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UNSATURATED ESTERS OF N-(β-HYDROXYETHYL) LACTAMS

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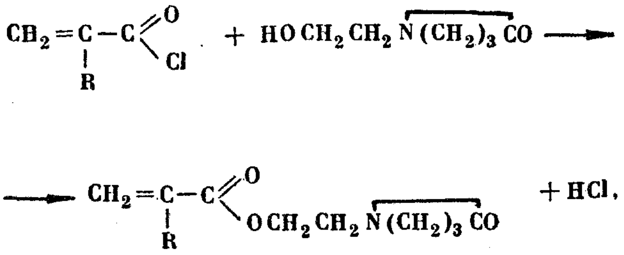
A general method is developed for synthesizing methacrylic esters with a 5-, 6-, or 7-membered lactam ring β to the carboxyl group, by reacting the sodio-derivatives of the lactams with β-chloroethyl methacrylate. The esters synthesized are prone to thermal polymerization, and able to copolymerize with other monomers in the presence of azodiisobutyronitrile. The following copolymers are prepared: β-(N-pyrrolidonyl) ethyl acrylate with methyl acrylate, β-(N-pyrrolidonyl) ethyl, β-(N-2-oxotetramethyleneimino) ethyl, and β-(N-2-oxopentamethyleneimino) ethyl methacrylates with methyl methacrylate.

Methacrylic ester polymers with an amino group β to the carboxyl group $CH_2 = C(CH_3)COOCH_2CH_2NRR'$, possess a number of properties of practical value [1]. They can be used as adhesives, coating resins, ion exchange resins, etc. Copolymers of such esters have higher softening temperatures.

Introduction of a lactam ring into a molecule often facilitates appearance of properties closely akin to those evoked by an amino group (linking to dyes, higher softening temperatures, etc.). Some properties due to the presence of a lactam group are specific. Hence it is of interest to synthesize unsaturated esters with a lactam ring substituent and study the possibility of polymerizing them.

Some of the present authors previously described [2, 3] the synthesis and certain properties of pyrrolidonylethyl acrylates. Synthesis was effected by reacting the appropriate acids or their chloroanhydrides with N(β-hydroxyethyl) pyrrolidone:



R=H; CH₃

N-(β-hydroxyethyl) derivatives of higher lactams, e.g., of piperidone and caprolactam, are accessible with difficulty, and formed in small yields [4, 5]. So it is not practical to synthesize acrylic esters based on piperidone and caprolactam by the method developed for pyrrolidone derivatives. The present work developed a method of preparing acrylic esters with a lactam ring β to the carboxyl, based on the capacity of alkali metal salts of lactams to react readily with halogen derivatives. The equation for the synthesis is:

$$CH_2{=}C(CH_3)COOCH_2CH_2Cl + Na\overline{N(CH_2)_nCO} \rightarrow$$
$$\rightarrow CH_2{=}C(CH_3)COOCH_2CH_2\overline{N(CH_2)_nCO} + NaCl.$$

β-(N-pyrrolidonyl) ethyl methacrylate I (n = 3) is prepared by this method, and so are β-(N-2-oxotetramethyleneimino) ethyl II (n = 4) and β-(N-2-oxopentamethyleneimino) ethyl III (n = 5) methacrylates.

It did not prove possible to prepare the starting β-chloroethyl methacrylate by a method which has been described [6], the reaction of ethylene chlorohydrin with methyl methacrylate (IV). The reactants were recovered unchanged. β-chloroethyl methacrylate was prepared by reacting ethylene chlorohydrin with methacrylic chloroanhydride [7], and converted to the methacrylic esters I-III. I-III are high-boiling, viscous liquids, with a low solubility in water, but readily soluble in organic solvents. Table 1 gives the conditions used for synthesis and the physical constants of the products.

Table 1 shows that ester yield is a function of lactam ring size, the yield falling as this increases. Increasing reaction time (up to 6 hr) at first promotes increased yield, but subsequently leads to formation of large amounts of tars (possibly because of thermal polymerization). On passing from a 5-membered to a 7-membered ring, the heat stability of the esters drops, and their proneness to thermal polymerization increases.

TABLE 1

$CH_2{=}C(CH_3)COOCH_2CH_2\overline{N(CH_2)_nCO}$

Experiment No.	Compound	n	Reaction time hrs.	Mp °C (mm pressure)	n_D^{20}	d_4^{20}	% ester yield
1	I	3	2.5	90— 95 ($1.2 \cdot 10^{-2}$)	1.4918	1.1206	30.1
2	I	3	4.0	90— 95 ($1.2 \cdot 10^{-2}$)	1.4920	1.1206	42.1
3	II	4	2.5	100—105 ($1.5 \cdot 10^{-2}$)	1.4985	1.1419	18.9
4	II	4	6.0	83— 88 ($1.1 \cdot 10^{-2}$)	1.4985	1.1419	49.0
5	III*	5	2.5	98—105 ($2.2 \cdot 10^{-2}$)	1.4993	—	16.1
6	III	5	4.0	98—105 ($2.2 \cdot 10^{-2}$)	1.4993	—	31.0
7	III	5	6.0	98—105 ($2.2 \cdot 10^{-2}$)	1.4993	—	51.0
8	III	5	9.0	75— 79 ($1.1 \cdot 10^{-2}$)	1.4993	—	10.8

* As III was highly viscous its specific gravity was not determined

A study was made of the polymerization and copolymerization with IV and with methyl methacrylate (V) of the esters prepared under the action of azodiisobutyronitrile. Copolymerization was carried out for various ratios of monomer at intensive conversions. Table 2 shows the relationships between concentrations of starting monomers, yield, and amount of monomer chains in the copolymers, and indicates the external appearance.

TABLE 2

Copolymerization of β-(N-pyrrolidonyl) Ethyl Acrylate (VI) with Methyl Acrylate (V)

M_1, mole fraction of V in the initial mixture	% N in the polymer or copolymer*	m_1, mole fraction of VI in the copolymer	Appearance of copolymer	Softening temperature °C	% yield of polymer** or copolymer
0.10	1.32	0.086	colorless, rubbery	250	71.4
0.25	2.96	0.229	colorless, rubbery	400	63.6
0.50	4.68	0.429	colorless, rubbery	450	55.3
0.75	6.21	0.671	colorless, rubbery	480	41.0
0.90	6.81	0.792	colorless, glassy	600	22.0
1.0	7.35	1.0	colorless, rubbery	500	71.6

*Average of two determinations. Found for VI: N 7.50; 7.19%, calculated for N 7.64%

**70% polymer yield when homopolymerizing V (M_2). Found: C 55.56; 55.59; H 7.10; 7.37%, calculated for C 55.9; H 7.03%.

Tables 2 and 3 show that copolymerization of VI with V, as well as of I, II, or III with IV, gives rise to copolymers in which the number of nitrogen-containing ester units increases as their concentrations in the initial mixtures increase, though the yield somewhat drops. Copolymer composition is close to that of the mixed monomers (figure). The solubilities of the copolymers were investigated, and it was found that partial solubility in dimethylformamide, ethanol, and dioxane was exhibited by copolymers between VI and V, for monomer ratios in the initial mixtures 0.1:0.9, 0.25:0.75, 0.5:0.5; by copolymers between I and IV for ratios 0.1:0.9, 0.25:0.75, by copolymers between II and IV for a ratio 0.099:0.901. The other copolymers, and also the homopolymers of the nitrogenous esters synthesized, are insoluble in organic solvents. Investigation of the copolymerization products shows that under these conditions there is no separate polymerization.

In particular, polymers of V and VI were not found in the copolymers. The copolymers prepared differ from the polymers of the starting monomers in solubility characteristics and have a higher softening temperature. The acrylic esters are characterized by having the highest softening temperature.

Experimental

Materials used were twice-distilled before use. VI was prepared by the method described in [1]. Bp 86-90° ($1.5 \cdot 10^{-2}$ mm); n_D^{20} 1.1305. α-Pyrrolidone bp 113-114° (14 mm); n_D^{20} 1.4880; d_4^{20} 1.1200. α-Piperidone bp 139-140° (15 mm); mp 39-40°. ε-Caprolactam bp 138-139° (12 mm); mp 68-70°. V, mp 80.5° (760 mm); n_D^{20} 1.4050; d_4^{20}

1.3984. IV, mp 100° (760 mm); n_D^{20} 1.4156; d_4^{20} 0.9360. β-chloroethyl methacrylate was prepared from ethylene chlorohydrin and methacrylic chloroanhydride [7], bp 78-80° (22 mm); n_D^{20} 1.4500, d_4^{20} 1.1105.

TABLE 3

Copolymerization of I, II, and III with IV

Monomer	M_1, the mole fraction of I to III in the starting mixture	% N in the polymer or copolymer	m_1, the mole fraction of I to III in the copolymer	Appearance of copolymer	Softening temperature °C	% yield of polymer or copolymer
I+IV	0.10	1.06	0.082	Colorless, hard, glass-like	510	82.0
	0.25	2.97	0.268	Colorless, hard, glass-like	500	75.3
	0.50	4.53	0.473	Colorless, hard, glass-like	500	58.0
	0.75	5.77	0.688	Colorless, hard, glass-like	470	40.0
	0.90	6.30	0.801	Colorless, hard, glass-like	470	26.0
	1.0	6.75	1.0	Colorless, hard, crystalline	450	57.5
II+IV	0.099	Traces	Traces	Colorless, hard, glass-like	490	79.6
	0.501	4.14	0.441	Colorless, hard, glass-like	450	46.5
	0.901	5.97	0.811	Colorless, hard crystalline powder	400	21.9
	1.0	7.04	1.0	Colorless, hard, brittle powder	350	39.9
III+IV	0.099	Traces	Traces	Colorless, hard crystalline powder	350	75.4
	0.506	3.15	0.313	Colorless, hard powder	400	37.1
	0.90	5.27	0.713	Colorless, hard powder	400	12.0
	1.0	6.18	1.0	Colorless, hard powder	400	34.3

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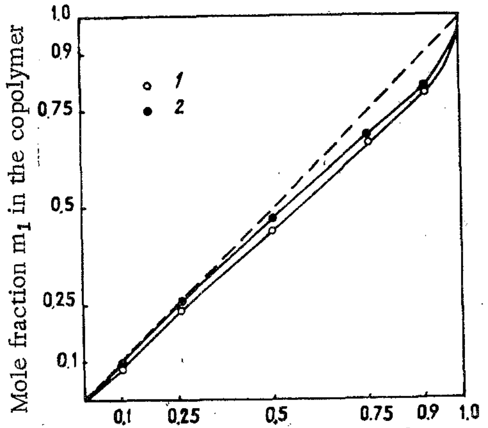
*Homopolymerization of IV (M_2) gives an 87.5% yield of polymer. Found: C 60.45, 60.01; H 8.3, 8.1%, calculated C 59.99; H 8.1%.

Preparation of II. The sodium salt of piperidone was prepared from 9.91 g (0.1 mole) piperidone in 30 ml dry toluene or xylene and 2.3 g (0.1 mole) sodium metal. 14.87 g (0.1 mole) β-chloroethylmethacrylate was added dropwise to it at 75-80°, and the reaction mixture then stirred for 2 hr 30 min. The mixture was cooled, the precipitate of sodium chloride filtered off, and washed a few times with dioxane. After distilling off the solvent, the residue was distilled in a high vacuum in a current of nitrogen and with the addition of an inhibitor (butyl gallate).



Composition of copolymers. 1) VI and V; 2) I and IV.

Piperidone was found as an impurity in the reactions products. To remove it, the unsaturated ester prepared was dissolved in diethyl ether, the solution washed with small quantities of distilled water, and then dried over sodium sulfate. The ester was further purified by chromatography on an activated carbon or alumina column. Purity was checked by thin-layer chromatography with a loose layer of Al_2O_3, activity grade II. A number of solvent systems were investigated, the best being ethyl acetate-diethyl ether 1:1 (an ether solution of the material being analyzed was placed on the plate). Iodine vapor was the visualizer. To study the products, R_f values were measured: piperidone R_f = 0.25; β-chloroethyl methacrylate R_f = 0.91; II R_f = = 0.74, bp 83 – 88° (1.1 · 10^{-2} mm); n_D^{20} 1.14985, d_4^{20} 1.1419, yield 49%. Found: N 7.01, 7.07%; MR_D 54.29. Calculated for $C_{11}H_{17}O_3N$: N 6.65% MR_D 54.47. II polymerized when heated, after 30 hr at 60° the thermal polymer yield was 12.1%. Found: N 6.05, 6.45%.

I and III were synthesized and isolated by the above method. ε-Caprolactam had R_f = 0.32. III: R_f = 0.85 bp 98 – 105° (2.2 · 10^{-2} mm); n_D^{20} 1.4993, yield 51.0%. Found: mol. wt. 224.76, 224.69 (in benzene); N 6.28, 6.47%. Calculated for $C_{12}H_{19}O_3N$, mol. wt. 225.28; N 6.22%. III underwent thermal polymerization after 30 hr at 60° giving 8.7% polymer. Found: N 6.27, 6.09%.

Polymerization and copolymerization procedure. Reaction was effected in sealed tubes filled with nitrogen, which were kept in a thermostat at 60° ±1° for 30 hr. The initiator was azodiisobutyronitrile, 0.2% by weight on the total weight of monomers. The polymer formed was dissolved in ethanol or chloroform and precipitated with diethyl ether or petroleum. The polymers and copolymers were dried to constant weight in a vacuum at 50-60°, and analyzed for nitrogen.

Copolymer composition was calculated from the nitrogen content. The results obtained are shown in Tables 2 and 3, and in the figure.

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