemical properties and data of elemental analysis of synthesized monomers

No.	Compound	Designation	Yield, %	T_{boil}, °C	n_D^{20}	d_4^{20}	ν, cm^{-1}	Elem. analysis (obtained/calcul., %) C	H	Si
I	$(CH_3)_2\underset{\underset{CH=CH_2}{\vert}}{Si}\overline{N(CH_2)_3C}O$	VDMSP	31	125/4 mm	1.4620	1.050	930	55.98/56.83	8.13/8.87	16.01/16.75
II	$CH_3(C_2H_5)\underset{\underset{CH=CH_2}{\vert}}{Si}\overline{N(CH_2)_3C}O$	VMESP	28	115/2 mm	1.4906	1.210	935	59.02/58.79	9.28/10.11	15.31/14.54
III	$CH_3(C_6H_5)\underset{\underset{CH=CH_2}{\vert}}{Si}\overline{N(CH_2)_3C}O$	VMPSP	22	172/4 mm	1.5320	1.072	965	67.5/68.12	7.35/7.19	12.14/13.12
IV	$CH_3(C_2H_5)\underset{\underset{CH=CH_2}{\vert}}{Si}\overline{N(CH_2)_5C}O$	VEMSC	27	155/1 mm	1.5008	1.131	940	62.56/63.12	9.95/8.89	13.27/14.54
V	$CH_3(C_3H_7)\underset{\underset{CH=CH_2}{\vert}}{Si}\overline{N(CH_2)_5C}O$	VMP$_2$SC	22	157/1 mm	1.4820	1.230	950	63.53/64.28	9.18/10.23	11.86/12.46
VI	$CH_3(C_6H_5)\underset{\underset{CH=CH_2}{\vert}}{Si}\overline{N(CH_2)_5C}O$	VMPSC	19	170/0.5 mm	1.5160	1.011	970	69.49/68.98	7.91/8.11	14.96/15.48
VII	$CH_3(C_3H_7)\underset{\underset{CH=CH_2}{\vert}}{Si}N(C_2H_5)_2$	VP$_2$MAS	49	107/1 mm	1.5080	0.998	920	59.20/62.19	11.2/12.23	19.7/18.43

being broadened, which indicates a marked slowing-down of the conformational transitions in the seven-membered lactam cycle of these compounds.

We carried out magnetooptic investigations of some organovinylsilyllactames. We have investigated the constants of magnetooptical rotation (MOR) as functions of the relation of the molecular mass M and the density ρ for some synthesized monomers and some commercial monomers employed in the work (Table II). The data of MOR for -caprolactam are given for the comparison.

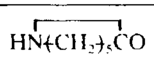
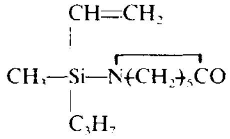
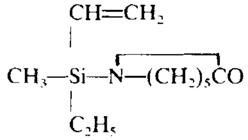
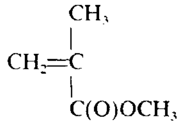
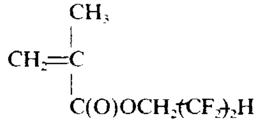
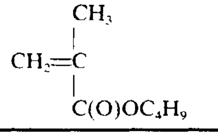
As it is evident, the experimental results demonstrate a good agreement with the theoretical dependence of M/ρ on the constant of MOR derived from Newton and Bertelot equations[2] and on the equation for the molecular MOR containing the value of polarization.

We also performed the reactions of copolymerization of the synthesized organovinylsilyllactams with styrol and methacrylates of different structure (organic methacrylates-methylmethacrylate (MMA), butylmethacrilate (BMA), fluorine- and silicium-containing methacrylates FMA and DMAMS) obtained using the procedures described in the article[3] and refined using standard procedures.[4]

Copolymerization of vinylsilyllactams with the above-mentioned monomers was

TABLE II

Functional dependence of the MOR constant on the ratio of molecular mass and density

No.	Compound	M/δ	Constant of CMR min/ECM
1.	 $HN(CH_2)_5CO$	109.78	−0.00316
2.	 $CH_3-\underset{C_3H_7}{\overset{CH=CH_2}{Si}}-N(CH_2)_5CO$	229.59	−0.00775
3.	 $CH_3-\underset{C_2H_5}{\overset{CH=CH_2}{Si}}-N-(CH_2)_5CO$	206.80	−0.00327
4.	 $CH_2=\underset{C(O)OCH_3}{\overset{CH_3}{C}}$	80.74	0.0131
5.	 $CH_2=\underset{C(O)OCH_2(CF_2)_2H}{\overset{CH_3}{C}}$	156.30	0.0129
6.	 $CH_2=\underset{C(O)OC_4H_9}{\overset{CH_3}{C}}$	140.78	0.128

carried out in soldered ampoules. The ampoules with monomers were preliminarily degassed with the mixture of peroxide initiators, such as dicumil (DCP) of 0.5 mass % and benzoyl (BP). For the separation of the copolymerization products from unpolymerized initial monomers, the reaction products were reprecipitated by hexane from the benzoyl solution and dessicated in the drying box at the temperature of 25°–30° until the constancy of mass.

The reaction of copolymerization of the vinylcontaining silyllactams with the styrol (St) was carried out at several ratios of monomers. The investigation of the reaction demonstrates that its rate, yield, η_{sp} and composition of the copolymers depend, in the main, on the ratio of monomers in the initial mixture, on the presence of organic radicals around the silicium atom in silyllactams and on the value of the lactam cycle.

For the estimation of the reactivity of the organovinylsilyllactams with styrol, the constants of copolymerization r_1 and r_2 were determined. The composition of copolymers was determined by the elemental analysis data (the contents of Si, %) and by the gas-liquid chromatography method.[5] The values of r_1 and r_2 were determined by Fainemann-Ross.[6] The obtained effective constants of copolymerization ($r_1 = 1.26$; $r_2 = 0.34$) confirm that the growing macroradical connects mainly the styrol molecule, whereby the statistical polymer is formed with basic chain enriched by the links of styrol as a more active monomer.

The researches demonstrate that with increasing silyllactam monomers fraction in the initial mixture, the copolymerization proceeds more slowly, with the formation of nonhighmolecular products and with a small yield. Thus, for example, the copolymerization of N-methylethylvinylsilyl-ε-caprolactam with styrol at the ratios of 90:10 , 70:30 and 50:50 (mass %) leads to the formation of two reaction products with η_{sp} of the order of 0.42, 0.30 and 0.26, respectively. The increase of the temperature above 120°C accelerates the copolymerization, but the elemental analysis data show that the copolymer composite is enriched by the organic monomer, which, probably, is connected with the predominantly proceeding reaction of styrol homopolymerization under the conditions of our experiment.

To substantiate the fact that the copolymer formation really happens at the copolymerization, we performed the investigation of MMD by the temperature

TABLE III

Conditions of the copolymer reaction of the organic vinylsilylactams and properties of the resulting copolymers (initiator-BP-DCP 0.5% + 0.5% at T = 100°)

No.	Parent monomers	Ratio of monomers in parent mixture mass, %	Yield of copolymers, % after 8 h		Temperature of copolymer melting, °C
1.	St:VMESC	10:90	46	0.08	
2.	St:VMESC	20:80	53	0.12	
3.	St:VMESC	30:70	60	0.23	
4.	St:VMESC	50:50	72	0.26	120–127
5.	St:VMESC	70:30	78	0.30	
6.	St:VMESC	90:10	81	0.42	
7.	$\text{St.VMP}_2\text{SC}$	50:50	66	0.28	130–139
8.	St.VMPhSC	50:50	58	0.25	143–150
9.	St.VMPhSC	50:50	64	0.23	134–140

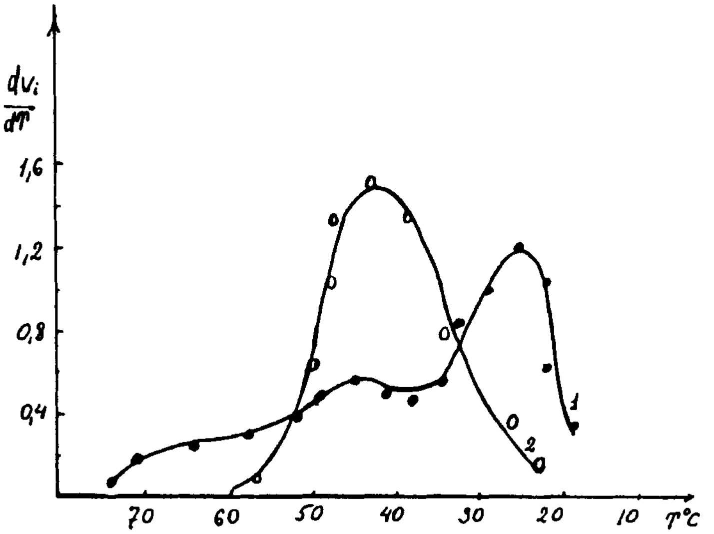


FIGURE 1 Curves of MMD for copolymers: 1) VDMSC:St (30:70 mass %); 2) VDMSC:St (10:90 mass %).

sedimentation method.[7] As the differential curves of the temperature sedimentation demonstrate (the points of turbidity, see Figure 1), under the conditions of copolymerization, the copolymer and the mixture of homopolymers are formed at relatively low temperature (75°C).

The synthesized copolymers represent transparent, colourless or light amber-coloured solid or rubber-type products which are soluble in benzene, toluene, chloroform, acetone. In the IR spectra of the fabricated copolymer N-(vinylmethylphenylsilyl)-ε-caprolactam with styrol (50%: 50 mass %), which was purified by the reprecipitation, side by side with the absorption maxima characteristic of the bonds Si—CH$_3$ (1260 cm^{-1}), Si—C$_6$H$_6$ (1610, 1500, 2011 and 3085 cm^{-1}), absorption maxima were detected in the region of 2040–2975 cm^{-1}, which are characteristic of the bonds →CH and)CH$_2$, as well as of the group —CH—CH$_2$.

After the solvent evaporation, most of the synthesized polymers constituted transparent elastic films on the solid surface, which loose their solubility after a prolonged heating at an elevated humidity. It seems to be connected with the hydrolysis of Si—N bonds at the temperature of 100°C by the air moisture with the production of silanol groups, their subsequent condensation leading to the formation of a three-dimensional structure. The contents of the gel fraction in the cross-linked polymer determined by Sohxlet apparatus, amount to 16.7% in chloroform.

The loss of solubility of copolymer on the base of bis(diethylamine)vinylmethylethylsilane with styrol at its heating with diphenylsilanediol (80%; 20 mass %) accompanied by diethylamine extraction speaks ipso facto in favour of such a proposition.

In the IR spectra of the cross-linked copolymer registered by means of its dispersing after freezing in liquid nitrogen and pressing with KBr, side by side with the absorption maxima characteristic of Si—N, C=O, Si—CH_3 bonds in this structure, we have found weak bands in the regions of 1060–1080 cm^{-1}, 1185 cm^{-1} which can be attributed to Si—O—Si and Si—C_6H_5 bonds, respectively. The formation of the cross-linked copolymer has been observed at the copolymerization of bis(diethylamine)-vinyl-methyl ethylsilane with styrol (80%, 20 mass %) in unsoldered ampoules in the air. It should be noted that the possibility of the involvement of lactam heterocycles in the formation of the three-dimensional structure by their opening via ⟩CO—NH— bonds is not out of question, as evidenced by relatively underrated yields of vinylcontaining silyllactams and by the formation of viscous resin-type products after vacuum distillation at their preparation.

The investigation of the copolymerization of N-vinylmethyl ethylsilyllactam with methylacrylates demonstrates that the yield and the specific viscosity of the obtained copolymers depend mainly on the volume of the radical of the complex-ester group of methacrylate (Table IV).

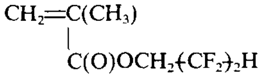
In consequence of the reaction, very viscous (except the product of the copolymerization with MMA) resin-type products with $\eta_{sp} = 0.10$–0.21 are formed.

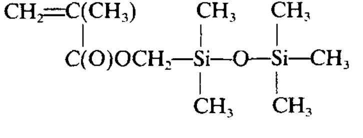
The thermomechanical properties and the thermooxygenational stability of some synthesized copolymers has been studied. Thermomechanical investigations of the obtained copolymers were performed on Höppler consistometer under the constant load of 125.0 gr and with the temperature growth rate of 1°C/min. As Figure 2 shows, the thermomechanical curves of the obtained copolymers characterize their moderate molecular masses. The appearance of the plateau region of highly elastic deformation with a low value of the relative deformation in the curve for the copolymer of vinyl methyl ethyl aminosilane with styrol (see Figure 2) at a relatively low specific viscosity of the copolymer $\eta_{sp} = 0.42$ seems to be connected with the formation of partly cross-linked copolymer which decomposes at the temperature

TABLE IV

Conditions of the copolymer reaction of the organic vinylsilyl-ε-caprolactam with methacrylate (50:50 mass %) and properties of the resulting copolymers (initiator BP-DCP 0.5%/0.5%)

No.	Parent monomers	Yield of copolymers, % after 8 h	η_{sp}	Physical state of the copolymers
1.	VMESC:MMA	70	0.23	solid transparent product
2.	VMESC:BMA	50	0.18	gum-like product
3.	VMESC:FMA[a]	53	0.21	transparent viscous
4.	VMESC:DMAMS[b]	44	0.10	resins

[a]FMA: 
$$\begin{array}{l}\mathrm{CH_2{=}C(CH_3)}\\ \quad|\\ \mathrm{C(O)OCH_2(CF_2)_2H}\end{array}$$

[b]DMAMS: 
$$\begin{array}{l}\mathrm{CH_2{=}C(CH_3)\quad CH_3\quad CH_3}\\ \quad|\qquad\qquad\quad|\qquad\quad|\\ \mathrm{C(O)OCH_2{-}Si{-}O{-}Si{-}CH_3}\\ \qquad\qquad\quad|\qquad\quad|\\ \qquad\qquad\mathrm{CH_3\quad CH_3}\end{array}$$

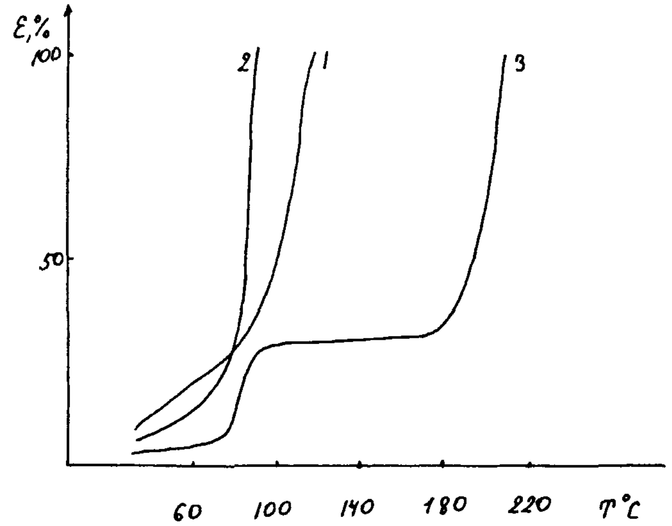


FIGURE 2 Thermomechanical curves for copolymers: 1) vinyl methyl phenyl silyl-ε-caprolactam with styrol, 2) vinyl methylethyl silyl-ε-carprolactam with styrol, 3) vinyl methylethyl silylamine with styrol.

above 180°C (the curves TGA in Figure 3) leading to the complete deformation of the sample.

Thermogravimetric analysis (TGA) of the obtained copolymers demonstrates that their thermooxygenational decomposition begins at the temperature above 180°, and for polystyrol—above 150°.[8] Such results confirm the occurrence of the chemical modification of polystyrol due to the introduction of silyllactam fragments into the macromolecule main chain.

Relatively early mass losses for the copolymer of styrol with vinylmethylethylaminosilane (Figure 3a, curve 3) seem to be connected with the processes of Si—N bond hydrolysis by the humid air with the release of the hydrolysis and condensation by-products, as evidenced by the appearance of a low-intensive exothermic spike in the differential thermal analysis (DTA) curves at 100°–120°. The basic processes of the copolymer thermooxygenational destruction are developed in the temperature interval of 180°–250°, as evidenced by the appearance of intensive endothermic peaks in the DTA curves in this temperature interval.

The influence of the organic setting of the silicium atom upon the thermooxydational stability has negligible manifestations.

CONCLUSIONS

The reaction of vinylorganochlorsilanes with ε-caprolactam and γ-pyrrolidone was investigated, and the corresponding vinyl-organosilyllactams were synthesized; their composition and structure were adjusted on the basis of the elemental analysis, IR and NMR spectra researches. For some of these compounds, the constants of the magnetooptical rotation were determined. Copolymerization of vinylorganosilyllactams and vinyl isopropyl methyl aminosilane with vinyl compounds (styrol, meth-

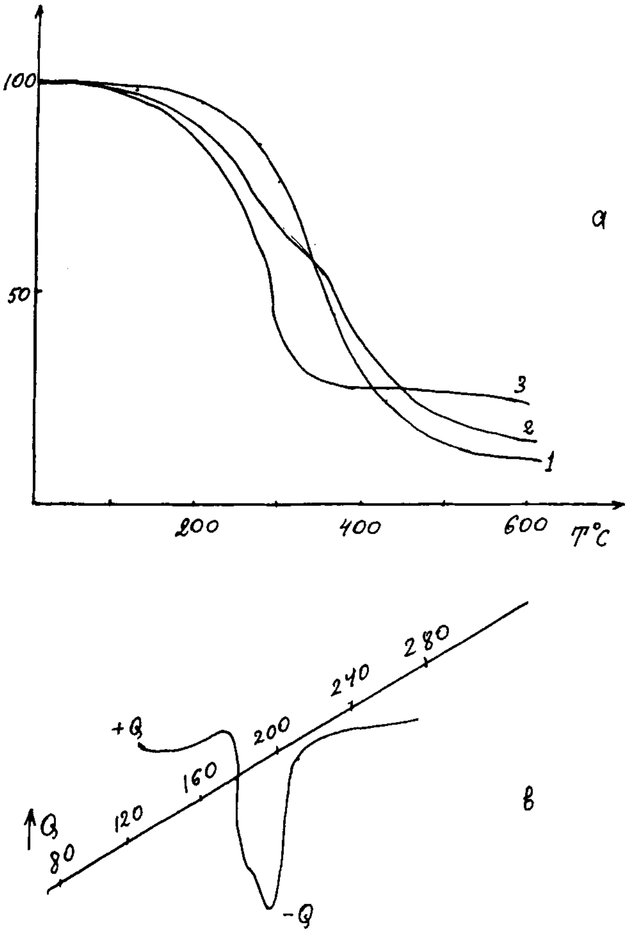


FIGURE 3 (a). Curves of TGA for copolymers: 1) vinyl methyl phenyl silyl-ε-caprolactam with styrol, 2) vinyl methyl ethyl silyl-ε-caprolactam with styrol, 3) vinyl methyl ethyl silylamine with styrol. (b) Curves of DTA for a copolymer on the base of aminosilane with styrol, 30:70 mass %.

ylmethacrylate, butylmethacrylate, fluorine- and silicium-containing methacrylates) was carried out, and the constants of copolymerization r_1 and r_2 were determined by Fainemann-Ross method. It is established that these reactions result in the production of soluble, transparent solid resin-type copolymers, wherein macrochains are upgraded by the links of more reactive monomers, in particular, styrol.

The thermomechanical properties and the thermooxygenational stability of the obtained copolymers were studied. It is established that the thermomechanical curves of copolymers are typical of polymers with moderate molecular masses. Thermogravimetric studies demonstrate that copolymers begin to destroy in the air above 180°C, which is higher than for corresponding organic homopolymers.

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