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Preparation of Phthalide-containing Methacrylates

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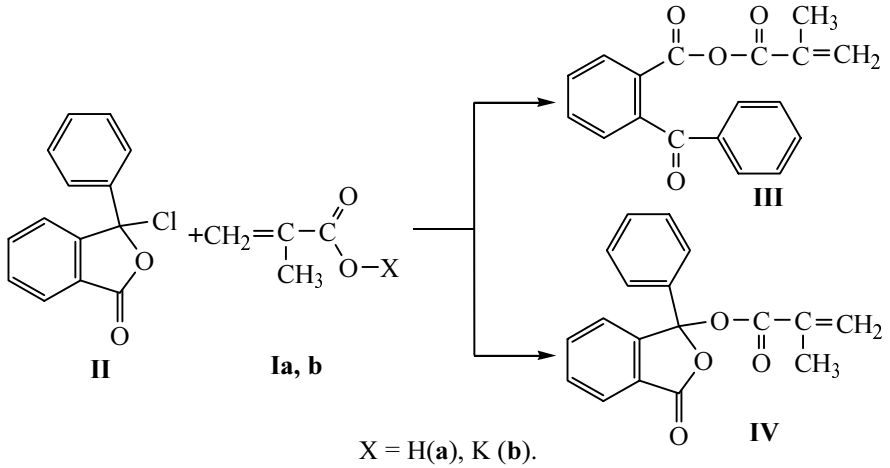
Abstract—Different unsaturated products of the synthesis of phthalide-containing methacrylates were obtained depending on the polarity of the reaction medium: In a donor solvent (pyridine) the phthalide ring is conserved in the product, in acetone or toluene its opening occurred.

Recently studies were activated of polymers containing substances or fragments thereof capable of changing the structure or physicochemical characteristics under the influence of external conditions (pressure, temperature, acidity of the medium etc.). Phthalides are of special interest in this respect. They are prone to the so-called ring-chain isomerism [1], and the transition between the isomeric forms occurs at variation of the external factors: temperature, pressure, acidity of the medium etc.

The phthalide-containing polymers possess outstanding electrophysical [2], and optical [3] characteristics, high heat resistance [4]. They are usually prepared by polycondensation. The high heat resistance of the polymers combines with high glass temperature and pour point, and also with low solubility in most industrially used organic solvents. On the contrary, many among vinyl polymers, in particular, polyacrylates, are characterized by low glass temperature and pour point and by good solubility, but possess low thermal stability. They are commonly prepared by the radical polymerization. Therefore in order to achieve modification of vinyl polymer properties it seems feasible to develop methods of incorporation (first of all at the polymerization stage) into the molecules of poly(meth)acrylates, polysterene and others of phthalides with versatile structures.

Phthalides may be incorporated into a polymer molecule in radical polymerization either involving them into initiation or chain transfer reactions [3] or by copolymerization with unsaturated phthalides. Aiming at preparation of poly(methyl methacrylate) modified with phthalide-containing compounds we carried out a synthesis of phthalide-containing methacrylates by reaction of methacrylic acid (**Ia**) [or



II **Ia, b** **III** **IV**

X = H(**a**), K (**b**).

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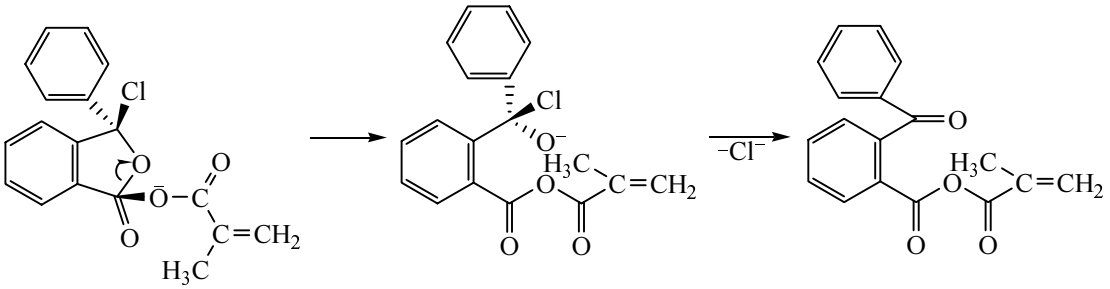
potassium methacrylate (**Ib**)] with 3-chloro-3-phenylphthalide (**II**).

It turned out that carrying out the reaction in a medium of various polarity it was possible to obtain either a product with conserved phthalide ring or with opening of the latter.

When the reaction between compounds **Ib** and **II** was performed in acetone it afforded in 87% yield mixed anhydride of *o*-benzoylbenzoic and methacrylic acid (**III**). In the ^{13}C NMR spectrum of the compound the signal from the third carbon atom of the phthalide ring is lacking. Thus the reaction occurred with the ring opening.

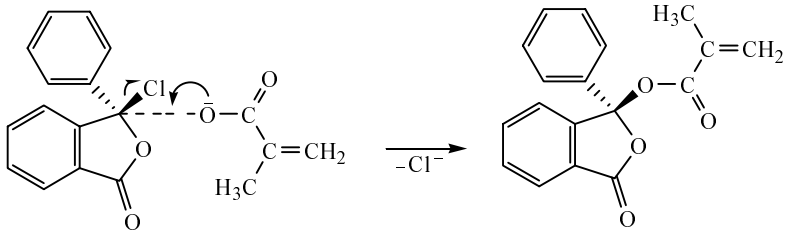


The reaction between compounds **II** and **Ib** proceeded as a nucleophilic substitution at the carbonyl carbon of the phthalide ring that had the largest chemical shift value in the ^{13}C NMR spectrum of this compound. Therefore the following structure of intermediate states seems to be the most probable.

The reaction is accompanied by potassium chloride separation.

In reaction of compounds **Ia** and **II** carried out in pyridine the main product obtained in 83% yield was 3-methacryloxy-3-phenylphthalide (**IV**), i.e., the phthalide ring was conserved in the course of the process. It means that the reaction proceeded at another reactive site.

On the one hand the acid dissociation in pyridine is enhanced by formation of pyridinium cation. On the other hand as suggests the reaction product structure the nucleophilic attack occurs on the sp^3-hybridized carbon of the phthalide ring. Apparently the carbonyl carbon is here blocked by interaction with pyridine. Therefore the nucleophile attacks another carbon of the phthalide ring also possessing excessive positive charge.



This suggestion is confirmed by the fact that the reaction between compounds **Ia** and **II** carried out in toluene afforded not ether **IV** but anhydride **III.**

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AMX-III-300 (at operating frequencies 300.13 and 75.47 MHz respectively) from 10–15% solutions in $CDCl_3$, internal reference TMS. Chemical shifts are reported in the δ scale (ppm). Mass spectra were measured on a mass spectrometer MKh-1306, ionizing voltage 70 eV, ionizing chamber temperature 150–200°C.

The reaction progress was monitored and the purity of compounds was checked by TLC on Silufol UV-254 plates. As eluents were used benzene–methanol, 93:7, and dichloromethane.

Methacrylic acid (**Ia**) was purified by vacuum distillation, bp 69–71°C (50 mm Hg).

Potassum methacrylate (**Ib**) was purified by recrystallization from ethanol.

3-Chloro-3-phenylphthalide (**II**) was prepared and purified along procedure described in [5], mp 57°C.

Anhydride of *o*-benzoylbenzoic and methacrylic acids (III). To a solution of 12.2 g (0.05 mol) of compound **II** in 70 ml of preliminary purified acetone was added a solution of 6.2 g (0.05 mol) of compound **Ib** in 120 ml of acetone. The reaction mixture was heated at reflux for 8–10 h; after 3 h of heating into the reaction flask several crystals of hydroquinone were added to prevent polymerization. Already in 30–50 min after the start of the run colorless crystals of KCl precipitated from the reaction mixture. After completing the heating and on cooling to –20°C the crystals were filtered off and dried, mp 768°C in conformity to the known melting point of KCl.

On evaporation of the solution colorless crystals precipitated that were filtered off and several times recrystallized from anhydrous ethanol. Yield 12.8 g (87%), mp 168–169°C. ^{1}H NMR spectrum, δ, ppm: 1.03 s (3H, CH_3), 5.30 s (2H, CH_2=), 7.3 m (9H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 21.37 q (CH_3–), 114.70 t (CH_2=), 123.60 s (C=CH_2), 157.31 s [O–C–(=O)–C], 164.28 s [Ph–C(=O)–O], 194.12 s [Ph–C(=O)–Ph], 126.4–137.3 m (Ph). Mass spectrum, *m/z*, (I_{rel}, %): 294 (6.8) [*M*]$^+$, 225 (87.3), 209 (100), 181 (43.9). Found, %: C 73.97; H 4.38. $C_{18}H_{14}O_4$. Calculated, %: C 73.46; H 4.79.

3-Methacryloxy-3-phenylphthalide (IV). To a solution of 12.2 g (0.05 mol) of 3-chloro-3-phenylphthalide in 100 ml of preliminary purified pyridine was added a solution of 4.4 g (4.3 ml, 0.05 mol) of methacrylic acid in 100 ml of pyridine. The reaction mixture was heated for 8–10 h at 60–70°C; after 0.5 h from the start of the run into the reaction flask several crystals of hydroquinone were added to prevent polymerization. On completion of the process the reaction mixture was diluted with 500 ml of water, and the products were extracted into ethyl ether. The ether extract was 4–5-fold washed with water, dried with anhydrous sodium sulfate, and the ether was evaporated. The reaction product precipitated as colorless crystals, it was filtered off, and recrystallized from ethanol yield 12.2 g (83%), mp 135°C. ^{1}H NMR spectrum, δ, ppm: 1.02 s (3H, CH_3–), 5.32 s (2H, CH_2=), 7.7 m (9H, arom.). ^{13}C NMR spectrum, δ, ppm: 21.34 q (CH_3–), 114.78 t (CH_2=), 123.48 s (C=CH_2), 163.12 s [O–C(=O)–C], 67.17 s [Ph–C(–O)–O], 165.07 s [Ph–C(=O)–O], 126.4–138.8 m (Ph). Mass spectrum, *m/z*, (I_{rel}, %): 294 (9.3) [*M*]$^+$, 225 (47.4), 209 (100). Found, %: C 73.17; H 4.57. $C_{18}H_{14}O_4$. Calculated, %: C 73.46; H 4.79.

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