

Color Changes Dependent on the Anisotropic Intercalation of Poly(diacetylenecarboxylates) in LDH Clay Hybrids

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Variation in the coloration of LDH clay-intercalated poly(diacetylenecarboxylates), i.e., poly- $[m,n]$ /LDH, was found to be dependent on the conformations of the carboxylates within the hybrid which were quite sensitive to the carbon numbers, m and n , in the alkyl chains.

The efficient polymerization of conjugated diacetylenes by UV or γ -ray irradiation has been previously reported.^{1,2} Since then, there have been many studies on diacetylene polymers owing to their unique and multi-functional properties.³ Especially, chromatic changeability has the potential for a wide variety of useful applications, e.g., in optical and memory devices. This property was found to be closely related not only to the extent of the conjugation over the polymerization backbone of the poly(diacetylenes) but also to the conformation of the side chains of the substituents with the backbone.⁴

It is generally understood that long alkyl chains, in this case linked to the poly(diacetylenes) and resulting in the formation of their aggregates, can induce a deep bathochromic shift due to their supramolecular conformations as well as the widespread conjugation of the poly(diacetylene) backbone.⁵⁻⁷ For weakly aggregated poly(diacetylene), a yellow to yellow-orange coloring attributed to short poly(diacetylene) conjugations could be observed.

We report here on the preparation of self-assembling aggregates of $\text{CH}_3(\text{CH}_2)_{m-1}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_{n-1}\text{CO}_2\text{H}$ (**mono- $[m,n]$** , $m, n = 5,11; 10,5; 16,1; 10,11$) in layered double hydroxide (LDH) clay which were observed to undergo various color changes upon polymerization. LDH, which is referred to by the chemical formula $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$, is capable of accommodating higher aliphatic acids in its interlayers not only by anion exchange with the Cl^- but also by the hydrophobic interaction of the guests. Although the relationship between the supramolecular aggregations and coloration has been previously reported, there have yet been few studies on poly(diacetylenes) hybridized in inorganic layered hosts such as LDH clay.

The coverage degrees (%) of the **mono- $[m,n]$** intercalated in the LDH were found to be dependent on the kind of **mono- $[m,n]$** and, at the same time, the intercalation degrees of the **mono- $[m,n]$** were observed to increase with the concentrations until reaching a saturation point, as shown in Figure 1. As a comprehensive reference for the diacetylene-LDH hybrids, e.g. "100%-mono- $[m,n]$ /LDH," is used to describe the hybrids treated with **mono- $[m,n]$** equivalent to the AEC (anion exchange capacity) of the LDH clays. It is clearly seen in Figure 1 that the coverage degrees for **mono- $[10,5]$** and **mono- $[5,11]$** were only about half that for **mono- $[10,11]$** , while **mono- $[16,1]$** showed the least efficient intercalation even though it possesses a long alkyl chain

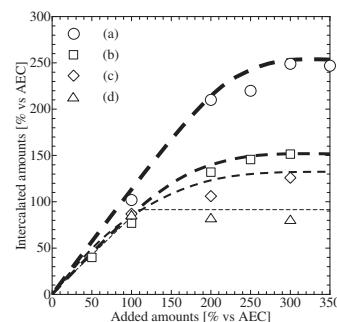


Figure 1. Intercalated amounts of **mono- $[m,n]$** against the added amounts: (a) **mono- $[10,11]$** ; (b) **mono- $[5,11]$** ; (c) **mono- $[10,5]$** ; and (d) **mono- $[16,1]$** .

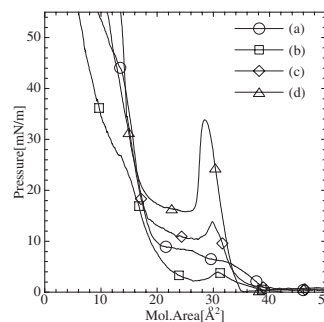


Figure 2. Surface pressure-area isotherms of **mono- $[m,n]$** measured at 5°C: (a) **mono- $[10,11]$** ; (b) **mono- $[5,11]$** ; (c) **mono- $[10,5]$** ; and (d) **mono- $[16,1]$** .

substituent similar to the other diacetylenecarboxylates. The extent of the steric hindrance suppressing the formation of guest carboxylate aggregations in the LDH was shown by analysis of the π -A curve. The existence of two discontinuous points, indicating the points of change in the alignment, could be observed upon an increase in the surface pressure (π), as shown in Figure 2. **Mono- $[16,1]$** and **mono- $[10,5]$** , with short methylene chain spacers located between the carboxyl and diacetylene groups, steeply increased their surface pressures at the cross-section point of ca. 35 \AA^2 per molecule, while **mono- $[5,11]$** and **mono- $[10,11]$** , with long terminal alkyl chains, slowly and gradually increased their surface pressures at ca. 40 \AA^2 per molecule and then steeply increased again at ca. 20 \AA^2 , indicating little steric hindrance against the compressions when the diacetylene substituents passed the initial point of abrupt change at ca. 40 \AA^2 .

The π -A profiles depicted in Figure 2 correspond well to the intercalation efficiencies so that **mono- $[5,11]$** and **mono- $[10,11]$** were shown to be more efficient than **mono- $[16,1]$** and **mono-**

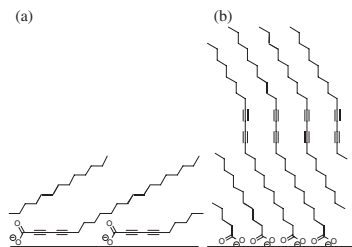


Figure 3. Alignments of **mono-[*m,n*]** on the water surface of a LDH instrument: (a) **mono-[16,1]**; and (b) **mono-[10,11]**.

[10,5]. The two former homologs can thus be considered attractive materials that can induce the efficient formation of organized aggregates when incorporated in LDH. On the other hand, since **mono-[16,1]** possesses a diacetylene group connected directly to the adjacent carboxylic group without a polymethylene spacer, only poorly organized aggregates could be formed due to the large cross section of the head group, as shown in Figure 3a. Analysis of the π -A profiles showed that **mono-[10,11]**, the most efficiently adsorbed in the LDH interlayers, exhibited two kinds of aggregation structures, i.e., loosely and tightly packed conformations, as shown in Figure 2. Moreover, ca. 250% **mono-[10,11]/LDH** may have a bilayer unit structure (Figure 3b), judging from the good correlation between the cross sections of the present **mono-[10,11]/LDH** and our previously reported highly organized bilayer-structured stearate/LDH hybrids.⁸

No reflection peaks in the XRD patterns of the 100% **poly-[5,11]/LDH** were observed, indicating the mostly irregular packing alignment of the carboxylates. On the other hand, a series of (00*l*) broad peaks appeared for the 200%- and 300% **poly-[5,11]/LDH** hybrids (spacing values of 35.6 and 42.6 Å, respectively), clearly indicating a recovery of their periodic and regular packing alignment within the interlayers. For the >200% **poly-[10,11]/LDH** hybrids (spacing value of 53.5 Å), a stereoregular polymerization took place within the LDH, and in fact, under conditions of excess intercalation, the **poly-[10,11]/LDH** hybrid developed deep blue coloring while still retaining the regularly packed conformation of the original **poly-[10,11]**.

Figure 4 shows the diffuse reflectance absorption spectra of the UV-induced polymerized hybrids of 300% **mono-[*m,n*]/LDH** having various alkyl chain lengths, while the total lengths were kept almost constant. All of the hybrid powders were placed in a quartz glass plate of 5-mm thickness and irradiated with UV light (>240 nm) using a 300-W xenon lamp at room temperature. It is noteworthy that all of the four **poly-[*m,n*]/LDH** hybrid powders in this work each possessed a characteristic color, i.e., from pale yellow to blue, according to the position of the ene-yne in each of the molecules.

The change in color for the **poly-[16,1]/LDH** hybrid (Figure 4d) was not very pronounced and only a light orange color appeared upon UV light irradiation, indicating irregular conformation and inefficient polymerization. For the **poly-[10,5]/LDH** (Figure 4c) and **poly-[5,11]/LDH** (Figure 4b) hybrids, both clearly turned red. Moreover, small amounts of blue components could be observed for **poly-[5,11]/LDH**. **Poly-[*m,n*]**, which possess long methylene chains between the carboxyl and diacetylene groups, were also observed to undergo

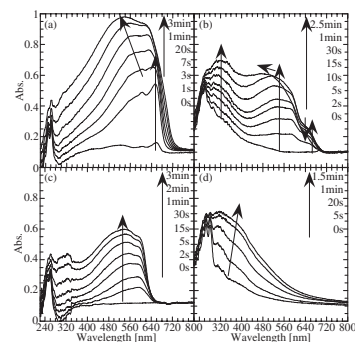


Figure 4. The diffuse reflectance spectra of poly(diacetylene-carboxylates) (**poly-[*m,n*]**) in the LDH interlayers: (a) **poly-[10,11]/LDH**; (b) **poly-[5,11]/LDH**; (c) **poly-[10,5]/LDH**; (d) **poly-[16,1]/LDH**.

bathochromic shifts in the absorption spectra, as can be seen in Figures 4b–4d. Especially for the case of **poly-[10,11]/LDH**, shown in Figure 4a, a typical bathochromic shift of the absorption spectrum could be seen due to the long methylene chain surfactant which plays an important role in the aggregation of the guest diacetylene compounds and profoundly affects their conformations through strong hydrophobic–hydrophobic interactions in water. It could, thus, be concluded that a well-oriented conformation is the major factor influencing efficient blue coloration and leading to efficient chromatic changeability and conductivity of the hybrid materials.

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