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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Development of the Conditions of Synthesis of *p*-Chlorophenyl Methacrylate of the Desired Purity Grade

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Abstract—The process of synthesis of *p*-chlorophenyl methacrylate by the reaction of *p*-chlorophenol with methacryloyl chloride was developed, identification and quantitative determination of admixtures in the targeted compound was carried out. The optimal conditions of the synthesis for obtaining the high quality monomer were developed.

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In the recent years increased the interest to organic glasses based on the methyl methacrylate (co)polymers with enhanced thermal stability and low water absorption that provides their reliable and prolonged exploitation under various conditions. Such glasses find application first of all in aviation and also in electrical engineering and car building industry [1, 2]. As (co)monomers for the modification of polymethyl methacrylate the most promising are the methacrylic esters with bulky cyclic fragments [2]. A special interest is paid to the methyl methacrylate coplymers with *p*-chlorophenyl methacrylate owing to high optical and strength characteristics, alongside enhanced thermal stability and low hygroscopicity [3]. However, it has been shown that when the *p*-chlorophenyl methacrylate is even slightly contaminated its physical and optical properties decrease, e.g., falls thermal stability due to plasticizing effect and appear optical defects like the glass turbidity. Hence, for producing organic glass with required set of properties a modifying monomer of high purity grade should be synthesized and used.

Unfortunately only scarce information was published so far on the synthesis of chloro-substituted phenyl methacrylates [4, 5]. It was only reported that reaction of *p*-chhlorophenol with methacryloyl chloride leads to *p*-chlorophenyl methacrylate with the yield 53% or less. The data on the content of contaminants in the ester and on their influence on the optical and physico-mechanical properties of the polymeric materials were not reported. The absence of the data on the features of manufacturing the high purity *p*-chlorophenyl methacrylate restricts the control over the synthesis and the possibility of optimal technological regimes.

The aim of this investigation is development of the method of *p*-chlorophenyl methacrylate synthesis with the minimal content of contaminants.

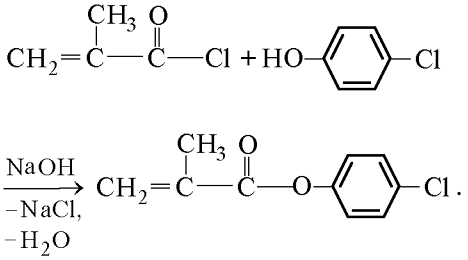
EXPERIMENTAL

The IR spectra were registered on a Specord M82 instrument in the region of 4000–400 cm^{-1} from thin films. The NMR spectroscopic investigations were carried out on a DPX-200 instrument with operating frequency 200 MHz for protons and 50 MHz for the ^{13}C nuclei. The samples were dissolved in deuterochloroform form Aldrich, internal reference TMS.

Chromatographic analysis was carried out on a gas chromatograph Chrom-5 with the flame ionization detector and glass column 2.5 m long and 3 mm in diameter, stationary phase Chromosorb WAW (0.16–0.20 mm) with 8% of poly(ethylene glycol)adipinate and 2% of H_3PO_4; the column temperature 170°C, the evaporator temperature 220°C, the hydrogen and nitrogen flow rate 30 ml min^{-1}. Calculation of the content of contaminants was performed using internal reference method, as the reference was used dimethyl succinate.

Methacrylic acid (TU 6-02-917-79, supplement 1), *p*-chlorophenol (TU 6-09-4935-80), organic solvents and other chemicals were corresponding to the technical documentation and were not purified additionally.

p-Chlorophenyl methacryate was prepared by acylation of *p*-chlorophenol with methacryloyl chloride by the Schotten – Baumann method [6]. The reaction was carried out in organic solvent in the presence of aqueous alkali:



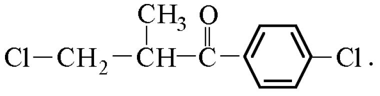
The gas chromatographic analysis of the obtained *p*-chlorophenyl methyl methacrylate showed that the monomer contained several contaminating substances with content of one of them up to 5 wt % (Fig. 1).

The most expectable contaminant is *p*-chlorophenyl β-chloroisobutyrate formed at the addition of hydrogen chloride to the C=C double bond of the methacrylate [7]:

To confirm this assumption we carried out authentic synthesis of *p*-chlorophenyl β-chloroisobutyrate by the hydrochlorination of methacrylic acid followed by reaction of β-choroisobutyric acid with thionyl chloride and of the formed β-chloroisobyutyryl chloride with *p*-chlorophenol [6].

The IR spectrum of the product obtained includes the band of vibrations of a C–Cl bond in an aliphatic group (ν=750 cm^{-1}) and the band of carbonyl group, the band is shifted to higher wavenumbers (ν=1766 cm^{-1}) that attests the absence of C=O conjugation with C=C bond.

In the ^{1}H NMR spectrum were not observed groups of the signal characteristic of *cis*- and *trans*-HC=C system (δ 6.34 and 5.76 ppm respectively) but there are the signals corresponding to the proton groups $CHCH_3$ (δ 3.09 ppm) and CH_2Cl (δ 3.76 – 3.80 ppm)



The side product concentrated in the bottoms after vacuum distillation of *p*-chlorophenyl methyl methacrylate had the characteristics analogous to those of *p*-chlorophenyl β-chloroisobutyrate prepared by the authentic synthesis. By comparison of the retention times at the chromatography of *p*-chlorophenyl methyl methacrylate and *p*-chlorophenyl β-chloroisobutyrate synthesized and isolated from the bottom we identified and determined quantitatively the content of saturated *p*-chlorophenyl β-chloroisobutyrate in the *p*-chlorophenyl methacrylate. It is this ester that works as a plasticizer at the (co)polymerization of *p*-chlorophenyl methacrylate and methyl methacrylate leading to a decrease in thermal stability and strength characteristics of organic glass.

The most probably, formation of *p*-chlorophenyl β-chloroisobutyrate is caused by the presence in the methacryloyl chloride of the saturated compound, β-chloroisobutyryl chloride. Metacryloyl chloride commonly is obtained by the reaction of methacrylic acid with thionyl chloride. In the course of reaction are formed gaseous products, including hydrogen chloride, capable of adding to the double C=C bond of α,β-unsaturated acids and respective acyl chlorides contrary to the Markovnokov rule [7]. As a result the saturated acyl chloride is formed. The gas chromatography analysis confirmed the presence of up to 5 wt % of chloroisobyutyryl chloride in the methacryloyl chloride produced by the above method.

For diminishing the content of unwanted impurity the thionyl chloride was replaced by benzoyl chloride [6] that afforded methacryloyl chloride containing 0.01–0.1 wt % only of chloroisobyutyryl chloride.

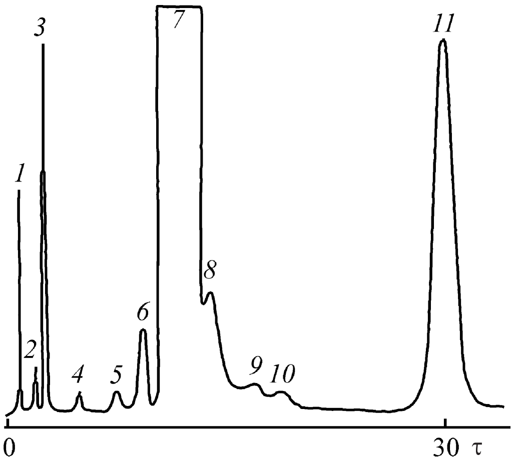


Fig. 1. Chromatogram of *p*-chlorophenyl methacrylate. τ is retention time (min). (*1*) toluene, (*2, 6, 9*) unidentified contaminants, (*3*) reference compound dimethyl succinate, (*4*) phenyl methacrylate, (*5*) *p*-chlorophenyl acetate, (*7*) *p*-chlorophenyl methacrylate, (*8*) 2,4-dichlorophenyl methacrylate, (*10*) *p*-chlorophenol, (*11*) *p*-chlorophenyl β-chloroisobutyrate.

Table 1. Influence of conditions of the synthesis of *p*-chlorophenyl methacrylate on the formation of contaminants and the product yield

T, °C	Mole ratio [*p*-chlorophenol] : [methacryloyl chloride]	Keeping duration, min	Total phenols, wt %	Content of *p*-chlorophenyl β-chloroisobutyrate, wt %	Yield of *p*-chlorophenyl methacrylate, %
5	1.0:1.0	30	0.0075	0.035	72
	1.0:1.0	60	0.0050	0.100	70
	1.0:1.3	30	0	0.750	70
10	1.0:1.0	30	0.0082	0.055	76
	1.0:1.0	60	0.0060	0.200	74
	1.0:1.3	30	0	0.780	66
15	1.0:0.8	30	0.7000	0.015	65
	1.0:0.8	60	0.5500	0.009	66
	1.0:1.0	0	0.0200	0.057	65
	1.0:1.0	30	0.0030	0.130	72
	1.0:1.0	60	0.0030	0.190	70
	1.0:1.3	30	0	0.900	70
20	1.0:0.8	30	0.6600	0.020	68
	1.0:1.0	30	0.0028	0.180	75
	1.0:1.0	60	0.0024	0.250	73
	1.0:1.3	30	0	1.200	70
30	1.0:1.0	30	0.0020	0.300	73
	1.0:1.0	60	0.0014	0.770	74

It is reasonable to assume that in this case the possibility of formation of *p*-chlorophenyl β-chloroisobutyrate during the synthesis of *p*-chlorophenyl methacrylate is practically excluded. However, at the optimization of technological parameters of the reaction of methacryloyl chloride with *p*-chlorophenol we found that in the *p*-chlorophenyl methacrylate this contaminant is present and its amount depends on the synthesis conditions. On raising the reaction temperature from 0 to 30°C does not increase considerably the *p*-chlorophenyl methacrylate yield but promotes more intense formation of *p*-chlorophenyl β-chloroisobutyrate (Fig. 1). When the process is conducted at 5°C the *p*-chlorophenyl β-chloroisobutyrate content is 0.03–0.04 wt %, that corresponds to approximate content of chloroisobutyryl chloride in the parent methacryloyl chloride, while in the reaction at 20°C its content grows 4–5-fold (to 0.15–0.20 wt %).

The fact of appearance of the saturated compound can be explained by the features of phenol acylation with acyl chlorides by the Schotten–Baumann method under the phase transfer reaction conditions [4]. Under these conditions hydrolysis can proceed of the acyl chloride [7] with the formation of hydrogen chloride that leads to formation of *p*-chlorophenyl β-chloroisobutyrate.

At higher temperature the hydrolysis rate increases resulting in the increased rate of HCl addition at the C=C bond of the methacrylate, consistently with the experimental data shown in Fig. 2.

It is expectable that the content of parent reagents also affects side reaction. Actually, excess of methacryloyl chloride, which, as was expected, is needed for the complete consumption of *p*-chlorophenol, leads to increased content of *p*-chlorophenyl β-chloroisobutyrate; the yield of *p*-chlorophenyl methacrylate increases therewith insignificantly (Fig. 3).

Thus, from the viewpoint of the desired monomer yield and the content of the unwanted saturated contaminant the optimal conditions of the synthesis are as follows: temperature in the range 5–10°C and equivalent ratio of the parent reagents, methacryloyl chloride and *p*-chlorophenol.

Besides, analysis of the obtained results and additional experiments allowed to conclude that 0.1 mole excess of alkali relatively to *p*-chlorophenol should be taken for the effective binding the hydrogen chloride formed at the hydrolysis of methacryloyl chloride.

By means of gas chromatography we found that the synthesized monomer can contain unreacted *p*-chloro-

Table 2. Characteristics of contaminants prepared in authentic syntheses

Contaminant	bp, °C	*P*, mm Hg	mp, °C	n_D^{20}	d_4^{20}	References
Phenyl methacrylate	83–84 67	4 1	–	1.5156	1.053	[4]
o-Chlorophenyl methacryate	104 89–90	4 2	–	1.5210	1.1390	[4, 5]
2,4-Dichlorophenyl methacrylate	–	–	5	–	–	[4, 5]
p-Chlorophenyl acetate	226–228	760	7–8	–	–	[9]

Table 3. Characteristics of the samples of *p*-chlorophenyl methacrylate

Yield of product, % %	Content of principal contaminants, wt%						Content of main product, %
	p-chloro-phenol	methacrylic acid	phenyl methacrylate	*p*- chloro-phenyl acetate	*p*-chloro-phenyl β-chloroiso-butyrate	peroxides [10]	
74	0.0065	0.0088	0.0076	0.0079	0.0738	absent	99.86
78	0.0033	0.0030	0.0113	0.0041	0.0116	0.0009	99.88
72	0.0043	0.0023	0.0172	0.0021	0.0243	0.0010	99.90
75	0.0083	0.0057	0.0074	0.00010	0.0357	0.0007	99.79
79	0.0059	0.0027	0.0061	0.0033	0.0421	absent	99.84

phenol, and sometimes phenol, *o*-chlorophenol and 2,4-dichlorophenol contaminating *p*-chlorophenol. Even little admixture of phenolic contaminants that exhibit inhibiting action [8] decreases the monomer polymerization activity that can result in composition ununiformity of the (co)polymer material and to deterioration of its optical and strength characteristics.

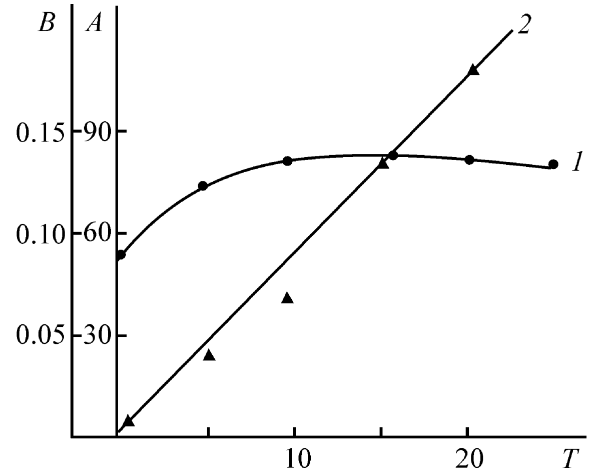


Fig. 2. Dependence of yield *A* (%) of *p*-chlorophenyl meth-acrylate (*1*) and content *B* (%) of *p*-chlorophenyl β-chloro-isobutyrate (*2*) on temperature *T* (°C). The methacryloyl chloride/*p*-phenol mole ratio equals 1, the reaction duration 2.5 h.

To provide practically quantitative reaction of phenols with methacryloyl chloride the reaction mixture after loading the reagents was kept for some time (Table 1). The optimal duration of keeping is found to equal to 30 min. Then the total content of residual phenols is not higher than 0.01 wt %, the content of *p*-chlorophenyl β-chloroisobutyrate also remains on the acceptable

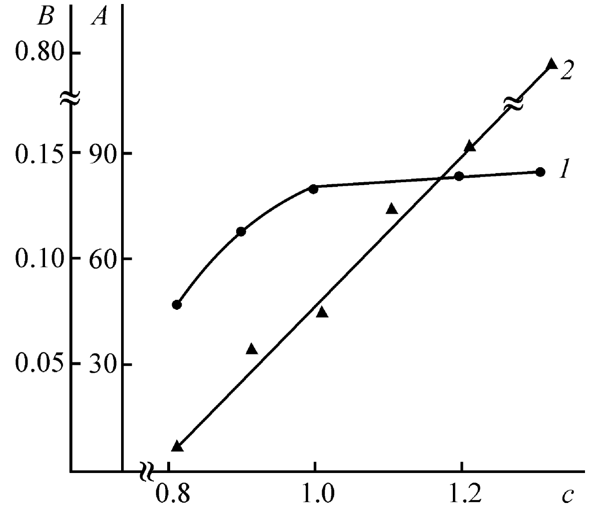


Fig. 3. Dependence of yield *A* (%) of *p*-chlorophenyl methacrylate (*1*) and content *B* (%) of *p*-chlorophenyl β-chloroisobutyrate (*2*) on the methacryloyl chloride / *p*-chlorophenol mole ratio *c*. The synthesis temperature 10°C, the reaction duration 2.5 h.

level, less than 0.1 wt %. Longer keeping leads to more complete consumption of phenols, but simultaneously to increased amount of *p*-chlorophenyl β-chloroisobutyrate, up to 0.2% and ever higher. The saturated compound in such amount affects negatively the glass properties.

These phenols also can react with methacryloyl chloride to form the corresponding methacrylates that were identified by means of authentic synthesis (Table 2). But these monomers do not restrict further polymerization of the target substance, but on the contrary take a part in it and, as established, practically do not affect the characteristics of the obtained polymer material.

Note that we also identified the *p*-chlorophenyl acetate formed in the process (Table 2). Its content in the *p*-chlorophenyl methacrylate is not significant and does not depend on the technological parameters of the synthesis. Its amount is defined by the amount of acetic acid contaminating the parent methacrylic acid and can be diminished to 0.001–0.10 wt% by vacuum distillation.

Identification of the contaminants in the *p*-chlorophenyl methacrylate both introduced with the raw material and formed in the process of the synthesis allowed to chose the optimal conditions of the synthesis of *p*-chlorophenyl merthacrylate. The developed method is based on the Schotten – Baumann reaction and the optimal temperature regime and ratio of reagents. For the better removing the unreacted initial compound the number of the alkaline washing of the reaction mixture was optimized. The reasons for exclusion of phenolic inhibitors were established and the inhibitors of other classes were applied providing the required polymerization activity of the monomer. For excluding reaction of the methacrylate with oxygen to form peroxide, a vacuum distillation under inert gas atmosphere was introduced.

As a result, the *p*-chlorophenyl methacrylate was synthesized with the yield no less than 72%; d_4^{20} =1.1823; n_D^{20} =1.5292–1.5300; mp 98–99°C/4–5 mm Hg. The IR spectrum, ν, cm^{-1}: 1740 (C=O); 1640 (C=C); 810, 1490, 1600, 3000, (*p*-chloro-substituted aromatic ring; 1250– 1050 (C–O–C). The ^{1}H NMR spectrum, δ, ppm: 2.05 (m, 3H, CH_3), 5.76 (m, 1H, *trans*-CH=C), 6.34 (m, 1H, *cis*-CH=C), 7.02 – 7.16 (m, 2H, 2,6-CH), 7.31–7.38 (m, 2H, 3,5-CH). The ^{13}C NMR DEPT spectrum, δ, ppm: 18.3 (CH_3), 123.0 (2,6-CH), 127.6 (CH_2=C), 129.5 (3,5-CH), 131.1 (4-CCl), 135.6 (CH_2=C); 149.4 (1-CO), 165.6 [C(O)O]. The characteristics of the monomer samples synthesized under the developed conditions are listed in Table 3.

Thus, the original complex modification of the known method allowed us to solve an important practical problem of synthesis of methacrylic monomer with a desired purity grade for the creation of polymers of special application. With the high purity *p*-chlorophenyl methacrylate as a modifying (co)monomer were obtained poly(methyl methacrylate) organic glasses with a complex of improved exploitation characteristics.

CONCLUSIONS

1. Main contaminants in the *p*-chlorophenyl methacrylate are identified, sources of their formation are elucidated and optimal condition for the exclusion of side processes are selected.

2. The method of synthesis of high purity *p*-chlorophenyl methacrylate with the yield 72% or higher and main component content 99.7–99.9% is developed.

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