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Designed Monomers and Polymers 0 (2009) 1–10
DESIGNED MONOMERS AND POLYMERS
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Synthesis of Methacrylate-Based Functional Monomers *via* Boron Ester Acidolysis and Their Polymerization

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Abstract
A new method is presented for the synthesis of functional methacrylate ester monomers. In this method, boron esters of appropriate alcohols were reacted with methacrylic acid to give corresponding methacrylic ester monomers. The monomers *N*,*N*-dimethylaminoethyl methacrylate (DAMA), 2-chloroethyl methacrylate (CEMA), 2-bromoethyl methacrylate (BEMA), 2-methoxyethyl methacrylate (MEMA) and butyl methacrylate (BMA) were prepared in a laboratory scale by a two-step one-pot process. In the first step, the corresponding boron esters were formed by azeotropic removal of water. Subsequently, addition of methacrylic acid and heating at 140–160°C in the presence of pyridine resulted in acidolysis of the boron esters, yielding the functional methacrylate ester monomers in acceptable yields (41–71%). The monomers obtained were characterized by ^{1}H-NMR and FT-IR spectra after isolation and purification. Their polymerizability was also demonstrated.

Keywords
Esterification, boron esters, functional monomers, radical polymerization

1. Introduction

Poly(methyl methacrylate) (PMMA) is an important commodity thermoplastic used extensively in various fields due to its optical clarity, hydrolytic stability and outstanding resistance against air oxidation. The principal commercial method for production of its monomer, methyl methacrylate (MMA) is still the acetone cyanohydrine process which dates back half a century [1]. This process is also applied for the production of higher methacrylates or other functional derivatives [2]. Direct esterification of methacrylic acid is proposed as an alternative industrial method [3]. Transesterification of MMA, on the other hand, is a less common way of preparing these monomers [4].

The use of methacryloyl chloride (MAC) seems to be mostly preferred for laboratory-scale preparation of methacrylate esters with desired functionalities

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DOI:10.1163/138577209X12486896623571

[5, 6]. However, the reaction with MAC needs dry conditions and extreme precautions. Difficulties in storage and handling of this material are additional drawbacks.

Herein, we describe an alternative method for laboratory scale preparation of some functional methacrylate ester monomers, namely, 2-chloroethyl methacrylate (CEMA), 2-bromoethyl methacrylate (BEMA), *N*,*N*-dimethylaminoethyl methacrylate (DAMA), 2-methoxyethyl methacrylate (MEMA) and butyl methacrylate (BMA). The method presented is based on acidolysis of boron esters with methacrylic acid. The reaction of boron esters with carboxylic acids was first described by Schiff more than 100 years ago [7, 8]. Synthesis of carboxylic acid esters by acidolysis of boron esters seems to be attractive due to easy preparation of the alkyl borates. However, this chemistry has been scarcely dealt with in the literature and only few reports are available [9, 10]. To the best of the authors' knowledge, there is no report dealing with application of this chemistry for preparing specifically methacrylate ester monomers.

In this work, a one-pot process using boron esters was developed as for the synthesis of the methacrylate ester monomers. Moreover, reaction conditions, isolation and spectral characterization of the monomers were reported in detail. Polymerizability of the resulting monomers was also tested by using a conventional radical initiator, 2,2′-azobis-(isobutyronitrile) (AIBN).

2. Experimental

2.1. Materials

All the chemicals used were analytical grade commercial products. Butanol (Merck), 2-chloroethanol (Aldrich), 2-bromoethanol (Aldrich), *N*,*N*-dimethylamino ethanol (Aldrich), 2-methoxy ethanol (Merck), 2,2′-azobis-(isobutyronitrile) (AIBN, Aldrich), methacrylic acid (Lancaster), sodium sulfate (Merck), pyridine (Merck), boric acid (Merck) and cross-linked poly(vinyl pyridine) resin (Reillex) were used as purchased.

2.2. Measurements

Gel-permeation chromatography (GPC) of the polymer samples were taken in tetrahydrofurane (THF) with a flow rate of 0.3 ml/min using an Agillant 1100 series instrument consisting of a pump, a refractive index-detector and Waters Styrogel columns (HR4, HR3, HR2). ^{1}H-NMR spectra of monomers and polymers were obtained by a Bruker 250 MHz NMR spectrometer, using $CDCl_3$ as solvent. FT-IR spectra were recorded on Perkin Elmer FT-IR Spectrum One B spectrometer.

2.3. Syntheses of the Monomers

Two methods (Method A and Method B) were employed for synthesis of the monomers. In Method A, boron esters were formed first by reaction of boric acid with appropriate alcohol in a canonical flat-bottom flask (250 ml) equipped with a

Dean–Stark trap and a reflux condenser. The water evolved was removed azeotropically with toluene and collected in the trap. Then, toluene was distilled off and reaction with methacrylic acid was conducted without isolation of the boron esters in the presence few milliliters of pyridine.

2.3.1. Method A

2.3.1.1. Synthesis of 2-Chloroethyl Methacrylate (CEMA). To the flask, there was added 40.7 ml (0.6 mol) 2-chloroethanol, 12.37 g (0.2 mol) H_3BO_3 and 50 ml toluene. The mixture was heated at 150°C while stirring with a magnetic bar. In this condition water removal was completed within 3–4 h. Then, toluene was distilled and recovered *via* reservoir of the trap. To the cooled mixture 51.5 ml (0.6 mol) methacrylic acid, 0.1 g hydroquinone and 3 ml pyridine were introduced and the reaction content was heated to 160°C for 12 h. No boric acid precipitation was observed in this case. The mixture was cooled to room temperature and poured into 300 ml water. The lower organic phase was separated by a separatory funnel and washed with 2% NaCl solution (3 × 150 ml). The crude product was dried over Na_2SO_4 and distilled (71–74°C/12 mmHg). The yield was 45.6 g (51.2%). Pure product was obtained by redistillation (70.5–72°C/12 mmHg), 37.2 g (41.8%) and the ^{1}H-NMR spectrum of CEMA, shown in Fig. 1, confirms the purity. ^{1}H-NMR, δ: 6.1 ppm (1H, s, $=CH_2$ *cis*), 5.5 ppm (1H, s, $=CH_2$ *trans*), 4.3 ppm (2H, broad s, $-COO-CH_2-$), 3.6 ppm (2H, broad s, $-CH_2-Cl$), 1.85 ppm (3H, s, $CH_3-C=C$).

2.3.1.2. Synthesis of 2-Bromoethyl Methacrylate (BEMA). The same procedure was followed for synthesis of this monomer starting from 2-bromoethanol. The

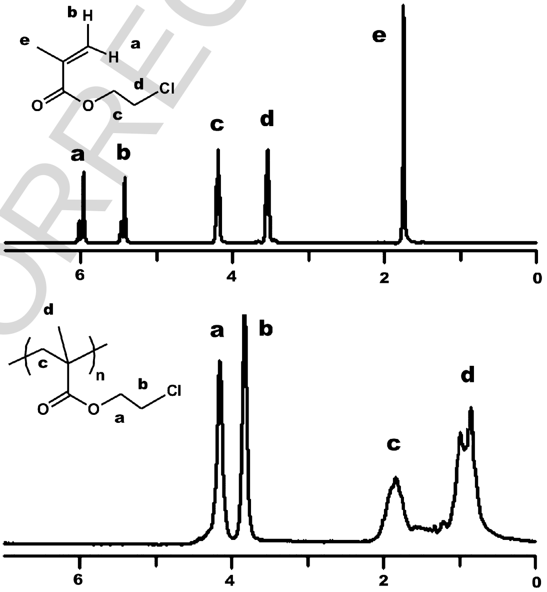


Figure 1. ^{1}H-NMR spectra of 2-chloroethyl methacrylate as synthesized and its polymer.

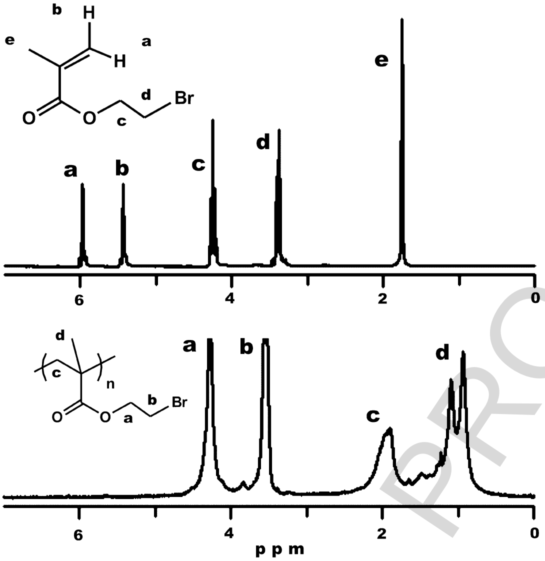


Figure 2. ^{1}H-NMR spectra of 2-bromoethyl methacrylate as synthesized and its polymer.

monomer was isolated by distillation under vacuum (96–99°C/11 mmHg). The yield was 71.2%. The ^{1}H-NMR spectrum of the product obtained in the first distillation revealed pure monomer and redistillation was not necessary as seen in Fig. 2.

^{1}H-NMR, δ: 6.0 ppm (1H, s, $=CH_2$ *cis*), 5.45 ppm (1H, s, $=CH_2$ *trans*), 4.3 ppm (2H, broad s, $–COO–CH_2–$), 3.4 ppm (2H, broad s, $–CH_2–Br$), 1.8 ppm (3H, s, $CH_3–C=C$).

2.3.1.3. Synthesis of N,N-Dimethylaminoethyl Methacrylate (DAMA). For the synthesis of this monomer, the general procedure described above was employed, except action of methacrylic acid in the second step was carried out in the absence of pyridine. Starting from 40.05 g (0.45 mol) *N*,*N*-dimethylamino ethanol and 9.28 g (0.15 mol) H_3BO_3, water was removed (8.1 ml) azeotropically with toluene. Then 38.7 g (0.45 mol) methacrylic acid was added in presence of hydroquinone (0.1 g) and heated to 50°C for 16 h.

Isolation of this monomer is difficult due to salt formation of the residual methacrylic acid with the monomer. Direct distillation of the mixture gave very low yields (6–11%).

To remove acid residues the reaction content was mixed with 120 ml dichloromethane and 28 g (0.7 mol) solid NaOH. The mixture was shaken with an orbital shaker for 3 h and filtered. The filtrate was transferred into round bottom flask and dichloromethane was removed by rotavapor. The residue was distilled under vacuum (75–76°C/8 mmHg). The yield was 42.6 g. Redistillation gave 29 g pure monomer (41.0%). ^{1}H-NMR, δ: 5.75 ppm (1H, s, $=CH_2$ *cis*), 5.2 ppm (1H, s, $=CH_2$ *trans*), 3.7 ppm (2H, broad s, $–COO–CH_2–$), 2.9 ppm (2H, broad s, $–CH_2–N$), 2.6 ppm (6H, s, $–N–CH_3$), 1.7 ppm (3H, s, $CH_3–C=C$).

2.3.1.4. Synthesis of 2-Methoxyethyl Methacrylate (MEMA). This monomer was synthesized by the same procedure described for CEMA, except that the reaction mixture was directly distilled without washing with water. From the reaction of 1.0 mol (76 g) 2-methoxyethanol and 0.33 mol (20.6 g) boric acid, 84 g crude product was obtained by distillation under vacuum (63–72°C/12 mmHg). The ^{1}H-NMR spectrum of this product shows presence metacrylic acid impurities up to 15%. To remove methacrylic acid, 50 g commercial poly(vinyl pyridine) resin (Reillex TM-425) was added into the product and it was left to stand for12 h in presence of hydroquinone as inhibitor. Redistillation of the filtered liquid (63–65°C/12 mmHg) gave pure monomer freed from methacrylic acid. Overall yield was 64.1 g (53.1%).

^{1}H-NMR, δ: 5.8 ppm (1H, s, $=CH_2$ *cis*), 5.3 ppm (1H, s, $=CH_2$ *trans*), 4.0 ppm (2H, broad s, $–COO–CH_2–$), 3.3 ppm (2H, broad s, $C–CH_2–O$), 3.1 ppm (3H, s, $–O–CH_2$), 1.7 ppm (3H, s, $CH_2–C=C$).

2.3.1.5. Synthesis of Butyl Methacrylate (BMA). The same procedure as given for synthesis of CEMA was followed in the synthesis of BMA. The monomer was isolated by washing of the reaction mixture and subsequent distillation (56–58°C/15 mmHg). The yield of redistilled monomer was 57.8%. ^{1}H-NMR, δ: 6 ppm (1H, s, $=CH_2$ *cis*), 5.5 ppm (1H, s, $=CH_2$ *trans*), 3.5 ppm (2H, t, $–COOCH_2–$), 1.9 ppm (3H, s, $CH_3–C=C$), 1.45 ppm (2H, m, $–O–CH_2–CH_2–$), 1.3 ppm (2H, m, $–CH_2–CH_3$), 0.8 ppm (3H, t, $–CH_2–CH_3$).

2.3.2. Method B

In this method, methacrylic acid was directly esterified by using catalytical amounts of boric acid. The same experimental setup was used in all reactions. A typical procedure is as follows: the alcohol (0.6 mol), methacrylic acid (0.6 mol) and 1.24 g (0.02 mol) H_3BO_3, 0.1 g hydroquinone and 50 ml toluene were charged to the reaction flask. The temperature of the oil bath was adjusted to 160°C and the mixture was stirred for 24 h.

The monomers were isolated by following the same procedures described above.

2.3.3. Polymerization of the Monomers

Polymerizabilities of the monomers, except DAMA, were tested simply by radical initiation with AIBN in 1,4-dioxane at 60°C for 3 h. Polymerization of DAMA was carried out in THF, since it is insoluble in dioxane. The polymers of CEMA (Fig. 1), BEMA (Fig. 2) and BMA were isolated by precipitation in water. Petroleum ether was used for precipitation of the polymers derived from DAMA and MEMA. The polymer structures were confirmed by comparison of their FT-IR spectra with those of the monomers reported in the literature.

^{1}H-NMR spectrums of synthesized polymers, in $CDCl_3$, are as follows;

- Poly(DAMA): δ, 1.1 ppm (m, 3H, $C–CH_3$), 1.6 ppm (broad m, 2H, CH_2), 2.7 ppm (broad m, 2H, $CH_2–N$), 2.3 ppm (s, 6H, $N–CH_3$), 4.1 ppm (broad t, 2H, $COOCH_2$). This spectrum is in agreement with that reported by You *et al.* [11].

- Poly(MEMA): δ, 0.8–1.3 ppm (m, 3H, C–CH_3), 1.8–2.1 ppm (broad m, 2H, CH_2), 3.40 ppm (s, 3H, OCH_3), 3.62 ppm (broad s, 2H, $COOCH_2$), 4.13 ppm (broad band, 2H, $COOCH_2$). The signal positions match with those of reported in the literature [12].
- Poly(BMA): δ, 0.8 ppm (broad s, 3H, CH_3 of butyl group), 1.0 ppm (broad s, 3H, –CH_3), 1.3–1.6 ppm (multiplets, 4H, middle CH_2–CH_2 protons of butyl group), 1.9 ppm (m, 2H, main chain CH_2), 4 ppm (broad band, 2H, $COOCH_2$). The same spectral data have been reported in the literature [13].

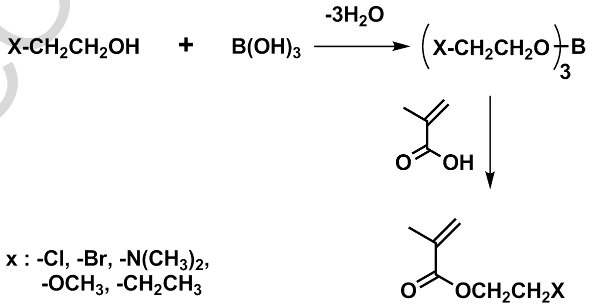
3. Results and Discussion

For the preparation of all monomers both methods were used and compared as related to the yield and simplicity of the process.

3.1. Method A

Five functional methacrylate esters were synthesized by acidolysis of appropriate boron esters with boric acid as depicted in Scheme 1.

Formation of boron esters by direct reaction of boric acid with alcohols, boiling higher than water, is relatively simple process. In contrast to usual esterification with sulfuric acid, removal of water in this reaction precedes smoothly, without discoloration of the reaction mixtures. The reaction in this step was followed by monitoring water evolved from equivalent boric acid/alcohol mixtures heated at 150°C. The water evolved was removed azeotropically with toluene and collected in a trap. Addition of methacrylic acid in the presence hydroquinone in the second step gave rise to the monomers. Except for the case of monomer DAMA, the reaction with methacrylic acid was very slow in this step. Overall process was performed in one pot. The yields attained were generally below 20%, even after heating for 36 h at 150°C. Conversion yields in the reaction mixtures were simply estimated by their NMR spectra. The integral ratios of the proton signals of carboxyl group at 10.3–10.7 ppm to those of the –OCH_2– group around 3.5 ppm were compared to estimate molar ratio of unreacted of methacrylic acid in the reaction mixtures.

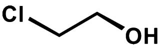
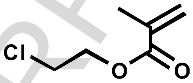
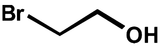
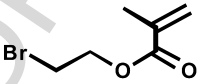
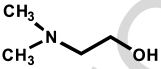
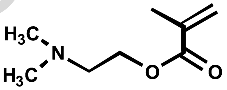
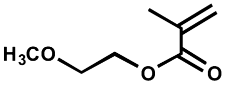
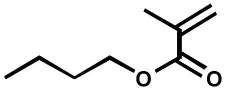


Scheme 1. Syntheses of the functional methacrylate ester monomers.

This inspection revealed that, conversion yields of DAMA were inherently higher than that of the other monomers. Higher yield of DAMA was considered to be due to presence of the tertiary amino group. It is quite likely that the enhanced yield is related to the role of the tertiary amine function present in the monomer which facilitates ionization of the carboxyl group in the organic phase and transfers the replaced proton. This claim was further supported by performing the same reaction with tri(butyl) borate and tri(methoxyethyl) borate in presence of pyridine. Indeed, in the presence of pyridine the conversion yields of BMA increased from 23% to 41.3% within 8 h (Table 1). Addition of pyridine was found to be useful to increase the reaction yields in the syntheses of the other monomers too. Therefore, the acidolysis reactions in this step were conducted in presence of pyridine (approx. 3 ml per 0.6 mol alcohol component).

Since the monomers DAMA and MEMA are miscible with water, simple washing procedures were not applicable to remove acid residues from the reaction mixtures. For instance, direct distillation of DAMA from the reaction mixture was impossible owing to salt formation between the tertiary amino group with unreacted methacrylic acid or with boric acid. In most cases no product was isolated by direct distillation of the reaction mixtures. It was found that addition of solid NaOH in dichloromethane is the best way to remove acid residues. Following distillation of the solution gave the monomer in appreciable yields (Table 1).

Table 1.
Monomer yields in Method A and Method B

Alcohol	Product	Reaction time (h)	Yield (%)	
			Method A (at 150°C)	Method B (after 24 h)
		12	41.8	17.7
		12	71.2	12.0
		16[a]	41.0	7.0
		12	53.1	14.3
		12/8	46–57.8/41.3	18.9

[a] At 50°C.

However, in the case of MEMA, treatment with solid NaOH did not work for the removal of acid residues. The NaOH added was dissolved in the mixture and resulted in polymerization even in presence of the inhibitor hydroquinone. Interestingly, a similar behavior was observed by adding solid Na_2CO_3 or K_2CO_3 as acid scavenger.

Dissolution of these salts can be ascribed to the host–guest complexation tendency of the two vicinal oxygen atoms in its structure. An alternative procedure was employed to obtain methacrylic-acid-free monomer. In this procedure, the mixture was distilled first and then, cross-linked poly(4-vinyl pyridine) was introduced to the crude product and left to contact overnight on a continuous shaker. The solid was filtered off and the product was redistilled under vacuum. The ^{1}H-NMR spectrum of the product showed no methacrylic acid residue and no alcohol component.

3.2. Method B

Direct esterification of methacrylic acid with these alcohols was also studied using catalytic amounts of boric acid (i.e., 1.2 g/0.6 mol). However, the monomer yields in the absence and presence of pyridine were always lower than 20% within 36 h. In order to inspect polymerizability of the monomers, they were simply subjected to radical polymerization by using AIBN as initiator at 60°C for 3 h. They were isolated by precipitation in petroleum ether.

3.3. Characterization of the Monomers and Their Polymers

Since the monomers DAMA, MEMA and BMA are commercially available, their ^{1}H-NMR spectra (see Experimental) were simply compared with those of the authentic samples and no further characterizations were made for assignment of their structures. Also, polymer structures of these monomers were verified by their NMR data given in the literature [11–13].

Being less common, the halogen containing monomers (CEMA and BEMA) and their polymers are discussed here. Figure 1 shows ^{1}H-NMR spectra of CEMA and its polymer obtained by radical initiation with AIBN.

The signals of the double bond protons appear at 6.0 and 5.45 ppm (for *cis* and *trans* protons, respectively). The methyl group protons exhibit a sharp singlet at 1.76 ppm. The triplets observed at 4.2 and 3.56 ppm are associated with the protons of O–CH_2 and –CH_2Cl groups, respectively. For the case of its polymer ($M_n = 56.5 \times 10^3$), the later signal shifts to 3.8 ppm, while the former being retained at the same position. Three protons of the methyl group give a broad doublet (instead of a singlet) in 0.8–1.2 ppm range, which imply partial isotacticity of the polymer structure. These signals must represent *mr* and *mm* sequences, respectively. The broad band centered at 1.85 ppm shows proton signals of CH_2 groups on the backbone. The ^{1}H-NMR spectrum of BEMA (Fig. 2) presents similar pattern. Thus, double-bond protons give two singlets at 6.0 and 5.45 ppm (for *cis* and *trans* protons, respectively). The sharp singlet at 1.8 ppm shows three protons of the methyl group. Proton signals of O–CH_2 and –CH_2Br groups gives two triplets at 4.3 and 3.4 ppm, respectively.

For the case of the polymer ($M_n = 66.3 \times 10^3$), the latter signal slightly shifts down-field and appears at 3.8 ppm. The position of the triplet at 4.3 ppm remains unchanged. The methyl group gives two signals at 0.95 and 1.1 ppm, which also imply partial isotacticity of the polymer structure. These signals must represent mr and mm sequences, respectively. Integral ratio of the two signals indicates existence of at least 30% of isotactic segments formed in the polymerization conditions studied. The protons of the CH_2 groups on the backbone do not give a singlet. Instead a multiplet is observed in the 1.4–2.1 ppm range due to presence of some isotactic sequences.

^{1}H-NMR spectra of the polymers derived from CEMA and BEMA were compared with those reported by Sugiyama *et al.* [6]. Although they used the same solvent ($CDCl_3$) in the NMR measurements, they reported slightly different chemicals shifts of the individual peaks for the two monomers. The FT-IR spectra of both polymers are almost the same. Typical C=O and C–O stretching vibration bands of the polymers appear at 1730 and 1140 cm^{-1}, respectively.

One important aspect of halogen containing monomers is branching in their radical polymerizations due to chain transfer by the haloalkyl groups involved. However, we have not found any detectible branch points in the NMR spectra of their polymers, probably due to negligible transfer efficiency of the haloalkyl groups of the monomers at the reaction temperature (60°C).

4. Conclusion

It has been demonstrated that the reaction of methacrylic acid with boron esters in the presence of pyridine gives methacrylate ester monomers in reasonable yields. In other words, boron esters act as alkylating agents for methacrylic acid. The acidolysis reaction described herein would be useful also as alternative pathway for preparing esters of ordinary carboxylic acids. Although the method was employed for the syntheses of methacrylate ester monomers with haloalkyl, tertiary amine and ether functions, it seems to be applicable in laboratory scale preparation of homologues monomers with various functions. The monomers CEMA and BEMA are of special interest as comonomer for easy modification and post cross-linking of their co-polymers by gamma irradiation [14]. Moreover, having polymerizable vinyl functions and initiating haloalkyl groups, these two monomers might be of interest especially in ATRP of acrylate monomers to prepare multi- or hyper-branched polymers, based on 'self-condensing vinyl polymerization' methodology. Polymers of MEMA are of special interest due to the temperature-sensitive solubility behavior of its homo-polymers in water. These will be subject of the further studies and will be reported elsewhere.

Acknowledgement

The authors wish to thank the Boron Research Institute of the Turkish Government for the financial support.

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