The Template Polymerization of 12-Methacryloyloxydodecanoate Ions in LDH Clay

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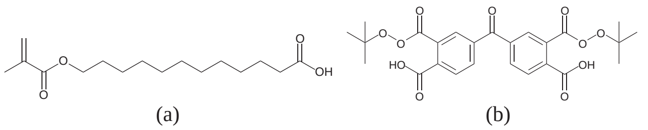
The LDH clay template polymerization of 12-methacryloyloxydodecanoate (MADA) ions under UV light irradiation resulted in the formation of preferential *meso* polymer ions through radical propagation in a parallel-oriented MADA hybrid assembly.

Alternatively stacked organic and inorganic hybrids have attracted much attention for their potential as unique photofunctional materials. Until now, there have been reports of organized hybrids using various anionic layered inorganic compounds such as clay minerals.[1–3] Among them, layered double hydroxide (LDH) characteristically has positively charged layers that can accommodate anionic guests within its interlayers by neutralizing the positively charged layers through ion-exchange.[4–7] LDH, i.e., $Mg_{4.5}Al_2(OH)_{13}Cl_2{\cdot}3.5H_2O$, possesses an anion exchange capacity (AEC) of 3.5 mequiv$\cdot$g^{-1} and ion exchangeable sites on the surface of its framework, i.e., 50.6 Å^2 per unit site. Moreover, clay interlayers of a two-dimensional nano space can be utilized as a photochemical anisotropic reaction field for organic materials.[1–4,8] We have previously reported that excessive amounts of long alkyl-chain aliphatic carboxylate ions can be accommodated to form self-assembling aggregates within the LDH interlayers by hydrophobic interactions as well as ion exchange with the guest anions.[8,9] Such laminated organic and inorganic hybrid materials were found to exhibit a unique framework in which the organic molecules could form highly organized assemblies. Moreover, high and efficient regio- and/or stereoselectivity could be observed depending on the conformations of the molecular assembly when these LDH hybrids were applied in template photochemical reactions.

In this work, the high and efficient regio- or stereospecific template polymerization of methacryl derivatives in a spatially restricted reaction field will be reported. A long alkyl-chained methacrylate derivative, 12-methacryloyloxydodecanoic acid (MADA), as shown in Chart 1a, was selected as the monomer for the stereo-controlled radical polymerizations in the LDH interlayers.

MADA was hybridized with LDH clay by the following procedures: An aqueous suspension of the sodium salt of MADA (5 mmol$\cdot$dm^{-3}) was mixed with sodium benzophenone-3,3′-di-*tert*-butylperoxycarbonyl-4,4′-dicarboxylate, i.e., a radical initiator (0.5 wt % vs MADA), as shown in Chart 1b. LDH powder of 200 mg was added to this stock solution (240 mL, 3 equiv. of LDH) and stirred for 3 days at room temperature. The hybrid precipitate was filtered and washed with ethanol, then dried in vacuo for 3 h to obtain fine white powder of 353 mg. The resulting hybrid is referred to as 300% MADA/LDH.



(a) (b)

Chart 1.

The XRD profiles (Figure 1) show that the lengths of the interlayer spaces for the MADA/LDH hybrids were dependent on the amount of MADA intercalated. The XRD patterns indicated that the interlayers of the hybrid were expanded when compared with the original interlayers without the carboxylate. Moreover, the peaks observed for the non-intercalated LDH did not appear in the XRD of the 300% MADA/LDH hybrid (Figure 1d), although new periodic signals (36 Å) attributed to the layered structure of the hybrids appeared, suggesting that a bilayer assembly was formed within the LDH on the basis of its molecular length (23.3 Å) and the framework thickness (4.8 Å).

Here, MADA could be intercalated into the LDH clays not only by ion-exchange but also by hydrophobic interactions. The intercalation efficiencies (%) of MADA into LDH were determined by elemental analysis and the results are shown in Figure 2. The efficiencies reached a saturation point of ca. 110% AEC of MADA when 350% of MADA against AEC was mixed with the LDH, although MADA is assumed to be structurally similar to typical surfactant carboxylates.

The MADA molecules in the hybrids were considerably tilted against the surface of the LDH framework. Judging from the MADA bilayer aggregates, one MADA molecule could occupy ca. 46.0 Å^2 on the LDH surface. However, since the cross-section of the *all-trans* methylene chain can be estimated to be ca. 18.6 Å^2, the MADA molecules are assumed to be arranged in a gauche form,[11] which is also supported by ν_{as} 2924 cm^{-1} for the IR spectrum of the hybrid.[12]

A MADA-saturated hybrid could be formed upon the addition of MADA into LDH in a 3:1 molar ratio, as shown in

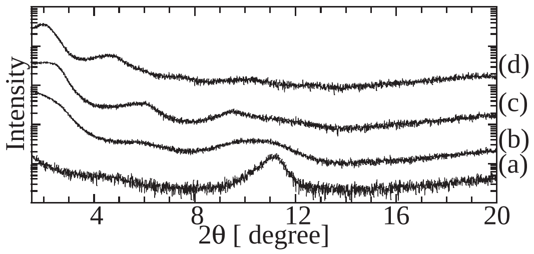


Figure 1. Interlayer distance of MADA/LDH hybrids against the amount of MADA added: (a) non-intercalated LDH; (b) 100% MADA/LDH; (c) 200% MADA/LDH; (d) 300% MADA/LDH.

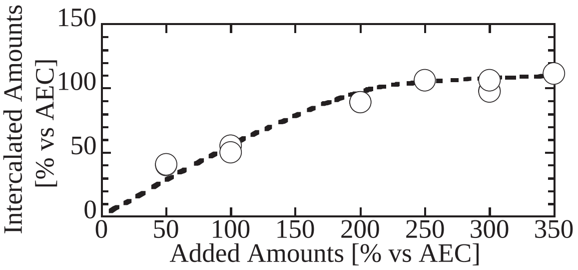


Figure 2. Plots for the amount of MADA intercalated against the amount added.

Figure 2, and under these conditions, the stereospecific tacticities of the MADA polymer were examined.

The hybrid powder (300 mg) were dispersed in distilled water (30 mL), placed in a quartz test tube (ϕ 20 × 300 mm length) and magnetically stirred under UV light irradiation (>330 nm) using a 300 W high pressure mercury lamp equipped with a KNO_3aq cut filter at room temperature. After 4 h irradiation, the white powder was filtrated and treated with 3 $mol{\cdot}dm^{-3}$ HCl to isolate the MADA polymer by decomposing the LDH framework. The resulting MADA polymers were extracted with chloroform, methylated with diazomethane, separated from the insoluble inorganic impurities through a GPC column, evaporated, dried in vacuo, and then analyzed by ^{13}C NMR with 30,000 iterative scans. The polymerization degree (N_D) of the poly(MADA) was observed to be 820 by comparing the GPC retention times of the standard poly(styrenes) of $N_D = 38$ and 480.

Figure 3 shows the ^{13}C NMR spectra in the region of the carbonyl groups for: (a) poly(MADA) and (b) commercially available non-regioselective poly(methacrylates) (Kishida Chem. Co., Ltd). Ten tactic pentads consisting of five monomer sequences have been assigned to the meso (*m*) and racemo (*r*) sequences for the poly(methacrylates),[10] abbreviated in combinations from "*mmmm*" to "*rrrr*", as shown in the peaks of the ^{13}C NMR spectra for the poly(MADA) and poly(methyl methacrylate) in Figures 3a and 3b, respectively. The tacticities were assigned by comparing the results with previous studies. Interestingly, the pentad peaks assigned to the *racemo*-rich sequences, i.e., *mrrm*, *mrrr*, and *rrrr*, could not be observed among the spectral peaks of the MADA, implying that the stereochemical control of the LDH interlayers was favorable for a *meso* conformational poly(MADA).

Figure 4 depicts the plausible models for the formation of *racemo* and *meso* conformation polymers in the MADA/LDH hybrids. The stereoselectivity is attributed to the MADA molecules which form bilayer aggregations in the hybrid and polymerization proceeded among the parallel-oriented molecules. In case (a), the vinyl groups of the two anti-parallel MADA molecules in the bilayer formed a *racemo* linkage (Figure 4a), whereas, for (b), the vinyl groups of the parallel-packed MADA formed a *meso* linkage (Figure 4b). The present template polymerization was, therefore, considered to proceed by coupling among the parallel-aligned MADA molecules on the surface of the LDH clays.

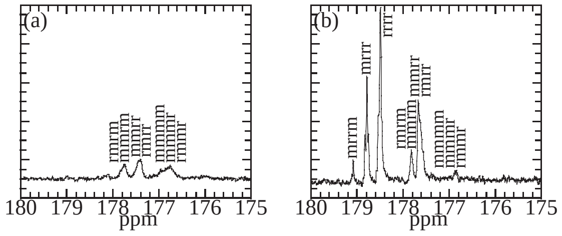


Figure 3. ^{13}C NMR spectra of the carbonyl carbons of the methacrylate group: (a) poly(MADA) isolated from the LDH hybrid; (b) methyl methacrylate polymer, $(C_5H_8O_2)_n$, with a polymerization degree (n) of $n \approx 6000$.

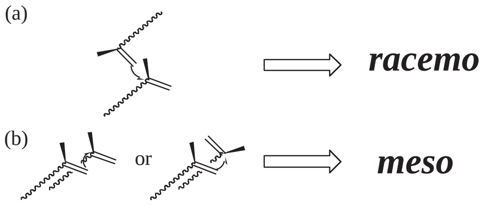


Figure 4. Models for the polymerization of the adjacent two MADA molecules in the LDH hybrid: (a) for the anti-parallel pair of MADA; and (b) the parallel pair of MADA.

In conclusion, the MADA/LDH hybrids prepared in this study were observed to undergo radical-initiated polymerization under UV light irradiation. Especially in the case of 110% AEC coverage of MADA in the LDH, a bilayer aggregate of the MADA assembly was formed within the interlayers and a regio-selective polymerization of *meso*-favorable conformers could be initiated. Consequently, a photo-induced template polymerization could proceed through the parallel alignment of the interlayer organic molecules within the LDH framework. LDH template polymerizations are, thus, seen to be promising in the preparation of heat resistant *meso*-polymers.

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