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STUDY OF THE KINETICS OF POLYMERIZATION AND COPOLYMERIZATION OF METHACRYLIC ACID SULPHOLANATE*

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The kinetics of polymerization of methacrylic acid sulpholanate (MAS) of its copolymerization with methyl methacrylate, styrene and methacrylic acid were investigated. An increased activity of MAS was noticed, when compared with the majority of known methacrylates, in the radical polymerization reactions.

SULPHUR containing polymers have a number of valuable properties, especially heat, temperature, light and chemical stability [1–4], large dielectric and physico-chemical characteristics [1, 5], good adhesion to various materials [6]. This

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type of polymer has been given much attention in recent years [7, 8, 10]. The polymerization of sulphur containing vinyl monomers and their copolymerization with various other monomers represents a very promising method of synthesizing sulphur containing polymers, and of modifying already widely used ones. The sulpholanates of unsaturated acids belong to the interesting monomers [9]. No information could be found in the literature to their polymerization kinetics. We therefore describe in this report the results of studying the radical homo- and copolymerization kinetics of MAS, and some of the properties of our products.

EXPERIMENTAL

The MAS $\left(\begin{array}{c} CH_2=C-COO-\boxed{} \\ | \quad\quad \searrow\diagdown \\ CH_3 \quad\quad SO_2 \end{array}\right)$ has a b p $=158°C/1$ mmHg; $n_D^{20} 1 5028, d_4^{20} 1 215,$

m.p $=39$–$40°C$. Elemental analysis gave: (%)· 47 0 C, 6 0 H, 15 8 S. The absorption bands found in the infrared (IR) spectra (cm^{-1}) are: 1132, 1143, 1287, 1328 (SO$_2$-groups); 1378, 1448, 2960 (CH$_3$-groups); 1400, 2920 (CH$_2$-groups); 947, 1017, 1630, 3020, 3040 (C=C bonds); 1132 (—COC-groups); 1715 (O=C-groups).

Styrene and methyl methacrylate (MM) were purified by the usual methods [11], the b.p. of styrene was $42°C/15$ mmHg, $n_D^{20}=1 5465$. The MM had b p $=46°C/100$ mmHg, $n_D^{20} 1 4130$. The methacrylic acid (MA) was dried over anhydrous calcium chloride and was thrice vacuum distilled; b p.$=44 5°C/2$ mmHg, $n_D^{20} 1 4315$. The azoisobutyrodinitrile (AIBN) was recrystallized three times from methanol and then vacuum dried to constant weight; m.p.$=102°C$. All the solvents used in the polymerizations were purified by the usual methods [12] and had the tabulated characteristics.

The kinetics of homo- and copolymerization were studied by dilatometry at low conversion (less than 10%) in the presence of AIBN (0·01% w/w) The dilatometers were fused after evacuation to 10^{-3}–10^{-4}mmHg. In all cases, with the exception of the determination of the order of reaction with respect to monomer, the monomer to solvent ratio used was 1 : 1. Contraction coefficient K of MAS was established after several tests from the polymer yield at $50°C$; it was 0 142. An estimate of K for the copolymerization was based on the additivity principle using the known values of K of other monomers [13, 14].

The polymers were purified by 3–4 reprecipitations followed by vacuum drying at $60°C$. The homopolymer was reprecipitated with sulphate ether from DMF. The solvents and precipitants used to purify the copolymers are given in Table 1. The copolymer compositions were determined by elemental analysis. The copolymerization constants were determined by the method described by Mayo and Lewis [15].

RESULTS

The kinetics of polymerization of MAS were studied in DMF, DMSO and benzene as solvents. There were difficulties in the latter due to the heterogeneity of the medium at higher MAS concentrations.

Table 2 and Figs. 1, 2 show that the nature of the solvent does not affect the rate of MAS polymerization. The orders of reactions with respect to monomer and initiator found graphically were 1 and 0·5 respectively (Fig. 1, 2), which indicates the presence of the usual mechanism of radical polymerization with a bimolecular chain termination. It was interesting to note that the rate of MAS polymerization exceeded that of numerous known methacrylates; this is probably

TABLE 1. THE PROPERTIES OF THE MAS COPOLYMERS (M_1) WITH SOME VINYL MONOMERS

M_2	Mole % of M_2 in copolymer	Soft. temp., °C	Flow temp., °C	Polymer purification		Solvents	Characteristic IR-spectral lines, cm^{-1}
				solvent	precipitant		
Styrene	100 88.87 80.16	107 134 144	153 150 170	Dioxane	Methanol	DMF, DMSO, dioxane, benzene, butyl acetate	1140, 1320 (SO_2-groups); 1190, 1720 (RCOOR'-groups); 1380, 1448 (CH_2-, CH_3-groups); 705, 760, 1448, 1597 (benzene groups)
MM	100 96.14 87.20 68.60	105 125 128 135	210 232 239 240	Benzene	Sulphate ether	DMF, DMSO. dioxane, benzene	1140, 1320 (SO_2-groups); 1165 (RCOOR'-groups); 1735 (CO-groups)
MAA	100 95.9 87.9 82.7	295 236 220 210	386 268 245 230	Ethanol	Sulphate ether	DMF, ethanol, water	1150, 1320 (SO_2-groups); 1720 (COOH-groups); 1380, 1480 (CH_2-, CH_3-groups)

due to the effect of the polar SO_2-group in the sulpholan ring producing steric hindrance to chain termination. The true activation energy E of the polymerization found by the graphic method was 23 kcal/mole (Table 2).

TABLE 2. THE MAS COPOLYMERIZATION KINETICS WITH AIBN AS INITIATOR ([AIBN]$=6.1 \times 10^{-4}$ mole/l.)

Solvent	Process temp., °C	$k \times 10^4$,* l. mole^{-1}·sec^{-1}	$k_\mathrm{D}/k_0^{1/2}$†
DMF	40	2·8	0·35
	50	2·8	0·48
	60	25	0·75
	70	56	0·10
DMSO	50	8·1	0·45
Benzene	50	—	0·43

* k—total rate constant of polymerization

† The k_D/k_0† of MAS was estimated analytically from $k=[f\ k_\mathrm{decomp}]^{\ddagger}\ k_\mathrm{P}/k_0^{\ddagger}$ (k_decomp—rate constant of AIBN decomposition which most of the authors give as being independent of the solvent type and monomer The k_decomp was here determined from $k_\mathrm{decomp}=1\ 29 \times 10^{15}$, $e-30,500/$ /RT [16] Value $f=0\ 5{-}0\ 7$ for AIBN [17], we took 0 7)

The studies of the kinetics of copolymerization with vinyl monomers, i.e. MM, styrene and MA, were carried out under homogeneous conditions The results are reproduced in Table 3 and Fig 3. The copolymerization constants r_1 are

TABLE 3. THE MAS (M_1) COPOLYMERIZATION WITH SOME VINYL MONOMERS (M_2) ([AIBN]$=6.1 \times 10^{-4}$ mole/l.)

M_2	M_2, mole%		r_1	r_2	$r_1 \cdot r_2$	Q	e	φ
	at start	in copolymer						
Styrene	97·14	88·87	1 5$\pm$0·1	0·22$\pm$0 01	0 33	2·0	0·26	25
	94 06	80·16						
	75·8	63·8						
MM	96 21	96·14	3 34$\pm$0 25	0 67$\pm$0 02	2 24	2 5	0 4	5
	92 06	87 20						
	80 9	68 60						
MA	96 6	95 9	1 0$\pm$0 1	0·83$\pm$0 02	0 83	—	—	600
	89 5	87 9						
	84 7	82 7						

evidence of the high activity of MAS in the copolymerizations. The explanation is, judging from the large Q-values calculated for MAS by the Alfrey–Price method [18] on the MAS copolymerization with MM and styrene, the increase of the conjugation energy of the monomer. The Q-value for MAS was not calculated, according to the results of its copolymerization with MA due to dependence of Q on the type of comonomer and medium in this case [19, 20].

The rate of the bulk copolymerization of MAS with styrene increased on raising the content of the first monomer in the original mixture (Fig. 3*b*). This

is probably the consequence of MAS radicals being more reactive than those of styrene. In the case of MM as comonomer in benzene as solvent (Fig. 3a), or MA in DMF (Fig. 3c) (using small MAS additions), the reverse was true, i.e. the rate of copolymerization dropped as the MAS content increased in the substrate. This indicates the MAS radicals to be less reactive than those of MM or MA.
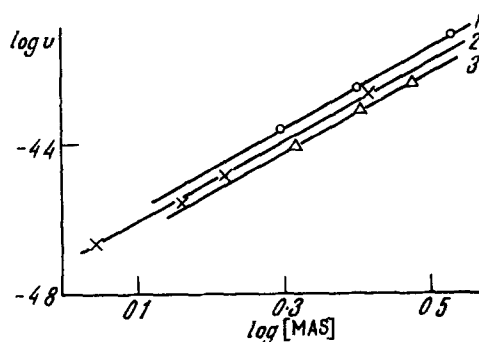

FIG. 1. The effect of the MAS concentration on the rate of polymerization v in: 1—DMF, 2—DMSO, 3—benzene at 50°C using 6.53×10^{-4} mole/l. AIBN.

The cross termination constants φ became smaller on changing from MAS–styrene to MAS—MM, while value of $r_1 \cdot r_2$ became larger (Table 3). This is explained by the monomers having different polarities in the first case, but similar ones in the second. There was in system MAS–MM the same tendency for cross termination ($\varphi = 5$). Undesirably large values of φ were encountered during the copolymerization of MAS with MA and the explanation must be sought in the solvent, i.e. DMF, which easily formed complexes with MA.
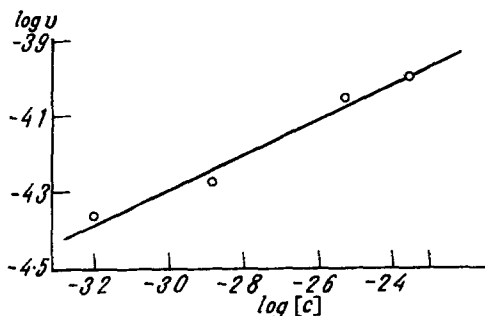

FIG 2. The effect of the initiator concentration c on the rate of the MAS polymerization in DMF at 50°C using 2.04 mole/l. MAS.

Poly-MAS is a white powder soluble in DMF and DMSO, but insoluble in benzene, acetone, chloroform, dioxane, butyl acetate, alcohols, paraffins. Typical IR-spectral absorption lines are (cm^{-1}): 1120, 1135, 1307 (SO$_2$-groups); 1185 (RCOOR'-groups); 1720 (CO-groups). The molecular weight (mol.wt.) of the

polymer produced in DMF at 60°C, determined by light-scattering, was 880,000 ($[\eta]=0.79$ in DMF at 20°C).

Thermomechanical testing showed two transition temperatures, i.e. the softening temp.=197°C, flow temp.=250°C, start of decomposition at about 240°C.
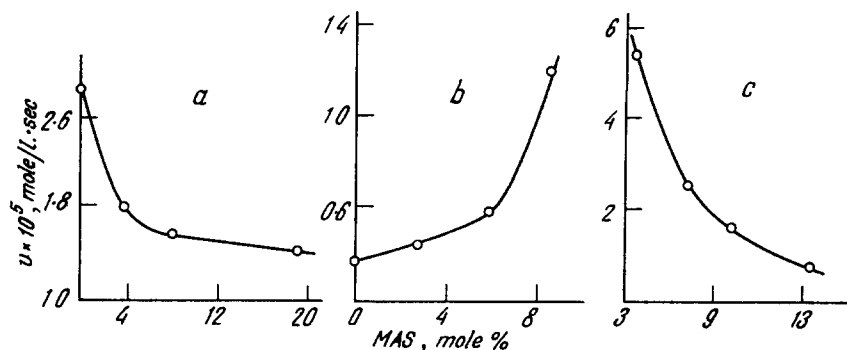

FIG. 3. The MAS copolymerization with MM in: a—benzene, b—its bulk copolymerization with styrene, c—and with MA in DMF; a—at 50°C; b—40°C; c—60°C; 0·01% w/w AIBN.

The copolymers were white powders. Table 1 shows the solubilities of the copolymers, typical IR-spectral absorption lines and the thermomechanical properties. The mol.wt of the MM copolymer containing 12·8% MAS produced in benzene at 50°C was 800,000. The insertion of the MAS units into the copolymer with styrene or MM raised the softening temperature and that of flow. The MA copolymers with MAS had lower softening and flow temperatures than the polymethacrylic acid alone.

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HOMO- AND COPOLYMERIZATION OF SILICON-CONTAINING LACTAMS*

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The polymerization of methylvinylsilyl-bis-ε-caprolactam (MVSC) and methyl-vinylsilyl-bis-γ-pyrrolidone (MVSP), and their copolymerization with methyl methacrylate (MM) or styrene, were studied. Some of the kinetic principles of these processes were also studied and the rate constants for the formation of gel were calculated.

The thermomechanical and thermogravimetric properties of the homo- and copolymers and their infrared spectra are also described.

THE aim of the work reported here was to study the polymerization of methyl-vinylsilyl-bis-ε-caprolactam (MVSC) and methylvinylsilyl-bis-γ-pyrrolidone (MVSP), and their copolymerizations with methyl methacrylate (MM) or styrene [1].

Bulk polymerization of MVSC and MVSP was carried out in the presence of 1% w/w dicumyl peroxide under a nitrogen stream at 120°C. These processes yielded crosslinked polymers as solid, elastic and transparent materials which were not soluble in organic solvents.