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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis and Polymerization of Unsaturated Phthalides

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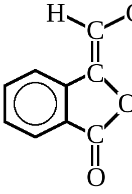
Abstract—Procedures were developed for preparing unsaturated phthalides: phthalideneacetic acid and methylene phthalide, which are promising monomers for radical polymerization. The structures of the monomers were studied, and their copolymerization with methyl methacrylate was performed.

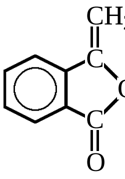
Much attention is given today to polymeric materials whose components change the structure and physicochemical properties, depending on external conditions (pressure, temperature, acidity of the medium, etc.). Of particular interest in this respect are phthalides showing ring–chain isomerism [1]. Phthalide-containing polymers exhibit unique electrical [2] and optical [3] properties, high heat resistance, and high softening points [4]. These polymers are most often prepared by polycondensation. However, their high heat resistance is combined with high glass transition and flow points, and also with poor solubility in the majority of industrially used organic solvents.

In contrast to phthalide-containing polymers, many vinyl polymers, in particular, polyacrylates have low glass transition and flow points and good solubility, but poor heat resistance. These polymers are most often prepared by radical polymerization. Therefore, it seems appropriate to modify vinyl polymers, such as poly(meth)acrylates, polystyrene, etc., with phthalides, and development of procedures allowing modification in the stage of synthesis is an urgent problem.

Phthalides can be incorporated into a polymeric molecule in the course of radical polymerization both via their involvement in chain initiation or transfer [3] and through (co)polymerization of unsaturated phthalides. With the aim to prepare poly(methyl methacrylate) modified with phthalide-containing compounds, we prepared two phthalide-containing monomers: phthalideneacetic acid **I** and methylene phthalide **II**:



I



II

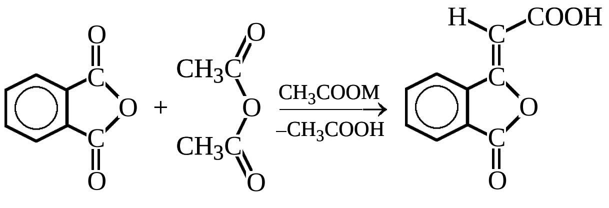
The monomeric purity is the necessary condition for their application.

EXPERIMENTAL

Phthalic anhydride was recrystallized from absolute ethanol before use; mp 239°C. Acetic anhydride was distilled; bp 140°C. The polymerization initiators, azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BP), were repeatedly recrystallized from methanol and vacuum-dried to constant weight.

Methyl methacrylate (MMA) was purified to remove the stabilizer by shaking with 5–10% KOH, washed with water to neutral reaction, dried over $CaCl_2$, and double-distilled in a vacuum. The fraction with bp 42°C (13.3 kPa) was used for polymerization.

Phthalideneacetic acid. Published data on synthesis of **I** and **II** are contradictory. Phthalideneacetic acid was prepared for the first time at the end of the XIX century [5–8], but its properties have been studied poorly. In this study, we prepared **I** by the Perkin–Gabriel reaction from phthalic and acetic anhydrides in the presence of a metal acetate:



The reaction was performed in several steps. First, a flask was charged with phthalic anhydride (2–3% excess relative to the reaction stoichiometry), acetic anhydride, and potassium acetate (20–30% excess relative to phthalic anhydride). The mixture was heated for 1.5 h on a boiling water bath. Then a tenfold vol-

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Table 1. Properties of **I** and **II**

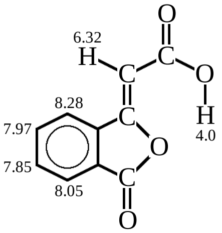
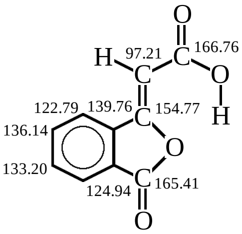
Compound	Found, % / Calculated, %		mp, °C	UV spectrum, λ, nm	IR spectrum, ν, cm^{-1}	NMR spectrum, δ, ppm	
	C	H				^1H	^{13}C
I	63.47 63.16	3.02 3.18	280	282 (C=C)	1705 (COOH) 1800 (C=O)		
II	74.16 73.97	4.02 4.14	56	311 (C=O and Ar)	1780 (C=O)	4.80 (*cis*-H) 5.25 (*trans*-H)	94.86 ($C=CH_2$)

Table 2. Geometries of **I** and **II**

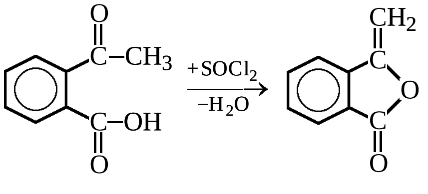
Bond	II		I	
	bond length, Å	bond angle, deg	bond length, Å	bond angle, deg
C=C	1.3	130.2 108.7*	1.3	122.7 108.8*
=C–H	1.1	130.2	1.1	119.6 115.6
=C–CO	–	–	1.5	115.8 124.8**
=C–O–	–	–	1.4	116.5
–O–H	–	–	1.0	109.9
Deviation from plane		No		–COOH, 58

* In the ring. ** Relative to the C=C bond.

ume of hot water was added, and the hot mixture was filtered. The precipitate was washed with hot water and ethanol. A light brown product was obtained; it was washed with a small amount of hot glacial acetic acid. After cooling and filtration, a yellow substance was obtained; its melting point, 249°C, is reasonably consistent with published data [6, 7]. The product was repeatedly recrystallized from glacial acetic acid in the presence of activated carbon. Colorless lustrous plates were obtained; mp 280°C (with decomposition). Further recrystallizations did not increase the melting point. The product was identified by IR, ^{13}C NMR, and ^1H NMR spectroscopy and by elemental analysis (Table 1).

Methylene phthalide. Synthesis of methylene phthalide and its polymers has been attempted by numerous researchers. However, either the suggested procedures gave the monomer in low yield (10–15%) or the product was unsuitable for polymerization because of the presence of inhibiting impurities.

In this study, to prepare and purify methylene phthalide, we chose the procedure described in [9]. It involved high-vacuum dehydration of acetophenone-*o*-carboxylic acid:



The product sublimes and is condensed as colorless needles, mp 56°C (yield about 60%); it is hygroscopic and sublimes in a vacuum at about 300°C (1–5 mm Hg). Some characteristics of **II** are listed in Table 1.

The kinetics of bulk polymerization was monitored gravimetrically [10]. The temperature was maintained at 60 ± 0.5°C. The composition was calculated from the analytical data.

The UV spectra (solutions in CH_3COOH) were recorded on a Shimadzu UV–VIS–NIR 3100 spectrometer using a 1-cm quartz cell. The IR spectra (mulls in mineral oil) were recorded on a Specord M-80 spectrophotometer (Germany). The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-400 spectrometer (300 MHz, CD_3OD, internal reference hexamethyldisiloxane).

The temperature of the decomposition onset was determined by the method of tangents with an MOM Q-1500D derivatograph (Hungary); sample weight 100 mg, heating rate 5 deg min^{-1}.

The probabilities of addition of propagating radicals with different structures of terminal units to comonomer molecules were calculated as described in [10].

The overwhelming majority of studies concerned phthalideneacetic acid are limited to its synthesis. In most cases, the acid was immediately subjected to thermal decarboxylation in a vacuum to obtain methylene phthalide [7, 8]. The properties and structure of the acid remained unknown, like those of methylene phthalide. Therefore, we first examined the structures of these compounds.

The ^1H NMR spectrum of **II** (Table 1) shows that the methylene hydrogen atoms (α-position relative to the phthalide ring) are nonequivalent (*cis* and *trans* arrangement relative to the oxygen atom of the phthalide ring).

In the case of phthalideneacetic acid, two isomers with the *cis* and *trans* arrangement of the carboxy group relative to the oxygen atom of the phthalide ring are possible. The nuclear Overhauser effect (η = 8%) observed on the aromatic proton (8.28 ppm, 3-position) upon irradiation at the frequency of the olefinic proton signal (6.32 ppm) unambiguously suggests steric proximity of these protons, i.e., the *cis* structure of the product. In other words, the synthesized phthalideneacetic acid is a pure *cis* isomer. Furthermore, the chemical shift of the carboxyl proton signal is unusually small, which may be due to interaction of this proton with the oxygen atom of the phthalide ring. Unfortunately, we failed to follow the changes in the chemical shift of this signal depending on the solvent polarity because of extremely low solubility of **I** in other solvents. However, the chemical shift varies with temperature: 25°C, 4.00 ppm; 30°C, 4.72 ppm; and 40°C, 5.73 ppm. This indicates that the intramolecular hydrogen bond in the acid molecule becomes weaker.

Table 3. Characteristics of copolymerization of MMA with unsaturated phthalides at 70°C [initiator azobis-(isobutyronitrile), 0.5 wt %] and decomposition (onset) temperatures of the copolymers

Phthalide content in monomer mixture, mol %	Initial copolymerization rate, % min^{-1}	Phthalide content in copolymer, mol %	T_{dec}, °C
Phthalideneacetic acid			
0	0.0950	0	190
10	0.0925	1.8	218
20	0.0800	3.3	226
30	0.0540	4.2	235
40	0.0220	6.9	230
60	0.0067	18.0	220
Methylene phthalide			
0	0.1070	0	190
10	0.1098	4.2	220
15	0.1064	7.0	228
20	0.1002	9.6	235
40	0.0891	21.6	240
60	0.0788	37.6	238
80	0.0745	60.2	242
90	0.0704	77.7	240

The molecular geometry of **I** and **II** was optimized by PM3 calculations. The results (Table 2) show that the oxygen atom deviates from the ring plane by approximately 2°; the bond angle at the ring oxygen atom is 108°, and the C–O bond length, 1.44 Å. An important result is that the phthalideneacetic acid molecule, in contrast to the methylene phthalide molecule, has functional groups that extend from the molecular plane; this must affect the electrical properties of **I** at elevated pressures and temperatures.

Unfortunately, we failed to prepare the homopolymer of phthalideneacetic acid by radical polymerization. However, we obtained copolymers of **I** with MMA. Some data on the reaction and copolymer compositions are listed in Table 3. It is seen that the copolymerization rate decreases with increasing content of **I** in the reaction mixture. This may be due to the fact that the purity of **I** is insufficient for radical polymerization. Therefore, we additionally performed repeated chromatographic purification of the mono-

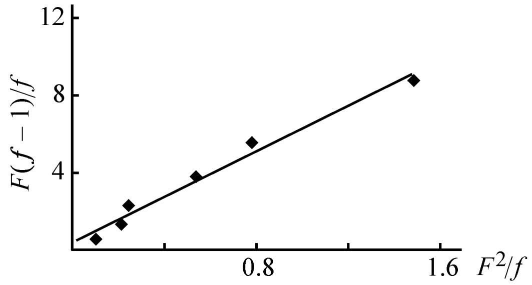


Fig. 1. Determination of the constants of MMA copolymerization with phthalideneacetic acid by the Fineman–Ross method.

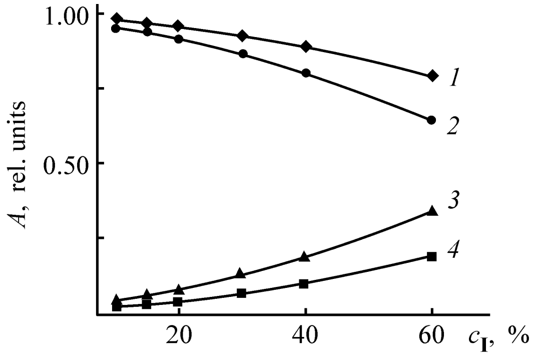


Fig. 2. Probability A of addition of a propagating radical with the of terminal unit (*1, 2*) MMA and (*3, 4*) phthalideneacetic acid to (*1, 3*) MMA and (*2, 4*) phthalideneacetic acid molecule. (c_I) Concentration of **I**.

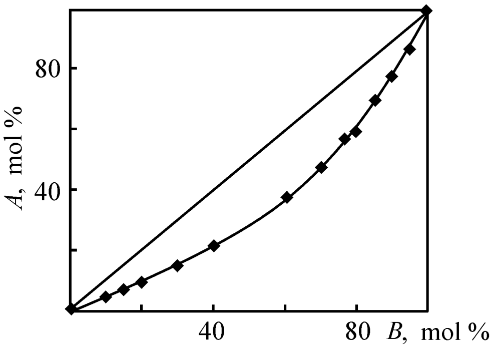


Fig. 3. Content *A* of methylene phthalide units in the copolymer vs. the content *B* of methylene phthalide in the initial monomer mixture.

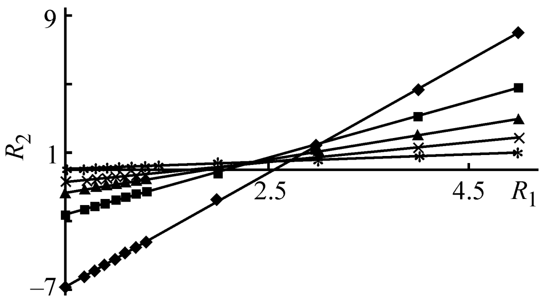


Fig. 4. Determination of the constants of MMA copolymerization with methylene phthalide by the Mayo–Lewis method.

mer. A certain increase in the copolymerization rate was, indeed, observed but attempted preparation of the homopolymer failed.

The constants of copolymerization of MMA with **I** were determined by the Fineman–Ross method [10] (Fig. 1) to be 0.36 ± 0.06 and 5.80 ± 0.08, respectively. Calculation of the probabilities of monomer addition to propagating radicals of various structures shows (Fig. 2) that incorporation of MMA into the chain is much more probable than incorporation of **I**.

At the same time, the copolymerization constants show that the monomers interact with each other (the product of the constants is significantly greater than unity), probably owing to their high polarity. Using the *Q*–*e* scheme, we calculated the parameters e = 1.26 (parameter characterizing the polarity of **I**) and Q = 0.79 (parameter characterizing the conjugation in the propagating radical with the radical center localized in the phthalideneacetic acid unit) [10]. Phthalideneacetic acid is close to MMA in the value of Q (Q_{MMA} = 0.74) but significantly exceeds it in polarity (e_{MMA} = 0.40), being in this respect close to acetonitrile (e = 1.20).

In contrast to phthalideneacetic acid **I**, methylene phthalide polymerizes in the presence of radical initiators, such as BP or AIBN. The reaction was performed in DMF in the presence of 3.7×10^{-3} M BP. The polymerization noticeably accelerated after reaching 30% conversion of the monomer (gel effect), suggesting the radical mechanism of the reaction. The polymer was precipitated with acetone and reprecipitated several times. Dry poly(methylene phthalide) has a high glass transition point (305°C), and its softening is accompanied by decomposition (as indicated by significant weight loss). We failed to prepare films from this polymer (under conditions similar to those used with other polymers) for studying electrical properties; therefore, it seems necessary to prepare copolymers of **II**, primarily with MMA.

A study of copolymerization of MMA with **II** showed that, with increasing content of **II**, the process decelerates but does not fully stop (Table 3), which allows preparation of the copolymer with different monomer ratios. Figure 3 shows that the copolymer is enriched in MMA units at any composition of the monomer mixture, and the ratio of the copolymerization constants meets the condition $r_1 > 1$ and $r_2 < 1$.

The copolymerization constants were determined by the Mayo–Lewis method [10] (Fig. 4) to be 2.69 ± 0.05 (for MMA) and 0.70 ± 0.07 (for **II**). In this case, too, the product of the copolymerization constants is greater than unity, suggesting mutual interaction of the monomers; however, it is apparently weaker than that with **I**.

Methylene phthalide is characterized by Q = 1.35 and e = +1.20. It is somewhat more polar than **I**, but its growing radical is more active in chain propagation.

As expected, the copolymers show higher heat resistance, compared to poly(methyl methacrylate) (Table 3). However, with increasing content of phthalideneacetic acid, the decomposition onset temperature starts to decrease, probably owing to decarboxylation.

CONCLUSIONS

(1) Procedures were developed for synthesis and purification of phthalideneacetic acid and methylene phthalide, promising monomers for radical polymerization.

(2) The structures of the phthalides were studied; phthalideneacetic acid has the *cis* structure.

(3) (Co)polymerization of unsaturated phthalides with methyl methacrylate was performed; the copolymerization constants and Q–e parameters were calculated; the activity of **I** and **II** as monomers was evaluated.

(4) The methyl methacrylate copolymers obtained show enhanced heat resistance.

ACKNOWLEDGMENTS

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