ISSN 1070-4272, Russian Journal of Applied Chemistry, 2010, Vol. 83, No. 4, pp. 738–741. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © O.I. Tuzhikov, T.V. Khokhlova, S.N. Bondarenko, S.A. Orlova, E.A. Abramova, 2010, published in Zhurnal Prikladnoi Khimii, 2010, Vol. 83, No. 4, pp. 686–689.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Reaction of Di-2-chloroethyl 2-Chloroethanephosphonate with Potassium Methacrylate

O. I. Tuzhikov[a], T. V. Khokhlova[a], S. N. Bondarenko[b], S. A. Orlova[a], and E. A. Abramova[a]

[a] *Volgograd State Technical University, Volgograd, Russia*
[b] *Volzhskii Polytechnic Institute, Volzhskii, Volgograd oblast, Russia*

Received June 24, 2009

Abstract—Reaction of di-2-chloroethyl 2-chloroethanephosphonate with potassium methacrylate at various component ratios was studied with the aim to prepare products containing methacrylate and vinyl functional groups. The structures of the compounds obtained were examined by ^{1}H NMR and IR spectroscopy and by gas chromatography–mass spectrometry.

DOI: 10.1134/S1070427210040300

Synthesis of phopshorus- and halogen-containing oligoester acrylates used as modifiers in preparation of fireproof composite polymeric materials was the subject of numerous studies [1–5]. Thermal polycondensation of 2-haloalkyl phosphates was examined, the reaction products were identified, and their characteristics were determined [1–4]. Bakhtina et al. [5] studied the reaction of dimethyl methanephosphonate with dichloroethane, trichloropropane, and dichlorodiethyl ether in the presence of catalysts at 120–250°C. The resulting phosphorus-containing oligomers were suggested for use both in the individual form (as protective coatings) and as fillers for a wide range of polymers.

Further development of studies in this field seems promising in the context of diverse specific requirements imposed on polymeric materials. Previous studies [6–9] showed that it is appropriate to examine polyfunctional organophosphorus acids with two or more polymerization-capable methacrylic groups. These compounds can be prepared from an available commercial product, di-2-chloroethyl 2-chloroethanephosphonate.

This study deals with the synthesis of 2-chloroethanephosphonic acid esters by the reaction of di-2-chloroethyl 2-chloroethanephosphonate with a methacrylic acid salt at various component ratios.

EXPERIMENTAL

Di-2-chloroethyl 2-chloroethanephosphonate **I** was prepared by isomerization of tri-2-chloroethyl phosphite on heating. As methacrylic acid derivative we used its potassium salt **II**. The reaction of **I** with **II** was performed at 120–140°C in dimethylformamide. To isolate the reaction products, the KCl precipitate formed in the process was filtered off, and the solvent was evaporated from the filtrate in a vacuum. The composition and structure of the synthesized products were confirmed by IR and ^{1}H NMR spectroscopy and by gas chromatography–mass spectrometry (GC–MS).

The ^{1}H NMR spectra of substances ($CDCl_3$ solutions) were recorded with a Varian Mercury-300 spectrometer operating at 300 MHz, internal reference HMDS; the IR spectra were taken on a Specord M-82 spectrometer. GC–MS measurements were performed with a Perkin–Elmer Clarus 500 device equipped with an MSD. The chromatographic separation was performed under the following conditions. Vaporizer temperature 260°C, initial column temperature 100°C. After 50 s, the column temperature was raised to 220°C at a rate of 15 deg min^{-1}, after which it was raised to 305°C at a rate of 8 deg min^{-1}. Column length 25 m, diameter 0.2 mm. Stationary phase Elite-17 MS, carrier gas He.

Esters derived from di-2-chloroethyl 2-chloroethanephosphonate and potassium methacrylate were prepared at the initial component ratios of 1 : 1, 1 : 2, and 1 : 3.

1 : 1 ratio. A four-necked reactor equipped with a stirrer, a reflux condenser, a thermometer, and a calcium chloride tube was charged with 40 g (0.074 mol) of di-2-chloroethyl 2-chloroethanephosphonate, 18.4 g (0.074 mol) of vacuum-dried potassium methacrylate, 25 ml of dimethylformamide (DMF), and 0.01 g of hydroquinone. The synthesis was performed at 130°C for 4 h. The KCl precipitate was filtered off on a glass frit. DMF was distilled off from the filtrate in a vacuum at 86°C. The reaction product was a light yellow viscous oil readily soluble in toluene, chloroform, and acetone. Yield of the phosphorus-containing product 46.5 g (98.5%).

1 : 2 ratio. The reaction was performed as described above, with 10 g (0.037 mol) of di-2-chloroethyl 2-chloroethanephosphonate and 9.18 g (0.074 mol) of potassium methacrylate. Yield of the phosphorus-containing product 13.09 g (95.7%).

1 : 3 ratio. The reaction was performed as described above with 80 g (0.296 mol) of di-2-chloroethyl 2-chloroethanephosphonate and 110.3 g (0.888 mol) of potassium methacrylate. Yield of the phosphorus-containing product 97.08 g (88.5%).

The physicochemical properties of the phosphorus-containing methacrylates prepared at various molar ratios of di-2-chloroethyl 2-chloroethanephosphonate and potassium methacrylate are given in the table.

The ^{1}H NMR spectrum of products **IIIa** and **IVa** (see scheme) obtained at equimolar product ratio contains signals at δ 1.80 and 1.84 ppm, corresponding to protons of the methyl group of the methacrylate moiety, and four singlets from protons bonded to the *sp*^{2}-hybridized carbon atom at δ 5.5–6.25 ppm. The signals at δ 5.57 and 5.94 ppm correspond to nonequivalent protons in the methacrylate moiety. The intensity of the proton signals from the unsaturated fragment exceeds the intensity of the proton signals from the methyl group of the methacrylate. This fact can be attributed to the formation of ethenephosphonate along with phosphorus-containing methacrylate, which is confirmed by the presence in the ^{1}H NMR spectrum of the typical ABX pattern from protons H_A, H_B, and H_X, with the coupling constants J_{AB} 2.2, J_{AX} 17.9, and J_{BX} 11.4 Hz. Appearance of signals corresponding to vinyl group protons (δ 6.15 and 6.25 ppm) and a sharp decrease in the signal from methylene protons of the chloroethyl group bonded to the P atom (δ 2.2 ppm) indicate that the methacrylate formation is accompanied by dehydrochlorination with the formation of the ethenephosphonate. It should also be noted that the signal at δ 4.18 ppm, corresponding to protons of methylene groups in the ester fragments of the phosphorus-containing methacrylate, increases relative to the signal from chloromethyl protons (δ 3.4 ppm). This fact confirms that di-2-chloroethyl 2-chloroethanephosphonate reacts with potassium methacrylate via chlorine atom.

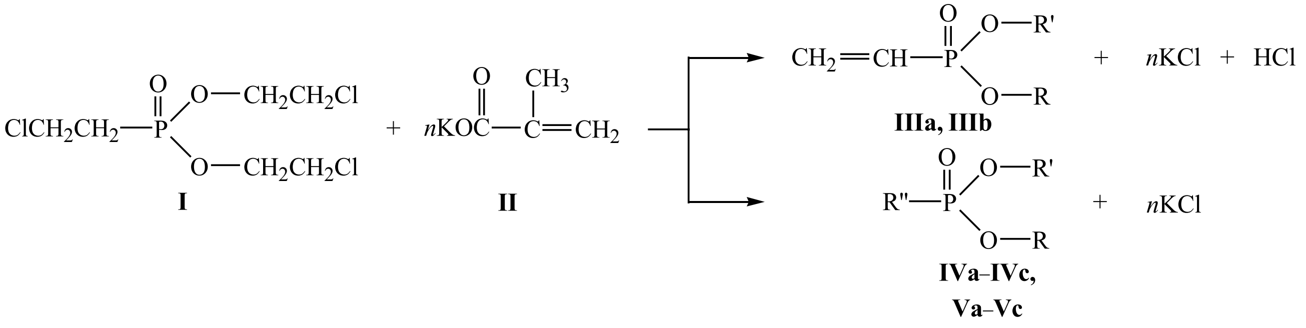
At 1 : 2 molar ratio of the isomerization product and potassium methacrylate, some specific features were revealed. In the range δ 5.5–6.5 ppm, two additional signals appear. They correspond in the intesity to the signals at δ 5.57 and 5.94 ppm, which confirms the formation of di-2-methacryloylethyl ethenephosphonate **IIIb**, the major product in this case. In addition, a weak signal remains at δ 3.64 ppm. This signal corresponds to protons of the chloromethyl group, which is confirmed by the 9.6% content of chlorine, determined analytically These data are indicative of the formation of di-2-methacryloylethyl 2-chloroethanephosphonate **IVb**.

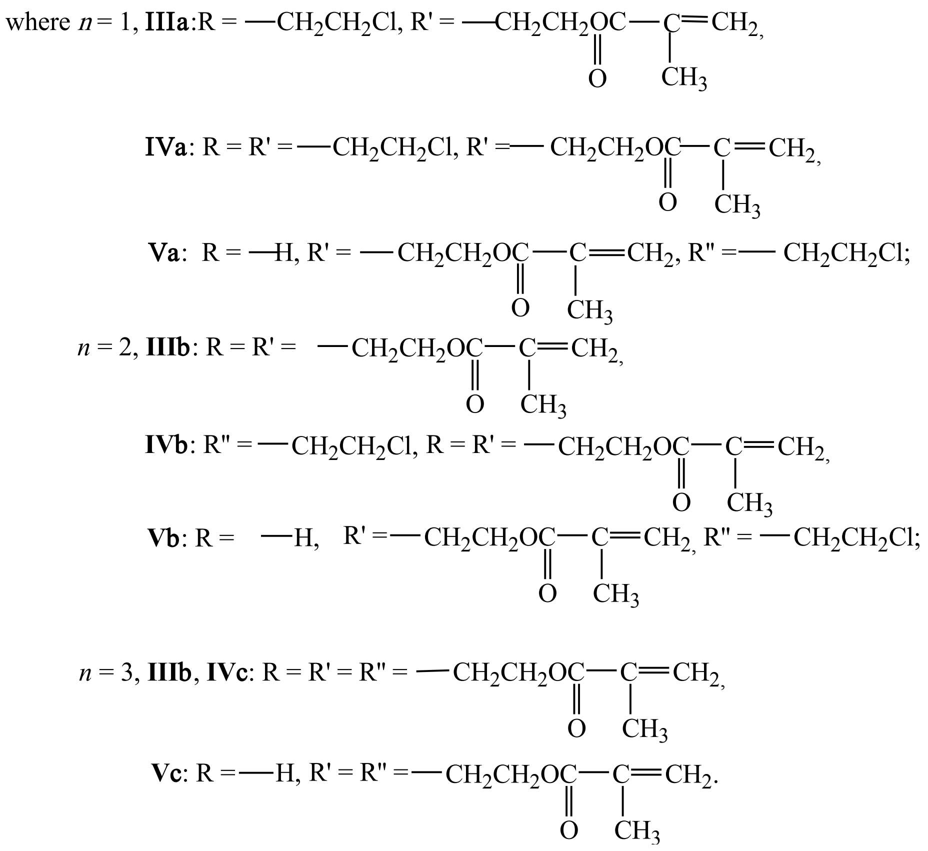
When the reaction was peformed at 1 : 3 molar ratio of the isomerization product to potassium methacrylate,

Physicomechanical properties of phosphorus-containing methacrylates

Molar ratio I : II	Molecular weight M	Reduced viscosity ν, St	Refractive index n_D^{20}	Density d_4^{20}, g cm^{-3}	Found, %/Calculated, %			
					C	H	Cl	P
1:1	382	30.2	1.4681	1.2548	$\underline{35.8}$ 36.1	$\underline{4.8}$ 5.0	$\underline{33.0}$ 22.2	$\underline{9.4}$ 9.7
1:2	356	28.4	1.4660	1.2405	$\underline{39.4}$ 38.7	$\underline{5.8}$ 5.2	$\underline{9.6}$ 8.8	$\underline{7.8}$ 8.1
1:3	332	24.7	1.4750	1.2446	$\underline{51.5}$ 50.3	$\underline{7.2}$ 6.6	$\underline{1.2}$ –	$\underline{7.9}$ 7.3

Scheme of the reaction of di-2-chloroethyl 2-chloroethanephosphonate with potassium methacrylate





where $n = 1$, **IIIa**: $R = -CH_2CH_2Cl$, $R' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$,

IVa: $R = R' = -CH_2CH_2Cl$, $R' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$,

Va: $R = -H$, $R' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$, $R'' = -CH_2CH_2Cl$;

$n = 2$, **IIIb**: $R = R' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$,

IVb: $R'' = -CH_2CH_2Cl$, $R = R' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$,

Vb: $R = -H$, $R' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$, $R'' = -CH_2CH_2Cl$;

$n = 3$, **IIIb**, **IVc**: $R = R' = R'' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$,

Vc: $R = -H$, $R' = R'' = -CH_2CH_2OC(=O)-C(CH_3)=CH_2$.

the intensity ratio of the signals of the CH_2= protons in the methacrylate and vinyl fragments increased considerably: from 2 : 1 to 5 : 1, with a decrease in the chorine content of the product to 1.2%. These facts are indicative of the predominant formation of di-2-methacryloylethyl 2-methacryloylethanephosphonate **IIIc** along with its ethenephosphonate analog **IVc**.

The IR spectrum of the product contains absorption bands corresponding to stretching vibrations of the following groups (cm^{-1}): >P–O–C– 930–1070; >P=O 1245; –C=C– 1630; –CH, –CH_2, –CH_3 in the range 2800–3100; –P(O)–O–C– 1100. Intense absorption at 2716 and 3400 cm^{-1} is characteristic of stretching vibrations of >P–O– and –OH groups in acids The presence of (>P–OH) groups (product **V**) is confirmed by potentiometric titration of the reaction product with a 0.1 N KOH solution. The acid number was 24.9 mg

KOH/g.

To evaluate the selectivity of the reactions under consideration, we performed a GC–MS study of the compositions of the reaction mixtures obtained at equimolar ratio of the isomerization product with potassium methacrylate. Chromatographic analysis revealed oligomeric composition of the reaction product. The major product is 2-chloroethyl 2-methacryloylethyl ethenephosphonate **IIIa** (72%), with di-2-chloroethyl 2-methacryloylethyl 2-chloroethanephosphonate **IVa** formed in a smaller amount (20%). Trace amounts of di-2-methacryloylethyl ethenephosphonate **IIIb** were also detected.

CONCLUSIONS

(1) Oligomeric phosphorus-containing products were prepared by the reaction of di-2-chloroethyl 2-chloroethanephosphonate with potassium methacrylate, performed at various component ratios.

(2) An IR and ^{1}H NMR study showed that the products contain methacrylate and vinyl functional groups. Therefore, they can undergo cross-linking with the formation of polymers suitable as modifiers for various composite materials.

REFERENCES

1. US Patent 4076303.
2. US Patent 3956431.
3. Korshak, V.V. and Shibalov, V.K., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1952, no. 2, pp. 214–216.
4. US Patent 4426336.
5. Bakhtina, G.D., Kryukov, N.V., Tuzhikov, O.I., et al., in *Khimiya i tekhnologiya elementoorganicheskikh monomerov i polimernykh materialov* (Chemistry and Technology of Organoelement Monomers and Polymeric Materials), Volgograd: Volgogr. Gos. Tekh. Univ., 1995, pp. 154–158.
6. Avanis'yan, Zh.G., Tuzhikov, O.I., Khokhlova, T.V., and Bondarenko, S.N., in *Khimiya i tekhnologiya elementoorganicheskikh monomerov i polimernykh materialov* (Chemistry and Technology of Organoelement Monomers and Polymeric Materials), Volgograd: Volgogr. Gos. Tekh. Univ., 1997, pp. 101–107.
7. Tuzhikov, O.I., Khokhlova, T.V., Bondarenko, S.N., et al*., Elastomery i plastiki s ponizhennoi goryuchest'yu* (Elastomers and Plastics of Reduced Combustibility), Volgograd: Volgogr. Gos. Tekh. Univ., 2005.
8. Tuzhikov, O.I., Khokhlova, T.V., and Tuzhikov, M.O., in *Khimiya i tekhnologiya elementoorganicheskikh monomerov i polimernykh materialov* (Chemistry and Technology of Organoelement Monomers and Polymeric Materials), Volgograd: Volgogr. Gos. Tekh. Univ., 2008, pp. 63–67.
9. Strauss, Ch.R. and Varma, R.S., *Top. Curr. Chem.*, 2006, vol. 266, p. 199.