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Synthesis and Radical Polymerization of Adamantyl Methacrylate Monomers Having Hemiacetal Moieties

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ABSTRACT: The design strategy and synthesis of bulky, hydrophobic, and thermally stable adamantyl methacrylate monomers with attached hydrophilic and acid labile three different types of alkyl (1°, 2°, 3°) hemiacetal side groups are described. Free radical polymerizations of the obtained monomers furnished the desired polymers with high molecular weights. The properties such as thermal stability, moisture stability, and acid sensitivity of the obtained adamantyl hemiacetal ester homopolymers were evaluated which showed strong structure−property dependence. The bond dissociation enthalpy of the obtained polymers depended on the electronic effects of the type of pendant hemiacetal ester side groups.

Introduction

Photolithography using chemical amplification technology has been a powerful tool so far in the advancement of microelectronic devices. The success story of this emerging technology is aided by the innovation of novel architecture to meet the demands of properties required to fabricate integrated circuits with continuously decreasing feature sizes. It is largely the successful etching of gradual smaller structures that have fueled the continued performance increases in microprocessors. The core chemical property utilized in the present state of art for chemical amplification is the acid sensitivity of the protective group unit in the various copolymer systems used as photoresists. The ideal features for designing a novel protective group unit for photoresist applications can be assigned as (1) high acid sensitivity, (2) good solubility in common organic solvents, (3) thermal stability to withstand the pre- and postexposure bakes, (4) high transmittance to the exposed wavelength of irradiation, (5) no outgassing during the deprotection step, and (6) high base solubility of the deprotected part.

In the meantime, hemiacetal esters as latent initiators have attracted enormous attention for their wide applications in developing adhesives and coating materials with simple procedures.[1] Their characteristic thermal stability (> 160 °C)[2] coupled with high acid sensitivity also makes them an attractive and potential candidate to be used as the protective group unit part in chemically amplified photoresist systems. However, there are only few reports using different hemiacetal ester moieties for such photoresist applications.[3] It might be due to the high acid and moisture sensitivity of hemiacetal polymers which raises serious concerns about easy decompositions on exposure to stringent conditions during resist formulations. Incorporation of rigid and bulky adamantyl groups to the side chain of various parent polymers are driving great interests due to its ability to tune the various chemical and physical properties of the polymers such as thermal properties, stiffness, glass transition temperatures (T_g), solubility, high density, resistance to oxidation, hydrophobicity, and crystallinity.[4] Therefore, the architecture of a sophisticated molecular system such as one having the highly acid sensitive hemiacetal ester functionality tethered to the thermally stable adamantane group might offer a plausible solution in developing a new and high-performance protecting group unit for chemically amplified resist systems with contrast characteristics like high thermal and moisture stability along with high acid sensitivity.

Herein, we report the synthesis and free radical polymerization of novel adamantyl methacrylate monomers having various types of alkyl hemiacetal ester moieties. Typically alkyl types of hemiacetal esters were synthesized in order to meet the requirement of imaging at 193 nm of light.[5] Different types of alkyl vinyl ethers (1°, 2°, 3°) were used to synthesize electronically and sterically different hemiacetal ester monomers in order to investigate structure−property relationship of the polymers. The fundamental properties of the polymers such as moisture stability, thermal stability, and acid sensitivity were examined, which are essential to evaluate their feasibility to function as possible protective group units for photoresist applications. It was found that all the polymers show good thermal stability along with high acid sensitivity. The comparative moisture and thermal characteristics of the polymers correlates to the electronic effects of the hemiacetal ester moieties.

Experimental Section

Instruments. All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian NMR spectrometer model Unity INOVA. Chemical shifts for ^{1}H and ^{13}C NMR were referenced to residual signals from DMSO-d_6 (^{1}H: δ = 2.54 ppm; ^{13}C: δ = 40.45 ppm) and $CDCl_3$ (^{1}H: δ = 7.27 ppm; ^{13}C: δ = 77.23 ppm). FTIR spectra were recorded on a JASCO FT/IR-5300 infrared spectrometer. High-resolution mass spectroscopy was performed on a JEOL LMS-HX-100 spectrometer. The melting point of the compound was measured with Stuart Scientific melting point apparatus SMP3. For thin-layer chromatography, aluminum sheets (Merck silica gel coated 60 F254) were used, and the plates were visualized with $KMnO_4$ solution in water. Molecular weight distributions of the polymers were estimated on a size exclusion chromatograph (SEC) (TOSOH HLC-8220 SEC system) with refractive index (RI) and ultraviolet (UV) detectors using chloroform as the eluent. The number- and weight-average molecular weights were calibrated using polystyrene standards with low polydispersity values. Thermogravimetric analyses (TGA) were performed on a Seiko TG/DTA 6200 at a constant heating rate of 10 °C/min under a nitrogen flow of 20 mL/min.

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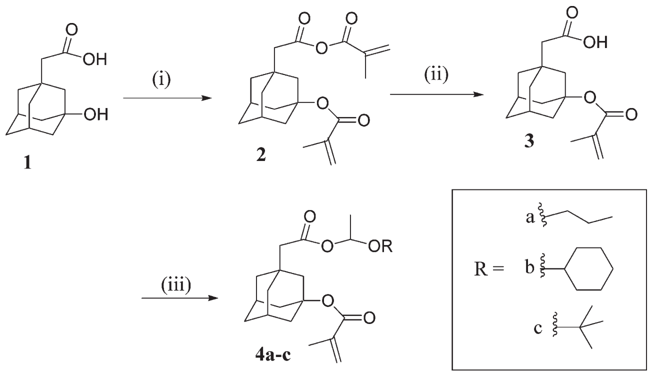
Scheme 1. Synthesis of Adamantyl Methacrylate Monomers with Hemiacetal Moieties[a]



[a] Conditions: (i) triethylamine, methacryloyl chloride, CH_2Cl_2, 0 °C−rt; (ii) pyridine, H_2O, rt; (iii) vinyl ether, bis(2-ethylhexyl)hydrogen phosphate, rt.

Materials. 3-Hydroxy-1-adamantaneacetic acid, bis(2-ethylhexyl)hydrogen phosphate, triethylamine, and pyridine were purchased from Wako Pure Chemical Industry (Osaka, Japan). Methacryloyl chloride was purchased from Tokyo Chemical Industry (Tokyo, Japan). (Trimethylsilyl)diazomethane (2.0 M) solution in diethyl ether was purchased from Aldrich. $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ (KYOWAAD 500SH) was obtained from Kyowa Chemical Industry Co. Propyl vinyl ether, cyclohexyl vinyl ether, and *tert*-butyl vinyl ether were purified by distillation. Methyl ethyl ketone (MEK) and dichloromethane (CH_2Cl_2) were dried over CaH_2 and distilled before use. Propylene glycol monomethyl ether acetate (PGMEA) was obtained from JSR Co. and used as received.

Synthesis of the Adamantyl Methacrylate Monomers and Their Corresponding Free Radical Polymerizations. See Supporting Information.

Tests for Moisture Stability. Typical procedure: Distilled water (2.5 mL) was added to 10 mg of the solid polymer dissolved in 2.5 mL of PGMEA, and the mixture was stirred for 7 days at room temperature. The resulting mixture was dried under vacuum, and the ^1H NMR spectrum of the obtained material was taken in $CDCl_3$.

Tests for Acid Sensitivity. Typical procedure: An aqueous solution of hydrochloric acid (0.5 M, 20 μL) was added to 10 mg of the solid polymer dissolved in 0.25 mL of THF, and the resulting mixture was stirred for 15 min at room temperature. The resulting mixture was precipitated in 1.0 mL of distilled water. The precipitate was collected, dried under vacuum, and then analyzed by ^1H NMR or IR spectroscopy.

Esterification of Poly-4a after Acid Exposure. 0.75 mL of DMSO and 0.25 mL of MeOH were added to 8 mg of dried polymer after acid hydrolysis of **poly-4a**. Then, 0.15 mL of 2.0 M solution of (trimethylsilyl)diazomethane in diethyl ether was added. The reaction was allowed to stir at room temperature for 12 h. The progress of the reaction could be observed by the bubbles of N_2 gas escaping from the reaction mixture. After the reaction, solid polymer precipitate could be observed sticking by the walls of the reaction vessel. The solution part of the reaction mixture was separated by decantation. The remaining solid precipitate was washed several times with diethyl ether, dried under vacuum, and then analyzed by ^1H NMR spectroscopy.

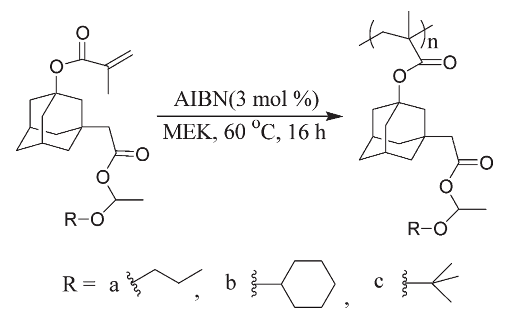
Results and Discussion

The adamantyl methacrylate monomers with hemiacetal side groups were synthesized by using 3-hydroxy-1-adamantane acetic acid as the starting precursor. The synthesis of the monomers follows a very simple and facile synthetic pathway as shown in Scheme 1.

The presence of both carboxylic acid group and hydroxyl group in the starting precursor **1** makes it feasible to attach two different functional groups (anhydride and ester) with varied reactivity in a single one-pot reaction. The more reactive anhydride group was then selectively hydrolyzed in the pyridine/H_2O system to obtain the adamantane acetic acid methacrylate monomer **3**. Finally, the methacrylate type adamantane acid monomer **3** on reaction with various types of vinyl ethers in presence of catalytic amount of bis(2-ethylhexyl)hydrogen phosphate yielded the desired methacrylate type adamantyl hemiacetal ester monomers **4a−c** in reasonable overall yields (27−32%).

The free radical polymerization of the obtained adamantyl methacrylate monomers with hemiacatal side groups were carried out in MEK using 3 mol % AIBN as initiator (Table 1).

Table 1. Polymerization of Adamantyl Methacrylate Monomers with Different Hemiacetal Ester Side Groups in MEK



entry	monomer	conv (%)[a]	yield (%)[b]	M_w	M_n	PDI[c]
1	**4a**	100	87	289 000	93 000	3.09
2	**4b**	100	73	475 000	134 000	3.54
3	**4c**	100	79	412 000	139 000	2.95

[a] Confirmed by ^1H NMR of the crude after 16 h of reaction. [b] Determined by the weight of the dried polymer after precipitation in hexane. [c] Determined by SEC using $CHCl_3$ as the eluent and polystyrene as the calibration standards.

Table 2. TGA Analyses of the Polymers

entry	polymer	% T_{d-5} (°C)
1	**poly-4a**	191
2	**poly-4b**	166
3	**poly-4c**	140

The hemiacetal monomers **4a−c** showed high polymerizability and good stability in the reaction conditions as evident from their high conversions and high yields without any decomposition (Table 1). The obtained homopolymers showed high solubility in common organic solvents like MEK, $CHCl_3$, toluene, DMF, and THF. The expected high transparencies of the polymers at 193 nm were also confirmed by UV analyses. The presence of bulky and high carbon containing adamantyl groups is expected to impart rigidity as well as good thermal and moisture stability to the hemiacetal ester polymers which is an important requirement for designing a photoresist with high etch resistance and longer shelf life. On the other hand, the presence of hydrophilic, highly sensitive acid labile hemiacetal ester group as the side chain of the bulky adamantyl moiety can assist to meet the solubility parameter in common organic solvents and is also expected to improve the acid sensitivity of the resist polymer. The thermal stability of the obtained hemiacetal polymers was tested by TGA analyses (Table 2) (for Figure, see Supporting Information.)

The difference in thermal stability of the hemiacetal ester polymers **poly-4a−c** can be correlated to the electron-donating ability of their corresponding alkyl groups or, in other words, to the relative stability of the resulting alkyl cation after decomposition. The higher the electron donation from the ester substituent, the higher will be the relative stability of the resulting cation and hence the lower will be the bond enthalpy of the ester bond resulting in lowering of the corresponding T_d. Since the efficiency

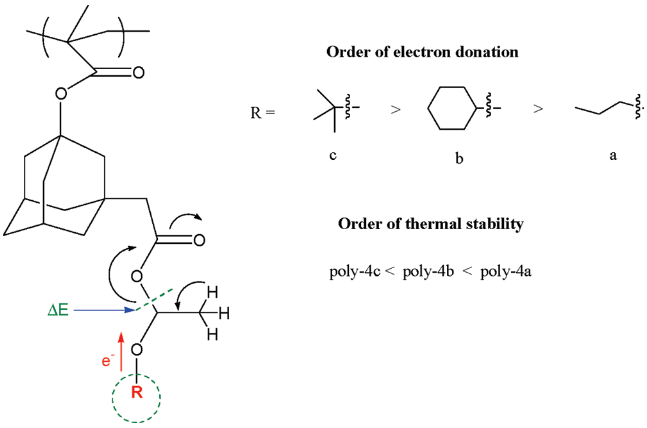


Figure 1. Dependence of bond dissociation energy on the electron-donating ability of side groups in hemiacetal ester polymers.

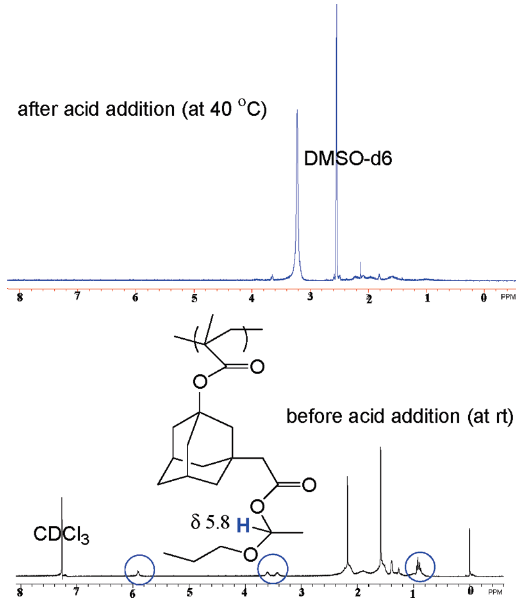


Figure 2. ^{1}H NMR of **poly-4a** before and after acid addition.

of electron donation from an alkyl group or the relative stability of alkyl cation varies as 3° > 2° > 1°, therefore the thermal stabilities of the obtained hemiacetal ester polymers justifies the observed expected order of T_d: **poly-4c** < **poly-4b** < **poly-4a**. Moreover, the observed weight loss in the TGA profile (see Supporting Information) closely corresponds to the weight of vinyl ethers which were expected to be generated by the proposed decomposition pathway (Figure 1) and thus verifying the selective degradation route of removal of the labile hemiacetal ester group at first. The thermal decomposition pathway is also supported by acid sensitivity data later.

To determine the moisture stability of the hemiacetal ester polymers **poly-4a**–**c**, solutions of each polymer in PGMEA were immersed in more than 4900 equiv of H_2O at room temperature and allowed to stir in the same condition for 7 days. The ^{1}H NMR of the samples before and after the study showed similar results to that obtained for thermal stabilities. **Poly-4a** and **poly-4b** showed no decomposition while **poly-4c** decomposed under the conditions as evident from the disappearance of the hemiacetal peaks around $\delta = 6.0$ ppm in the ^{1}H NMR (see Supporting Information). Thus, **poly-4a** and **poly-4b** showed exceptional stability to moisture while **poly-4c** decomposed on exposure to high moisture content due to lowering of the dissociation enthalpy of the hemiacetal ester bond as a result of higher electron-donating effect of the attached *tert*-butyl group.

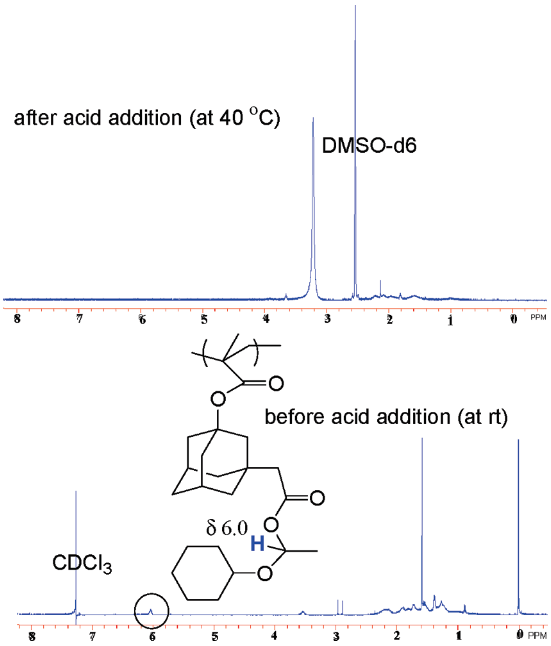


Figure 3. ^{1}H NMR of **poly-4b** before and after acid addition.

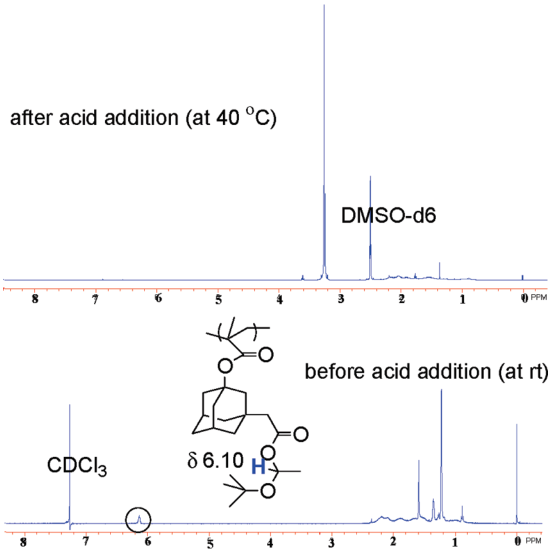


Figure 4. ^{1}H NMR of **poly-4c** before and after acid addition.

The acid sensitivity of the polymers **poly-4a**–**c** was evaluated by addition of aqueous HCl to polymer solution in THF. The dried polymers obtained after 15 min reaction with an aqueous solution of 0.5 M HCl in THF were found to be insoluble in most of the common organic solvents at normal temperature which made it difficult to analyze the obtained materials by ^{1}H NMR spectroscopy. However, the solubility of the polymers increased to some extent in DMSO at higher temperature, thereby making it feasible to measure the ^{1}H NMR of the decomposed compounds in DMSO-d_6 at 40 °C. Although the intensities of ^{1}H NMR signals of the polymers after acid addition were not very distinct even at 40 °C, the clear absence of the hemiacetal ester peaks around $\delta = 6.0$ ppm justified the high acid sensitive nature of the synthesized adamantyl type hemiacetal ester polymers (Figures 2–4). The high acid sensitivities of the hemiacetal ester polymers were further confirmed by the 88% esterification

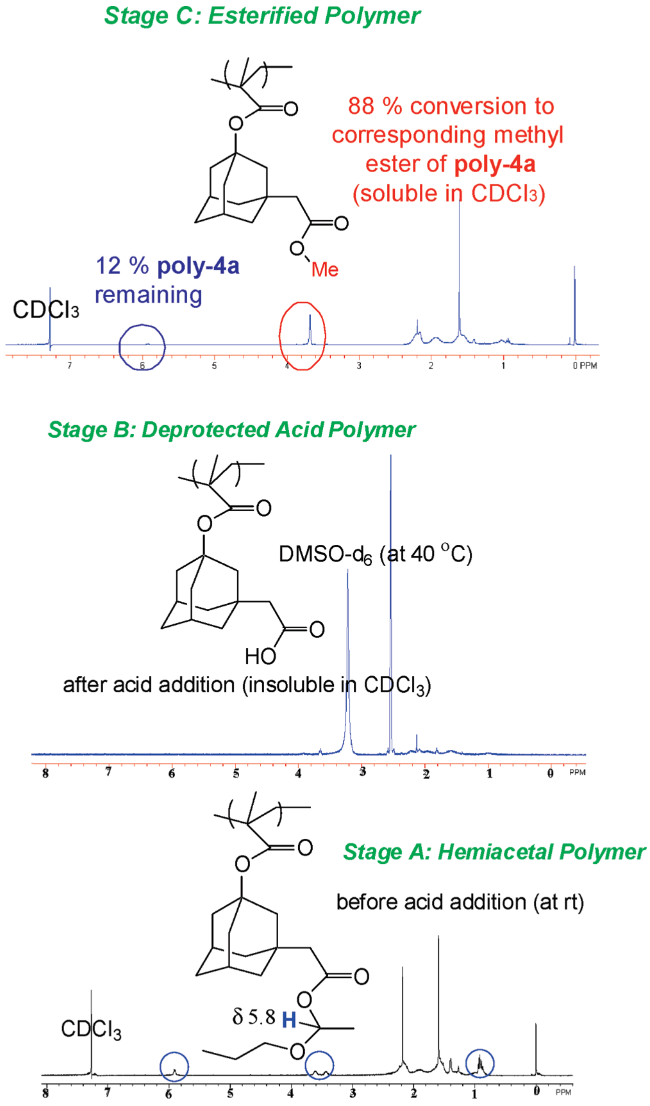


Figure 5. ^{1}H NMR of **poly-4a** before acid addition (stage A), after acid addition (stage B), and after methyl esterification of the hydrolyzed polymer (stage C).

reaction of the insoluble hydrolyzed polymer obtained after reaction of **poly-4a** with acid (Figure 5). The ^{1}H NMR of the newly obtained soluble ester polymer in $CDCl_3$ clearly showed the transformation of the insoluble hydrolyzed polymer into the corresponding methyl ester by the absorbance of a new −OMe peak around $\delta = 3.65$ ppm. 12% of **poly-4a** was detected to be unreacted during the acid hydrolysis reaction which might be due to the rapid insolubility induced in the polymer system as a result of hydrolysis. **Poly-4a** was chosen as the preferred representative test polymer for this reaction as it demonstrated the best thermal stability profile in comparison to **poly-4b** and **poly-4c** and thus can be generalized. Furthermore, the clear difference in the IR spectra of the dried polymers before and after acid exposure measured at room temperature reconfirms the decomposition of hemiacetal ester bond and formation of acid group by its typical broad absorption around 3300−2500 cm^{-1} (see Supporting Information).The insolubility of the polymer in common organic solvents after acid addition might be the result of cross-linking in the partially decomposed polymers via ionic interaction of the polar acid groups or hydrophobic interaction between the adamantyl moieties. However, the weight of the dried polymers after treatment with acid corresponded to almost quantitative loss of the hemiacetal ester side groups. Moreover, the hemiacetal ester polymers were insoluble in the standard developer solution for resist formulation (2.38% tetramethylammonium hydroxide) before reaction with acid whereas the polymers which were obtained after reaction with acid showed high solubility in the standard developer solution. The selective solubility of the polymers in the developer basic solution before and after reaction with acid reassures the highly sensitive acid-catalyzed decomposition of the hemiacetal ester moiety and formation of acid group, thereby also satisfying one of the basic requirements for resist formulation.

Conclusions

In summary, adamantyl methacrylate monomers having hemiacetal ester side groups were synthesized. Free radical polymerizations of the obtained monomers at 60 °C proceeded to give the corresponding polymers with high molecular weights in high yields. The obtained hemiacetal ester polymers showed high acid sensitivity with selective deprotection of the hemiacetal ester side groups when exposed to acid. The comparative moisture and thermal stability of the bulky hemiacetal ester polymers exhibited strong structure−property interdependence with the bond enthalpy of the hemiacetal ester polymers progressively decreasing with increase in electron donation from the substituted ester group. The easy synthetic pathway, high polymerizability of the monomers, good thermal and moisture stability of the homopolymers along with high acid sensitivity, and strong structure−property dependence ideally fit into the characteristic properties required for designing potential protective group units for photoresists.

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Supporting Information Available: Syntheses of the adamantyl methacrylate monomers (**3**, **4a−c**), free radical polymerizations of the obtained methacrylate type adamantyl monomers with hemiacetal side groups (**4a−c**), comparative TGA curve of the obtained hemiacetal ester polymers (**poly-4a−c**), ^{1}H NMR spectra showing moisture stabilities of polymers (**poly-4a−c**) in PGMEA, and IR spectra showing acid sensitivities of polymers (**poly-4a−c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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