224 | Macromol. Symp. 2006, 240, 224–231 DOI: 10.1002/masy.200650827

The ATRP Synthesis of the Potential Thermoplastic Elastomer Poly(methyl methacrylate)–b-(lauryl methacrylate)-b-(methyl methacrylate) Hitherto Unrealized by Ionic Polymerization

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Summary: The triblock copolymer poly(methyl methacrylate-b-lauryl methacrylate-b-methyl methacrylate) {P(MMA-b-LMA-b-MMA)} has been synthesized by a two stage atom transfer radical polymerization in bulk at near room temperature (ca. 35 °C) using CuCl/pentamethyldiethylenetriamine (PMDETA)/tricaprylylmethylammonium chloride (Aliquat®336) complex as the catalyst and 1,2-bis (bromoisobutyryloxy)ethane (BIBE) as the initiator for the polymerization of LMA in the first stage. The same catalyst was also used for the polymerization of MMA in the second stage. The dynamic mechanical thermal analysis of a sample with the middle block $M_n = 82000$ and each end block $M_n = 14500$ showed typical features of a thermoplastic elastomer.

Keywords: atom transfer radical polymerization (ATRP); block copolymer; poly(lauryl methacrylate); poly(methyl methacrylate); thermoplastic elastomer

Introduction

Triblock copolymers with a rubbery middle block and glassy end blocks exhibit the properties of thermoplastic elastomers[1]. The first such copolymers which became also commercially successful are the well known SBS and SIS (S = styrene, B = butadiene, I = isoprene). They are polymerized by the living anionic polymerization (LAP) route[2]. Following their commercial success and the scientific interest they generated other anionically made triblock copolymers were also investigated for TPE properties [3].

Subsequently, following the discovery of living carbocationic polymerization the triblock copolymer poly(styrene-*iso*butylene- styrene) was synthesized which proved to be a thermoplastic elastomer with somewhat lower mechanical properties than SBS or SIS[4,5].

It was quite natural that triblock (meth)-acrylate copolymers will also be looked into. Indeed, a host of these triblock copolymers with several rubbery poly (alkyl acrylate)s as the middle block and PMMA as the end blocks were synthesized by the LAP route and their properties studied [6–8]. Subsequently, the atom transfer radical polymerization (ATRP) method was used in view of the ease of synthesis the method provides [9,10].

Among the poly(alkyl methacrylate)s the poly(lauryl methacrylate)(PLMA) has a low T_g ($T_g = -65\,°C$)[11] which is comparable to those of poly(n-butyl acrylate) or poly(*iso*octyl acrylate). Triblock copolymers with PMMA as end blocks and PLMA as middle block are therefore likely to have the properties of thermoplastic elastomers. Previously, the LAP route was used to synthesize this triblock copolymer but without much success. Thus, Anderson et al. ended up with a broad MWD copolymer (PDI = 3.56) using 1,1-diphenylhexyl lithium (DPHLi) initiator in THF at −78 °C[12]. The high PDI was attributed to the low solubility of LMA at

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$-78\,^{\circ}C$ in THF. Nakagowa et al. used toluene as the medium of polymerization to overcome the solubility problem at $-78\,^{\circ}C$. t-BuLi/triethylamine was used as the initiator by them. The polymerization was very slow. The molecular weights of the block copolymers were low, $M_n < 23{,}000$, although the PDI was reasonably good, being ≤ 1.22[13]. Subsequently, the insolubility problem in THF was avoided working at a temperature higher than $-78\,^{\circ}C$. Thus, Raghunadh et al. used ligated anionic polymerization in THF at $-40\,^{\circ}C$. Use of LiCl, $LiClO_4$ or dilithium triethylene glycolate as additives in these ligated polymerizations provided very good control on LMA polymerization leading to PLMA of $PDI \leq 1.10$ [14]. However, block copolymerization of LMA and MMA with PLMA anion as the macroinitiator led to polymers with broad MWD. This result was attributed to low crossover initiation efficiencies and the instability of the living PLMA anion at the relatively high temperature of $-40\,^{\circ}C$[14]. Thus, the synthesis of the triblock copolymer by the LAP route remained unrealized.

Besides LAP, the group transfer polymerization (GTP) was also used, but only diblock copolymers of low molecular weights were reported [15]. Furthermore, the control was lost when polymers with $M_n > 50000$ were targeted [16].

In this work we have used the ATRP method [17–20] to synthesize the target triblock copolymer. The copper mediated ATRP of higher alkyl methacrylates requires the use of highly hydrophobic ligands in the catalyst complex to overcome the heterogeneity problem in the medium arising out of the use of the highly hydrophobic monomer [21–24]. In some situations highly hydrophobic initiators were also needed [24]. On the other hand, we found that the CuCl/ PMDETA complex, a commonly used inexpensive ATRP catalyst, goes into solution in LMA in the presence of a catalytic amount of Aliquat®336 (AQCl) at ambient temperature [25]. This catalyst system was used earlier by us in the bulk ATRP of MMA at ambient temperature [26]. Recently, we reported that the same system also works very well for the ATRP of higher alkyl methacrylates viz., LMA and stearyl methacrylate at ambient temperature [25]. Accordingly, this method has been used in this work to synthesize the target triblock copolymer.

Experimental

Materials

LMA (Aldrich, 96%) and MMA (BDH) were washed with 5% aqueous NaOH solution, dried over anhydrous $CaCl_2$, then vacuum distilled and stored under nitrogen at $-15\,^{\circ}C$. PMDETA (99%) and Aliquat®336 both Aldrich products were used as received. CuCl (98%, BDH) was purified by washing with 10% HCl in water followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. The difunctional initiator BIBE was prepared according to a literature method [27].

Synthesis of α,ω-Dichloro PLMA (Cl-PLMA-Cl)

A representative example is given below.

In a nitrogen purged test tube (8 × 2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.018 g, 0.043 mmol) and CuCl (0.0022 g, 0.022 mmol). Nitrogen purging was continued for 10 min following which the tube was closed with a rubber septum which was secured by a Cu wire. LMA (0.868 g, 3.42 mmol) previously purged with nitrogen was next introduced into the tube with a nitrogen purged gas-tight syringe. The mixture was stirred magnetically for 30 min to prepare a homogeneous solution. PMDETA (0.004 g, 0.022 mmol) followed by BiBE (0.0078 g, 0.022 mmol) were then injected in. The polymerization was conducted at $35\,^{\circ}C$ with stirring. For kinetic studies separate polymerizations were run for different times. After the desired time periods the contents of the tubes were diluted with 1 ml THF and poured into 300 ml methanol. The separated polymer was isolated, redissolved in THF and reprecipitated into excess methanol. It was finally dried in a vacuum oven at $45\,^{\circ}C$ for 48 h, and weighed. The M_n and PDI of the polymer were 42000 and 1.28 respectively at 98% conversion achieved in 9 h.

Synthesis of Triblock Copolymer poly (MMA-b-LMA-b-MMA)

A representative example is as follows.

In a nitrogen purged test tube (8×2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.013 g, 0.031 mmol), CuCl (0.0008 g, 0.008 mmol) and Cl-PLMA-Cl (0.381 g, 0.008 mmol, Mn = 49000 and PDI = 1.25). Nitrogen purging was continued for 10 min following which the tube was closed. Nitrogen purged MMA (0.376 g, 3.76 mmol) was next added into the vessel. The PLMA macroinitiator was allowed to dissolve completely in MMA for 24 h. PMDETA (0.0014 g, 0.008 mmol) was then injected into the tube and mixed with the solution using a vortex mixer for 5 min. The polymerization was conducted at 35 °C unstirred. For kinetic studies separate polymerizations were run for different times. After the desired time periods the contents of the tubes were diluted with 1 ml THF and poured into 300 ml methanol. The polymer was isolated, purified and dried as described in the case of PLMA. Conversion was 86% in 16 h. The M_n and the PDI of the triblock copolymer were 84,000 and 1.14 respectively.

Characterization

Molecular weight and molecular weight distribution:

It was apprehended that the gpc method will not give correct molecular weights in view of the expectedly large difference in hydrodynamic volumes between PLMA and the calibration standard PMMA. The molecular weights were therefore determined by the viscometric method using the θ solvent n-amyl alcohol at 29.5 °C. The intrinsic viscosity was determined by the single point method using equation (1)[28].

$$[\eta] = \frac{\sqrt{2\eta_{\mathrm{sp}} - 2\ln \eta_{\mathrm{rel}}}}{\mathrm{c}} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, η_{rel} is the relative viscosity at concentration C in g / dl unit and η_{sp} is the specific viscosity. The viscosity average molecular weight (M_v) was calculated using the following Mark-Houwink relation [29] with $[\eta]$ in dl/g units.

$$[\eta] = 3.48 \times 10^{-4} M_{\mathrm{w}}^{0.5} \tag{2}$$

As the polymers are of low polydispersity, $M_v \approx M_w$. The number average molecular weight M_n was therefore calculated from M_w using the PDI values of the samples which were determined by gpc.

The gpc was performed at room temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer and Waters Ultrastyragel columns of 10000, 1000, 500 Å pore size which were preceded by a prefilter. HPLC grade THF (Spectrochem, India) was used as the eluent at a flow rate of 1 ml/min. Before injection into the gpc system the polymer solutions were treated with cation exchange resin Dowex® 50 W (Fluka) to free them from Cu salts. They were then filtered through a prefilter-filter combination system compatible with organic solvents. PMMA standards were used for calibration.

Dynamic Mechanical Analysis

Dynamic mechanical properties were measured with a (DMA Q800, TA Instruments) dynamic mechanical analyzer. The temperature sweep experiments were carried out at 1 Hz (ramp mode, heating rate of 2 °C/min) using a film tension clamp for sample mounting

Results and Discussion

The triblock copolymer was prepared in two stages. In the first stage a α,ω dichloropoly(lauryl methacrylate) (Cl-PMMA-Cl) was prepared in bulk by ATRP at 35 °C using BIBE as the difunctional initiator and CuCl/PMDETA/AQCl as the catalyst system. Figure 1 shows the first order kinetic plots for the disappearance of the monomer (plot of $\ln[M]_0/[M]$ vs t where $[M]_0$ and $[M]$ are monomer concentrations at time t = 0 and t respectively) for two different molecular

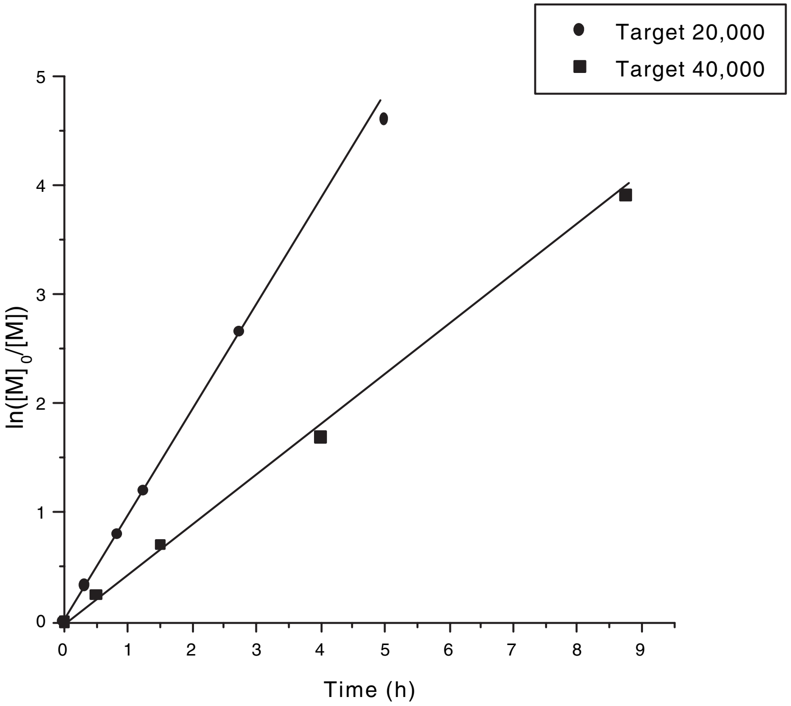

Figure 1.

ln $[M]_0/[M]$ vs. time plots for the ATRP of LMA in bulk with two different target molecular weights at 35 °C. $[LMA]_0 = 3.42$ mol/dm^3, $[CuCl]_0 = [PMDETA]_0 = [BiBE]_0 = 0.043$ mol/dm^3, $[AQCl] = 0.086$ mol/dm^3, for target $M_n = 20000$ and $[LMA]_0 = 3.42$ mol/dm^3, $[CuCl]_0 = [PMDETA]_0 = [BiBE]_0 = 0.022$ mol/dm^3, $[AQCl] = 0.044$ mol/dm^3 for target $M_n = 40000$.

weight targets viz., $M_n = 20{,}000$ and 40,000 corresponding to 100% conversion of monomer to polymer [30]. The figure shows that the plots are linear in both cases which indicates that the polymer radical concentration remains constant throughout the polymerization[17–20]. This fulfills one of the criteria for living polymerization.

Figures 2 and 3 show the evolution of M_n and the polydispersity index (PDI) with conversion for the lower and higher M_n targets respectively. The experimental M_n values are to some extent greater than the theoretical values represented by the straight lines in the figures [30]. The percentage deviation is largest for the lowest conversions, decreases gradually with increase in conversion and becomes less than 10% at the highest conversions (98–99%). This is a consequence of the dead polymer formed at low conversions before the persistent radical (the cupric complex) concentration is built up to the equilibrium concentration level [31,32]. Also, the percentage deviation of the M_ns from the theoretical values is greater for the lower target molecular weight system (Figure 2) than for the higher target one (Figure 3). This is due to the fact that in the former system a higher persistent radical concentration was required to be built up since the polymer radical concentration in the equilibrium regime was higher in this system than in the latter system. Hence, more dead polymer was formed in the former system prior to the establishment of the equilibrium regime. Elsewhere, we have shown that the above mentioned deviation is greater for higher alkyl methacrylates than for the lower alkyl ones. Also, the deviation is smaller with a bifunctional initiator than with a monofunctional one. These results have been explained[25].

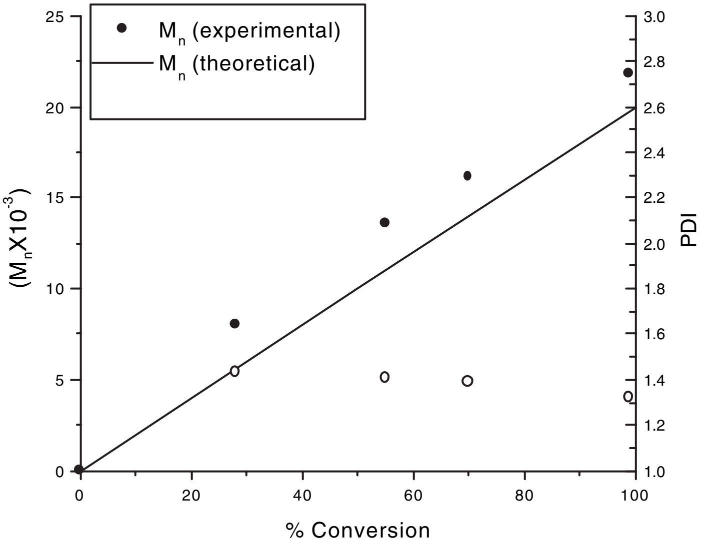

Figure 2.
Evolution of M_n and PDI with conversion for the system with target $M_n = 20000$ at 100% conversion. The closed symbols refer to M_n and the open symbols refer to PDI.

The PDI for both the systems decreases slowly with conversion as is required by the theory [19,31–34] and reaches ca. 1.3 at the highest conversions. In our recent work on the ATRP of higher alkyl methacrylates using a monofunctional initiator we have shown that the PDI decreases with the use of some amount (ca. 20 vol% of monomer) of a solvent like THF or anisole which provides better solubility environment for the cupric complexes[25].

In the second stage of the synthesis of the triblock copolymer the difunctional PLMA was used as the macroinitiator in the bulk

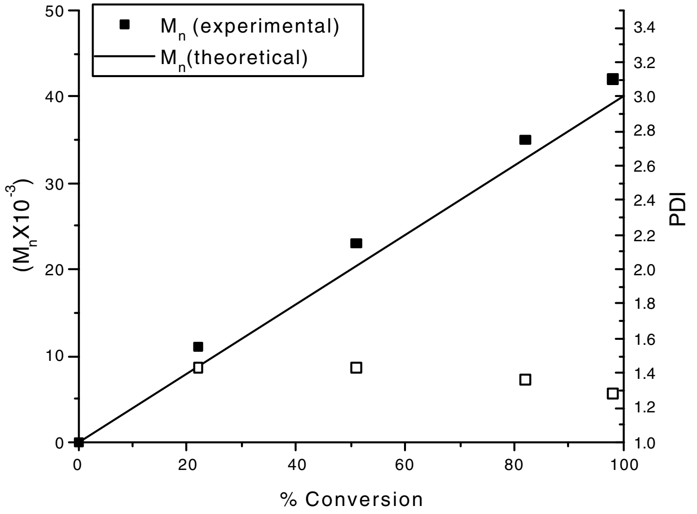

Figure 3.
Evolution of M_n and PDI with conversion for the system with target $M_n = 40000$ at 100% conversion. The closed symbols refer to M_n and the open symbols refer to PDI.

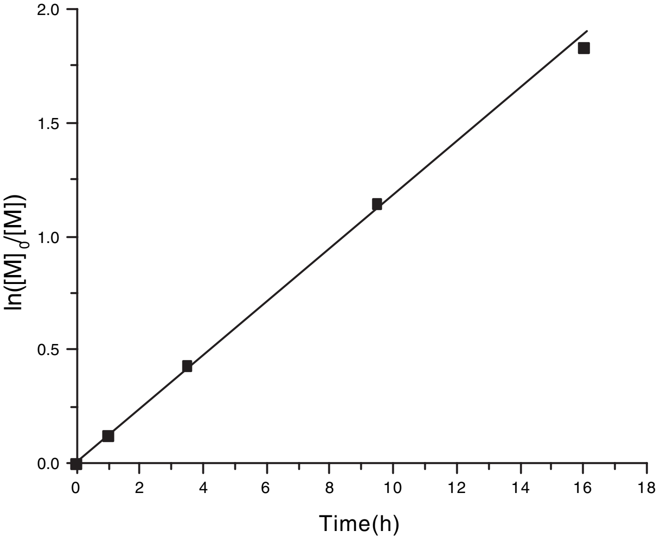

Figure 4.
ln[M]$_0$/[M] vs. time plot for the ATRP of MMA using Cl-PLMA-Cl as the macroinitiator in bulk at 35 °C. [MMA]$_0$ = 9.4 mol/dm^3, [CuCl]$_0$ = [PMDETA]$_0$ = [Cl-PLMA-Cl]$_0$ = 0.019 mol/dm^3 and [AQCl]$_0$ = 0.076 mol/dm^3.

ATRP of MMA at 35 °C using CuCl/PMDETA/AQCl complex as the catalyst.

Figure 4 shows the first order kinetic plot for the disappearance of monomer in the bulk ATRP of MMA using Cl-PLMA-Cl ($M_n = 49000$) as the macroinitiator for the second stage polymerization. The plot is linear indicating a constant concentration

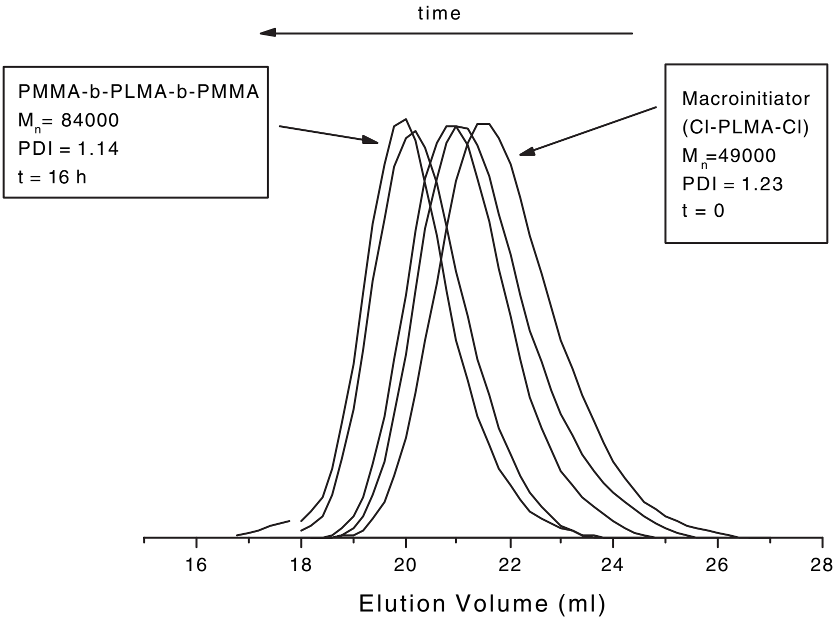

Figure 5.
Evolution of GPC traces of the triblock copolymers synthesized from Cl-PLMA-Cl macroinitiator. The recipe is same as given in Figure 4.

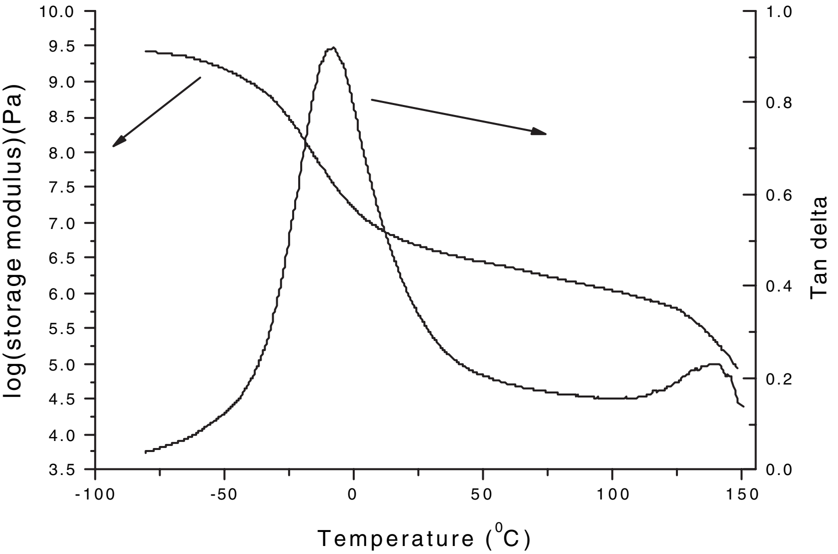

Figure 6.
Plot of log storage modulus (1 Hz, 2 °C / min) and tan delta vs. temperature of a PMMA-b-PLMA-b-PMMA triblock with 14.5k-82k-14.5k as the blockwise M_ns.

of polymer radicals throughout the polymerization.

Figure 5 shows the evolution with time of the molecular weights and the molecular weight distributions (MWD) in the form of gpc traces for the triblock copolymer. The gpc traces are unimodal and they laterally shift toward high molecular weights with increase in conversion. These facts indicate efficient initiation. Also, true to the theoretical requirement the MWD decreases with conversion [19,31–34].

The evidence of the formation of the triblock copolymer is obtained from the dynamic mechanical thermal analysis. Figure 6 shows the temperature variation of the storage modulus (G') and tan δ from −80 to 150 °C of one sample with the following blockwise M_ns PMMA (14.5k)-PLMA (82k)-PMMA (14.5k) (where k stands for a factor of 1000). The PMMA content is 26% by weight. A higher molecular weight PLMA has been used as the central block for this triblock copolymer than those targeted in kinetic studies (Figures 1 to 4). This is because the contamination of the block copolymer with dead PLMA becomes less with the increase in target M_n of the living PLMA as has been discussed with results given in Figures 2 and 3. The dynamic mechanical behaviour is typical of triblock thermoplastic elastomers which show two glass transitions (one for the rubbery block and the other for the glassy block), a rubbery plateau between them and a terminal zone after the T_g of the hard block. A detailed study of the thermomechanical properties and the morphology of the polymers will be published elsewhere.

To conclude, this study shows that the triblock copolymer P(MMA-b-LMA-b-MMA) is easily synthesized in bulk ATRP using CuCl/PMDETA/AQCl as the catalyst complex at ambient temperature.

Acknowledgement: Thanks are due to the Council of Scientific & Industrial Research, Government of India for financial support.

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