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Dependence of polymerization ability of maleimidophenyl methacrylates on π-electron structure of maleimide fragments

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New maleimidophenyl methacrylates with different substituents in maleimide fragments were synthesized and their structures were confirmed by nuclear magnetic resonance spectroscopy. The kinetics of radical thermoinitiated homopolymerization of these monomers in N,N-dimethylformamide (DMF) solutions in the presence of AIBN at 80 °C have been investigated with dilatometry. Substituents variation in the maleimide units gave us the opportunity to systematize the results obtained. It was found that not only the unsubstituted maleimide groups take part in a cross-linking processes during the thermoinitiated radical polymerization of these monomers, but also the monomer with $X_1 = H$, $X_2 = CH_3$. Other monomers formed linear polymers. For monomers with tetrahydrophthalimide larger substituent cross-linking processes are observed after homopolymerization of methacrylic group. The activity of synthesized compounds has been discussed.

Key words: *phenyl methacrylates; radical polymerization; self-copolymerization; cross-linking*

1. Introduction

Significant interest has been focused on monomers that contain two or more different reactive groups, which can independently take part in diverse polymerization processes. Such polyfunctional monomers afford the possibility, at least at principle, of carrying out selective polymerization reactions consecutively involving each type of active group while keeping other groups intact. It is along these lines that efficient routes exist for the preparation of graft-copolymers, reactive homopolymers and copolymers which can be modified by means of polymer-analogous transformations, curing or vulcanization without the introduction of any additives.

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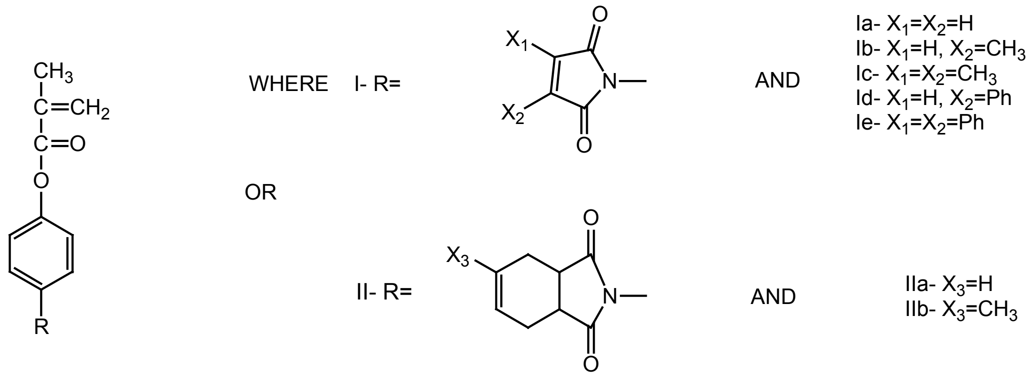
In this paper, we present some bifunctional monomers based on *p*-aminophenol. The common formula of these compounds is shown in Scheme 1 (some monomers of this type (IIa and IIb) were synthesized previously [1, 2]).



Scheme 1

The first ones can be considered as being simultaneously monomers of phenyl methacrylates and of phenyl maleimide. They are highly active in radical polymerization [3]. The second ones are known as strong electron-acceptor monomers with e-factor (Q-e scheme) near 2 [4]. They are very active in copolymerization with electron donor monomers [5] and can be used as photoinitiators for acrylate monomers [6]. Maleimides with substituted double bonds, for example, by one chlorine atom [7] homopolymers are unknown, but copolymerization is possible. Dimethyl maleimide double bond was previously found to be inactive also in copolymerization [8]. These phenomena were not studied previously in detail.

Imidophenyl methacrylates (Scheme 1) which have two double bonds of different activity when exposed to an elevated temperature or UV-irradiation are able to take part in polymerization processes and cross-linking reactions.

2. Experimental

The procedure of synthesis of these monomers includes two stages. 4-hydroxyphenylmaleimides or 4-hydroxyphenyltetrahydrophthalimides were synthesized by condensation of equimolar quantities of *p*-aminophenol and corresponding anhydride in concentrated acetic acid as a solvent. The condensation was carried out at the boiling point of acetic acid in a glass reactor with a condenser during 5–9 hours. After the completion of the condensation reaction, the resulting mixture was poured into water. In the case of maleic, citraconic and phenylmaleic anhydrides corresponding monoamides were formed.

The synthesis of the monomers was carried out by heating appropriate initial imides or monoamides with 30 mass. % excess of methacrylic anhydride in the presence of concentrated sulphuric acid (H_2SO_4) as a catalyst and phenothiazine as the inhibitor of polymerization. For 4-hydroxyphenylmaleamide, 4-hydroxyphenylcitraconylamide, and 4-hydroxyphenyl-2-phenylmaleamide imides cycles were formed at the same time of the methacrylation. After the completion of the reaction of methacrylation the resulting mixture was poured into water. Recrystallization was carried out in a toluene–hexane (1:1) mixture. Monomers are soluble at room temperature in acetone, alcohols, 1,4-dioxane, DMF, under the heating in toluene, CCl_4 and insoluble in hexane and water.

The structures of the synthesized compounds were confirmed by nuclear magnetic resonance spectroscopy (H^1 NMR; Bruker-100 NMR spectrometer). The solvent used for sample preparation was acetone-d_6. Tetramethylsilane was used as a reference for peak assignments.

In H^1 NMR spectra of monomers Ia–Ie the fragment of methacrylate group was found as signals of methyl protons at 2.07, 2.05, 2.02, 2.06, 2.28 ppm and signals of methylene protons at 5.77, 5.88, 5.84, 5.85, 5.86 ppm (*trans*-protons) and 6.35, 6.33, 6.31, 6.33, 6.34 ppm (*cis*-protons) for (Ia), (Ib), (Ic), (Id) and (Ie), respectively. The maleimide fragments of Ia, Ib and Id were found by the signals of protons X_1 (see Scheme 1) at 6.85, 6.68 and 7.04 ppm for these monomers, respectively. The substituents in maleimide cycles were found by the signals of methyl protons at 2.12 ppm for Ib, at 2.05 ppm for Ic, or by the signals of phenyl protons at 7.55–7.8 ppm for Id. For Ie the substituents in maleimide cycle were found by signals of phenyl protons at 7.3–7.68 ppm, which give common signals with protons of phenylene ring. For other monomers, the protons of phenylene ring were found as multiplets at 7.22–7.48 ppm for Ia, at 7.25–7.52 ppm for Ib, at 7.1–7.38 ppm for Ic, at 7.23–7.5 ppm for Id.

For study the polymerization ability of these monomers, the kinetics of radical thermoinitiated homopolymerization in solutions with addition of AIBN were investigated with dilatometry. The polymerization was carried out in DMF solutions (5 mass. % concentration to monomer) at the temperature of 80 °C in the atmosphere of argon.

3. Results and discussion

At the formation of polymers from the synthesized compounds, the significant distinctions in kinetics of the polymerization are observed (Fig. 1). The monomers (Ia) and (Ib) were found to form polymers of a three-dimensional structure, and for the compound (Ib) the cross-linked polymer formation begins at the conversions more than 10%. For (Ia) the linear polymer is not formed. High velocity of the polymerization and significant conversions of polymer based on (Ia) are connected with high activity of non-substituted maleimide double bond, which allows it to enter the processes of copolymerization [9]. Actually, this is a ‘self-copolymerization’ of the monomer on two bonds. For the monomer (Ib) the completion of the reaction at earlier stages and slower polymerization (in comparison with (Ia)) are possible to be explained by a dominant interaction of methacrylic double bond and rather small participation in polymerization processes of the double bond of citraconylimide. Thus, the introduction even of a small substituent essentially reduces the activity of double bond of such a type. The formation of a cross-linked structure indicates that the double bond of citraconylimide is capable of copolymerization. Cross-linking at later stages allows one to select conditions of a selective course of the reaction with the purpose of reception of linear polymers extremely on the methacrylic bond.

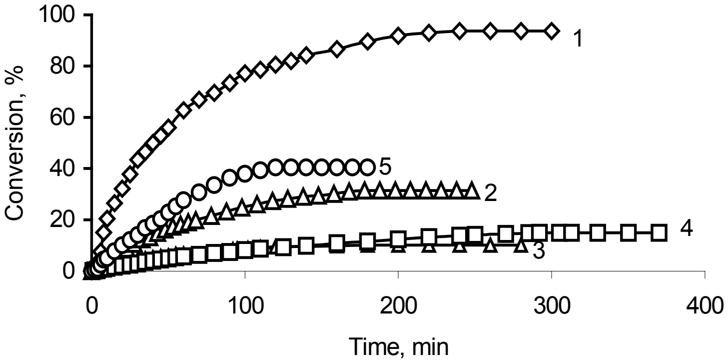
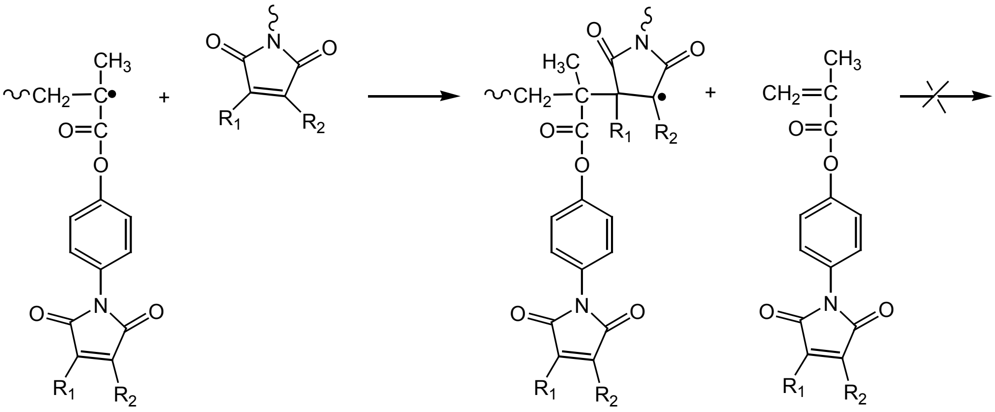


Fig. 1. Kinetic curves of thermoinitiated radical homopolymerization of: 1) Ia, 2) Ib, 3) Ic, 4) Id, 5) Ie in solutions at 80 °C (5 mass. % concentration to monomer in DMF, 1 mass. % AIBN from weight of monomer)

Anther case is observed for monomers (Ic) and (Id), which in such conditions are polymerized with low rates and yields (no more than 15%). The compound (Ie) is polymerized with a high yield (40%). This fact seems to be rather unusual (especially if one compares the polymerization ability of (Ib) and (Ic), (Id) and (Ie)). By a more detailed analysis of the results obtained, it is possible to make the following suggestions. The first one is that in compounds of such structures both bonds (methacrylic and maleimide) can participate in polymerization. The second one is that the character of the interaction on these bonds depends on the presence and nature of the substituent near a double bond of maleimide. For monomers (Ic) and (Id), low polymerization ability may be explained by the fact that the deactivation of a growing or starting initiating radical occurs owing to the addition to a replaced maleimide. A new radical, due to steric hindrances, is unable to continue both kinetic and material chains (Scheme 2).

For monomer (Ie) high conversions and formation of extremely linear polymers are explained by similar reasons: the active centre due to steric hindrances does not interact with a double bond of 2,3-diphenylmaleimide fragment (Scheme 3).

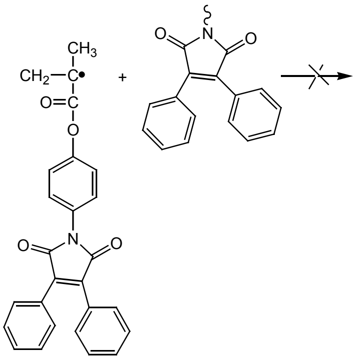
Therefore, for this monomer the deactivation of an active centre, as in a case of compounds (Ic) and (Id), and cross-linking, as for monomers (Ia) and (Ib), become impossible. A similar behaviour of monomers with substituted double bonds as the agents of chain transfer, particularly for monoterpenoids, was observed earlier [10].



Ic - $R_1=R_2=CH_3$
Id - $R_1=H$, $R_2=Ph$

Scheme 2

In the case of monomers with the tetrahydrophthalimide substituent (IIa and IIb), the tetrahydrophthalimide units were found to take part in cross-linking processes during the thermoinitiated radical polymerization of these monomers. The influence of temperature on the thermoinitiated radical polymerization of IIa is shown in Fig. 2.



Scheme 3

On the kinetic curves, two stationary parts are observed: in the initial part A the inclination angle (as well as calculated kinetic parameters) increases with the temperature and only one linear polymer product is obtained. Cross-linking processes are not observed. In the stationary part B, the increasing temperature does not lead to sufficient changes of the inclination angle. After the stage B of polymerization, partially insoluble products were obtained. With temperature increase, the stationary part A decreases and the cross-linking process is increased, probably simultaneously with the polymerization (part B).

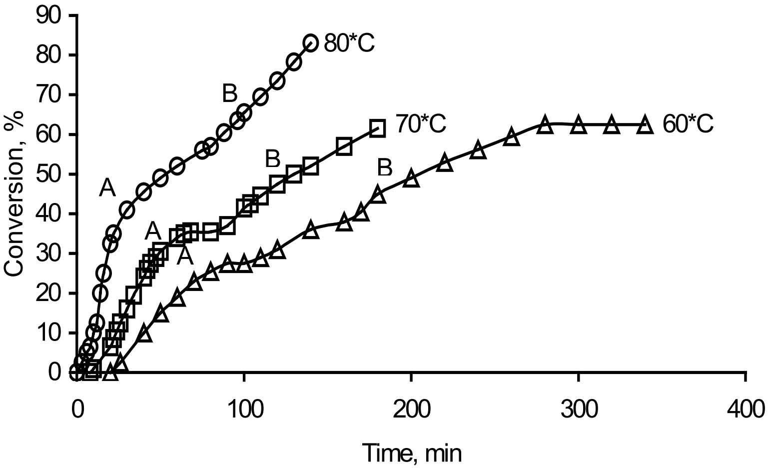


Fig. 2. Kinetic curves of thermoinitiated radical homopolymerization of IIa in solutions at different temperatures

At the stationary parts of the experimental curves, some kinetic parameters of the thermoinitiated radical homopolymerization were calculated. The ability of monomers to the polymerization was evaluated by the total rate of polymerization (V_p) and total constant of polymerization (K_Σ). The total constant of polymerization was found from the equation

$$V_P = K_\Sigma [\mathrm{I}]^{0.5}[\mathrm{M}]$$

where [I] is the concentration of the initiator, [M] – the concentration of the monomer, K_Σ – total constant of polymerization, in which the influence of monomer and initiator concentrations are excluded. Kinetic parameters for the synthesized monomers are given in the table.

In the case of tetrahydrophthalimidophenyl methacrylates (IIa and IIb), the introduction of imide substituent leads to the increase of K_Σ value due to its significant influence as an electron acceptor. Simultaneous increase of the steric factor does not play any significant role. The influence of the nature of a substituent on polymerization ability of maleimidophenyl methacrylates was reported earlier, the introduction of maleimide substituent also increases K_Σ, but the character of changes of total constants of the polymerization depends on the nature of the substituent in maleimide cycle.

Table. Kinetic parameters of thermoinitiated radical homopolymerization of monomers (80°C, 5% mass. % solution of monomer, 1 mass. % AIBN from weight of monomer)

Code of monomer	Molecular weight	$V_p \cdot 10^4$ mol/(dm^3·s)	$K_\Sigma \cdot 10^3$
Ia	257	–	–
Ib	271	0.5525	5.42175
Ic	285	0.19275	1.989
Id	333	0.1537	1.8534
Ie	409	0.72542	10.74
IIa	311	0.63	6.8
IIb[1]	325	–	3
PhMA[1, 2]	164	0.52	1.1

[1] 10 mass. % solution of monomer in DMF.

[2] Phenyl methacrylate.

4. Conclusions

The polymerization ability of phenyl methacrylates with tetrahydrophthalimide and maleimide fragments was found to be dependent on the π-electron structure of imide fragments. It was found that in the case of monomers with maleimide substituent (monomers Ia–Ie), the maleimide units can participate in the polymerization, and in some cases (Ia, Ib) in copolymerization with methacrylic groups. In the case of monomers with tetrahydrophthalimide group, its units can take part in cross-linking processes after a previous homopolymerization of methacrylic group.

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