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Abstract

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PHOSPHORUS-CONTAINING AMIDES OF ACRYLIC AND METHACRYLIC ACIDS

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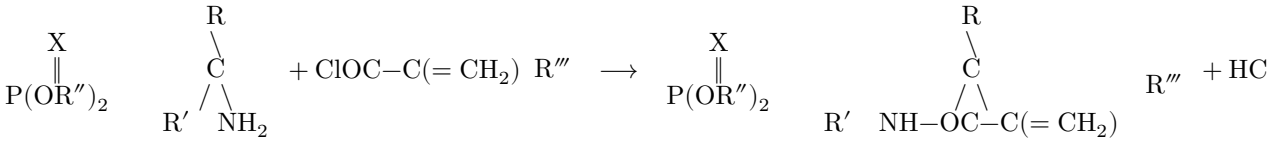
Previously we described the synthesis and properties of phosphorus-containing esters of acrylic and methacrylic acids. Polymers obtained on the basis of these esters are transparent solid products, in most cases sparingly soluble or insoluble in organic solvents, noncombustible or possessing reduced combustibility ([1]).

In the present work we synthesized phosphorus-containing amides of acrylic and methacrylic acids, starting from the acid chlorides of these acids and various aminophosphine and aminothiophosphine esters.



where R and $R' = \mathrm{H}, \mathrm{CH_3}, \mathrm{C_2H_5}$; $R'' = \mathrm{CH_3}, \mathrm{C_2H_5}$; n-$\mathrm{C_3H_7}$; iso-$\mathrm{C_3H_7}$; $R''' = \mathrm{H}, \mathrm{CH_3}$; $X = \mathrm{O}$ or S.

The reactions were carried out in the presence of an equimolecular amount of triethylamine in an ether solution. The yields of phosphorus-containing amides were from 40 to 80%. Their characteristics are given in Table 1.

Dialkylphosphonoisopropyl- and dialkylphosphono-butylamides of acrylic and methacrylic acids are either crystalline or paraffin-like substances, or thick liquids colored brown. All of them dissolve in water and in organic solvents: acetone, dioxane, alcohols, formic acid, and other solvents.

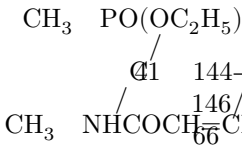
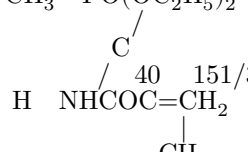
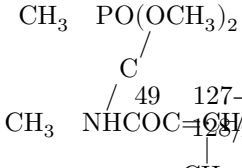
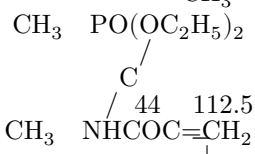
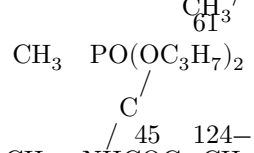
Dialkylthiophosphonoisopropyl- and dialkylthiophosphonobutylamides of methacrylic acid are fairly mobile liquids having a yellowish or greenish color, insoluble in water, soluble in ether, benzene, alcohols, chloroform, and dimethylformamide.

Fig. 1. Dependence of the rate of polymerization of methacrylic acid amides. 1 –dimethylphosphonoisopropylamide (1.5 mole % DNAIMK), 2 –diethylphosphonoisopropylamide (1.5 mole % DNAIMK), 3 –diethylthiophosphonoisopropylamide (2.5 mole % DNAIMK).

Dialkylphosphonoisopropyl-, dialkylphosphonobutylamides of methacrylic acid readily polymerize in the presence of benzoyl peroxide at 70° with formation of solid, brittle polymers. Under analogous conditions the corresponding thio analogs either do not polymerize at all or polyme-

Table 1

Dialkylphosphono- and dialkylthiophosphonoisopropyl- and isobutylamides of acrylic and methacrylic acids

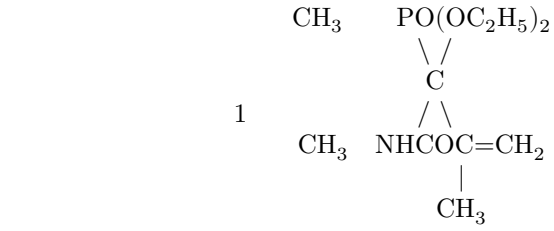
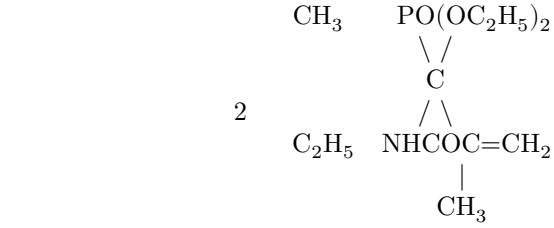
No.	Compound	Yield, %	B.p., °C (pressure in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	P content, % found	P content, % calculated
1		41	144–146/3 M.p. 66	–	1.4718	–	–	12.38	12.50
2		40	151/3.5	1.1011	1.4650	62.44	62.40	12.51	12.45
3		49	127–128/2	–	1.4730	–	–	12.81	13.19
4		44	112.5 113/1 M.p. 61	–	–	–	–	11.82	11.78
5		45	124–125/2	1.0723	1.4697	75.75	76.24	10.54	10.65

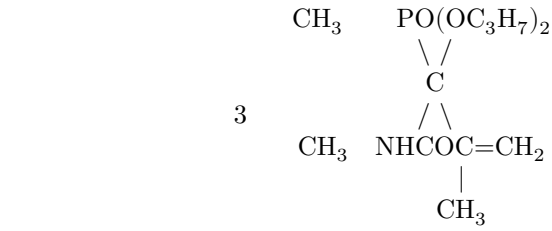
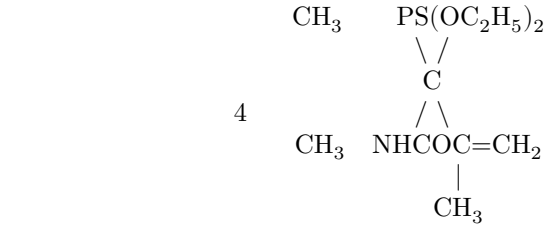
No.	Compound	Yield, %	B.p., °C (pressure in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	P content, % found	P content, % calculated
6	CH_3 / C_2H_5 — $PO(OC_2H_5)_2$ / C / $NHCOC(CH_3)=CH_2$	59	127–129/2	1.0850	1.4710	71.39	71.63	11.09	11.18
7	CH_3 / CH_3 — $PS(OC_2H_5)_2$ / C / $NHCOC(CH_3)=CH_2$	78	120.5 121/1.5	1.0802	1.4918	74.76	74.50	10.74	11.11
8	CH_3 / C_2H_5 — $PS(OC_2H_5)_2$ / C / $NHCOC(CH_3)=CH_2$	79	140–141/2	1.0730	1.4959	79.66	79.13	10.21	10.57
9	CH_3 / CH_3 — $PS(O\text{-}n\text{-}C_3H_7)_2$ / C / $NHCOC(CH_3)=CH_2$	78	118.5 119/5	1.0402	1.4809	83.85	83.74	10.22	10.11
10	CH_3 / C_2H_5 — $PS(O\text{-}n\text{-}C_3H_7)_2$ / C / $NHCOC(CH_3)=CH_2$	77	136–137/2	1.0543	1.4903	87.96	88.35	9.36	9.67

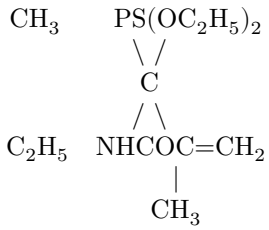
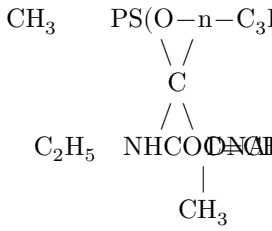
polymerize very slowly. More rapid polymerization of all phosphorus-containing amides of methacrylic acid proceeds at 70° in the presence of dinitrile of azoisobutyric acid (DINAIMK). The results obtained are presented in Fig. 1. As can be seen from the figure, dimethylphosphonoisopropylamide meth-

Table 2

Characteristics of polymers of dialkylphosphono- and dialkylthiophosphonoisopropyl- and isobutylamides of methacrylic acid

No.	Monomer	Duration of polymerization, h	Polymer yield, %	Properties of the polymers
1		2	81.4	Hard, brittle, yellowish; swells in alcohols and water; insoluble in petroleum ether, benzene, acetone
2		6	62	Hard, brittle; soluble in alcohols, water, dimethyl-formamide; insoluble in benzene, acetone, dioxane, petroleum ether

No.	Monomer	Duration of polymerization, h	Polymer yield, %	Properties of the polymers
3		4	65	Hard, brittle, brown; soluble in methanol, water, formic acid; insoluble in acetone, benzene, chloroform, petroleum ether, dimethyl-formamide
4		12	55.7	Hard, greenish; soluble in methanol, ethanol, dimethyl-formamide, acetone, benzene, dioxane, chloroform; insoluble in petroleum ether, water, formic acid

No.	Monomer	Duration of polymerization, h	Polymer yield, %	Properties of the polymers
5		15	38.5	Hard, greenish; soluble in dimethylformamide, dichloroethane, benzene, chloroform, dioxane; insoluble in methanol, water, petroleum ether, formic acid
6		3(2% KMnO4)	45	Hard, brittle, greenish; soluble in methanol, ethanol, formic acid, water, dimethylformamide; insoluble in petroleum ether

[[unclear: beginning of word]]acrylic acid polymerizes considerably faster in comparison with diethylphosphonoisopropylamide of methacrylic acid. Diethylthiophosphonoisopropylamide of methacrylic acid polymerizes at approximately the same rate as its oxygen analog, but in the presence of a larger amount of initia-

tor.

Fig. 2. Thermomechanical curves of amides of methacrylic acid. **1** – dimethylphosphonoisopropylamide, **2** –diethylphosphonoisopropylamide.

The purification of polymers of dialkylphosphonoisopropylamides of methacrylic acid was carried out by extraction with acetone; the polymer of diethylthiophosphonoisopropylamide of methacrylic acid dissolved in acetone and was precipitated from solution with formic acid. The polymers were dried in a vacuum drying oven to constant weight. Polymers were also obtained from other monomers; their characteristics are given in Table 2. Polymerization in all cases was carried out at 70° in the presence of 1.5 wt.% dinitrile of bisazoisobutyric acid.

Thermomechanical curves were recorded for dimethyl- and diethylphosphonoisopropylamides of methacrylic acid (Fig. 2). As can be seen from Fig. 2, they thermo-

stable up to a temperature of 150–190°; upon further increase in temperature, strong foaming of the polymers occurs, apparently associated with their partial decomposition and the evolution of gaseous products.

Experimental Part

Esters of α-aminoalkylphosphonic and α-aminoalkylthiophosphonic acids were obtained by heating equimolecular amounts of an aldehyde or ketone and dialkyl phosphite or dialkyl thiophosphite in a saturated alcoholic solution of ammonia at 100° for 3 h. ([2,3]).

Preparation of the dimethyl ester of α-aminoisopropylphosphonic acid. 14.5 g of acetone and 27 g of dimethyl phosphite in 100 ml of a saturated solution of ammonia in absolute ethyl alcohol were heated in sealed tubes on a boiling water bath for 40 min. Then the excess alcohol and ammonia were distilled off from the reaction mixture, and the residue was distilled in vacuo. 17.5 g of the dimethyl ester of α-aminoisopropylphosphonic acid was obtained (43% yield). B.p. 87–88°/4, n_D^{20} 1.4355, D_4^{20} 1.0630, MR_D found 41.08, calculated 39.59.

$C_5H_{14}O_3PN$.	Found %:	P 18.62; 18.44
	Calculated %:	P 18.56

Preparation of the dipropyl ester of α-aminoisopropylphosphonic acid. 5.8 g of acetone, 16.6 g of dipropyl phosphite, and 60 ml of a saturated alcoholic solution of ammonia were heated in sealed tubes on a boiling water bath for 3 h. After distilling off the excess ammonia and alcohol, the residue was distilled in vacuo. 8.9 g of the dipropyl ester of α-aminoisopropylphosphonic acid was obtained (40% yield). B.p. 95–96°/4, n_D^{20} 1.4360.

$C_9H_{22}O_3PN$.	Found %:	P 14.13
	Calculated %:	P 13.9

Reactions of acid chlorides of acrylic and methacrylic acids with esters of α-aminoalkylphosphonic acids. In a three-necked flask equipped with a stirrer and reflux condenser are placed 0.25 mole of an ester of an α-aminoalkylphosphonic or thiophosphonic acid, 0.25 mole of triethylamine, 250 ml of dry ether, and 0.5 g of cuprous chloride. To the reaction mixture, with stirring, an ethereal solution of 0.25 mole of acryloyl or methacryloyl chloride is gradually added. Heating of the reaction mixture is observed. The mixture is stirred for several more hours and left overnight. On the following day the precipitate of triethylamine hydrochloride is filtered off, and the residue, after addition of hydroquinone to it, is distilled in vacuo.

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Note: Figure translations are in progress. See original paper for figures.