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Interlamellar Grafting of γ-Methacryloxypropylsilyl Groups on Magadiite and Copolymerization with Methyl Methacrylate

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Organically modified magadiite has been prepared by grafting γ-methacryloxypropylsilyl (γ-MPS) groups to the interlayer surface. γ-Methacryloxypropyltrimethoxysilane as silylating reagent was reacted with dodecyltrimethylammonium-exchanged magadiite. Formation of the organic derivatives of magadiite was confirmed by XRD, IR, ^{29}Si CP-MAS NMR, and ^{13}C CP-MAS NMR. Copolymerization of the grafted groups with methyl methacrylate yielded a novel type of layered silicate−organic intercalation compound with covalently bound polymers in the interlayer space. This is in contrast to conventional clay−polymer systems where ionic interactions between silicates and organic modifiers are dominant.

Introduction

Various types of hybrids can be prepared by intercalation of guest species into inorganic layered materials. Guest species can assume unique properties which cannot be realized in their solution and bulk states due to the interactions with layers and their interlamallar packing modes. Many fundamental and applied studies were conducted to explore various unique features of these hybrids.[1]

A layered polysilicate magadiite ($Na_2Si_{14}O_{29} \cdot nH_2O$,)[2,3] accommodates various organic substances to form intercalation compounds.[4−7] Magadiite[8,9] has reactive silanol groups in its interlayer space. Organic groups can be grafted to these groups by reaction with organochlorosilanes to modify the interlayer space. These reactions were also performed with organically modified magadiite. Trimethylsilylation was performed on magadiite after swelling with DMSO and NMF.[10,11] Bulkier silyl groups as well as trimethylsilyl groups can be grafted on dodecyltrimethylammonium-exchanged magadiite.[12−17]

The grafted organic groups reported so far have been limited to alkyl and phenyl groups. Here we report a new type with silyl groups containing C═C bonds. The presence of double bonds in the interlayer region enables (1) grafting of further functional groups and (2) the formation of novel layered silicate−polymer nanocomposites. Recently clay−polymer nanocomposites have attracted increased attention because of their unique mechanical and chemical properties,[18−22] in which clay minerals were modified by organoammonium ions. Although magadiite−polymer systems were also reported,[23−25] no reports were found on the formation of silylated magadiite−polymer nanosystems where the

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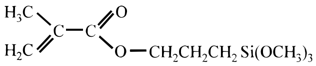

Figure 1. γ-Methacryloxypropyltrimethoxysilane.

surface of the layered silicate and polymer chains were linked covalently. We already reported silylation of magadiite with allyl groups,[14] but partial dissociation of allyl groups can occur during the grafting reaction.

In the present study, γ-methacryloxypropylsilyl (γ-MPS) group was used as a polymerizable silyl group for the modification of magadiite. Methyl methacrylate (MMA) monomers were subsequently intercalated into the γ-MPS-modified magadiite and copolymerized with the grafted groups in the interlayer space. The surface modification with γ-MPS for amorphous silica and the copolymerization with MMA were studied.[26−31] The smallest particle size of the amorphous silica was 20−30 nm. In contrast, each silicate layer of magadiite is about 1 nm thick. Therefore, magadiite is very suitable for the preparation of homogeneous silicate−polymer nanocomposites if the each layer is effectively modified with the polymers.

Experimental Section

Silylating Reagents and MMA. γ-Methacryloxypropyltrimethoxysilane (Figure 1) (Chisso Co., Sila-Ace S710) was used as a silylating reagent. The ^{29}Si NMR spectrum of the reagent showed only a single peak at −42 ppm, indicating the absence of impurities due to the hydrolysis and polymerization. The ^{13}C NMR spectrum of the reagent showed the γ-MPS groups and all the chemical shifts coincided with those of a reference.[32] Therefore, the reagent was used as received. MMA was distilled just prior to use to remove the polymerization inhibitor.

Synthesis of Na−Magadiite and Ion Exchange. Na−magadiite was prepared according to a previous report.[3] The XRD pattern of Na−magadiite was identical with the reported diagram.[33] Ion exchange with dodecyltrimethylammonium (C_{12}-TMA) cations was performed as previously reported.[12] The XRD pattern of the C_{12}TMA−exchanged product (C_{12}TMA−magadiite) indicated a basal spacing of 2.87 nm.[12] The IR spectrum (2850−3020 cm^{-1}; C−H stretching modes of methyl and methylene groups) also indicated the introduction of C_{12}-TMA ions. The amount of C_{12}TMA per $Si_{14}O_{29}$ unit was 1.6. The ^{29}Si CP/MAS NMR spectrum of C_{12}TMA−magadiite was similar to that for Na−magadiite, indicating the retention of the silicate framework.

Grafting of γ-MPS Groups. C_{12}TMA−magadiite was dehydrated at 100 °C for 2 h under reduced pressure. The sample (1 g) was then mixed with 100 mL of ethanol and 11.8 mL (~50 mmol) of γ-methacryloxypropyltrimethoxysilane. The mixture was refluxed for 48 h under nitrogen and the refluxing was repeated by using a fresh silylating agent. The product (γ-MPS−magadiite) was washed several times with ethanol and acetone and dried in air for 2 days.

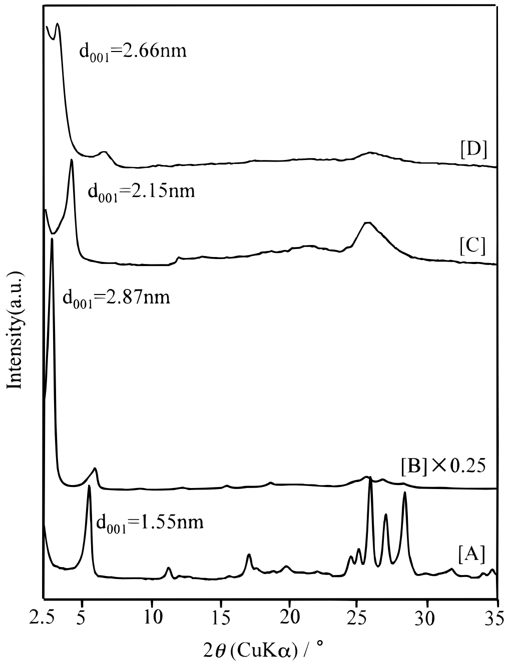

Figure 2. X-ray diffraction patterns of (A) Na−magadiite, (B) C_{12}TMA−magadiite, (C) γ-MPS−magadiite, and (D) PMMA−γ-MPS−magadiite.

γ-MPS−Magadiite−Poly(methyl methacrylate) Nanocomposite. γ-MPS−magadiite (1 g) was mixed with 30 mL of distilled toluene, 11.8 mL (~50 mmol) of MMA, and 0.13 g of recrystallized 2,2′-azobisisobutyronitrile. The mixture was stirred at 60 °C for 72 h under N_2 to bring about radical polymerization. After polymerization, toluene was removed under reduced pressure and the opaque material obtained was dispersed in a large amount of methanol. The white solid was extracted with 150 mL of toluene for 72 h in a Soxhlet apparatus to remove free poly(methyl methacrylate) (PMMA). This final product is designated as PMMA−γ-MPS−magadiite.

Characterization. X-ray powder diffraction was conducted with a MAC Science MXP^3 diffractometer (graphite monochromated Cu Kα). ^{13}C and ^{29}Si liquid-state NMR spectra were measured on a JEOL EX-270 spectrometer with 45° pulse at the resonance frequencies of 67.80 and 53.54 MHz, respectively. Tetramethylsilane was used as an internal reference. ^{13}C and ^{29}Si solid-state NMR spectra were recorded on a JEOL GSX-400 spectrometer with 45° pulse at the resonance frequencies of 100.40 and 79.30 MHz, respectively. Adamantane and poly(dimethylsiloxane) were used as the external references. CHN analysis was performed by a Perkin-Elmer PE-2400II instrument. Thermogravimetry (TG) curves were recorded on a Mac Science 2000S analyzer under a dry air flow at a heating rate of 10°/min. SEM images were obtained by a Hitachi S2500CX micrograph by an accelerating voltage of 25 kV.

Results and Discussion

Grafting of γ-MPS Groups onto the Interlayer Surface. γ-MPS−magadiite was a white powder which could be dispersed in toluene whereas Na−magadiite is not dispersible in organic solvents.

The basal spacing of γ-MPS−magadiite before washing is 2.15 nm (Figure 2C), suggesting the incorporation of γ-MPS groups into the interlayer region. Although the basal spacing of the product decreased to 2.01 nm after washing, the value is still larger than that of Na−magadiite, indicating the immobilization of γ-MPS groups. Because the difference in the basal spacings between γ-MPS−magadiite (2.15 nm) and H−magadiite

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Table 1. Elemental Composition of γ-MPS−Magadiite and PMMA−γ-MPS−Magadiite

	mass %					
	C[a]	H[a]	N[a]	Si and O[b]	grafted γ-MPS, mol/mol $Si_{14}O_{29}$	copolymerized MMA, mol monomers/mol $Si_{14}O_{29}$
γ-MPS−magadiite	13.7	2.3	ca. 0	79.6	1.2	
PMMA−γ-MPS−magadiite	28.3	4.2	ca. 0	54.1	(1.2)	4.9

[a] Obtained by CHN elemental analysis. [b] Obtained by thermogravimetry (on the basis that the sample heated to 900 °C consisted only of silicon and oxygen).

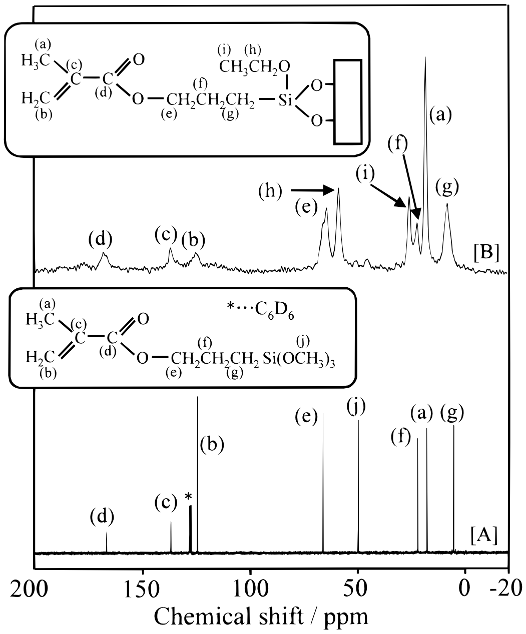

Figure 3. ^{13}C NMR spectra of (A) γ-methacryloxypropyltrimethoxysilane (liquid state) and (B) γ-MPS−magadiite (solid state, CP/MAS).

(an acid-treated magadiite, 1.12 nm[11]) is 1.03 nm, γ-MPS groups are interdigitated each other with the organic chains almost perpendicular to the silicate sheets. The chain length of a γ-MPS group is 1.0 to 1.1 nm.

The IR spectrum of γ-MPS−magadiite (not shown) shows two bands due to C=O stretching at around 1720 and 1695 cm^{-1}. While the band at 1720 cm^{-1} is assigned to relatively free carbonyl groups, the band at a lower wavenumber corresponds to C=O groups hydrogen bonded with silanol groups.[34] Consequently, a part of γ-MPS groups may interact by hydrogen bonds in a way that the organic chains are parallel to the silicate layers. The CHN data of γ-MPS−magadiite (Table 1) indicate that the amount of remaining C_{12}TMA ions is virtually zero because the nitrogen content is nearly zero and, therefore, the amount of immobilized γ-MPS groups is 1.2/$Si_{14}O_{29}$ unit.

The ^{13}C CP/MAS NMR spectrum (Figure 3B) shows the peaks for (CH_2=) at 125 ppm, (=$C(CH_3)$−) 137 ppm, and *C*=O at 168 ppm. The peaks at 26 and 59 ppm, which did not appear in the spectrum of γ-methacryloxypropyltrimethoxysilane (Figure 3A), are ascribable to (1) ethanol as solvent, (2) ethoxy groups formed by esterification of silanol groups with ethanol, or (3) ethoxy groups transesterified with unreacted methoxy groups of the alkoxysilane.[35]

The ^{29}Si CP/MAS NMR spectrum (Figure 4B) shows several peaks of the T units such as $T^1[Si(OSi)(OR')(OR'')R]$ at −45 ppm, $T^2[Si(OSi)_2(OR')R]$ at −57 ppm, and $T^3[Si(OSi)_3R]$ at −66 ppm and the signals due to the silicate framework of magadiite at −100 ppm ($Q^3[Si(OSi)_3OR]$) and at around −110 ppm ($Q^4[Si(OSi)_4]$). The chemical shift of the T^0 unit of the starting silylating reagent is about −42 ppm. The broadness of the peak due to the T^2 unit indicates that the environment around the silylating agent on the interlayer surface is not identical, which is possibly due to polymerization of adjacent silyl groups with T^1 units and/or the peculiar interlayer surface nature of magadiite. The intensity of the Q^3 peak decreased remarkably, which is also an evidence that the interlayer surface silanol groups are modified by γ-MPS groups forming new Q^4 units.

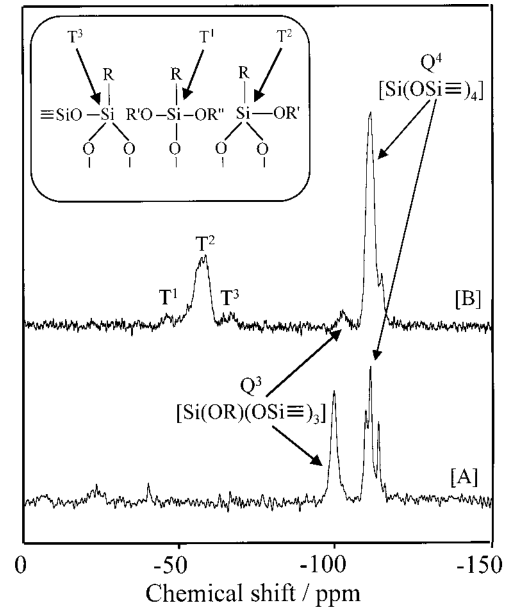

Figure 4. ^{29}Si CP/MAS NMR spectra of (A) Na−magadiite and (B) γ-MPS−magadiite.

We removed water adsorbed in C_{12}TMA-magadiite and from the solvent to avoid hydrolysis and condensation of γ-methacryloxypropyltrimethoxysilane during the grafting reaction. Thus $-OCH_3$ groups should not be converted to −OH groups as is frequently found in sol−gel processes. The amount of C_{12}TMA ions in C_{12}TMA−magadiite is lower than the total amount of silanol groups, indicating that there are free silanol groups. We propose the mechanism of the grafting (Figure 5): (1) Free silanol groups react with the organoalkoxysilane to form grafted silyl groups in the interlayer space with the generation of methanol. (2) The methanol and ethanol (solvent) can react with neighboring silanol groups to form alkoxy groups and water. (3) The generated water can interact with C_{12}-

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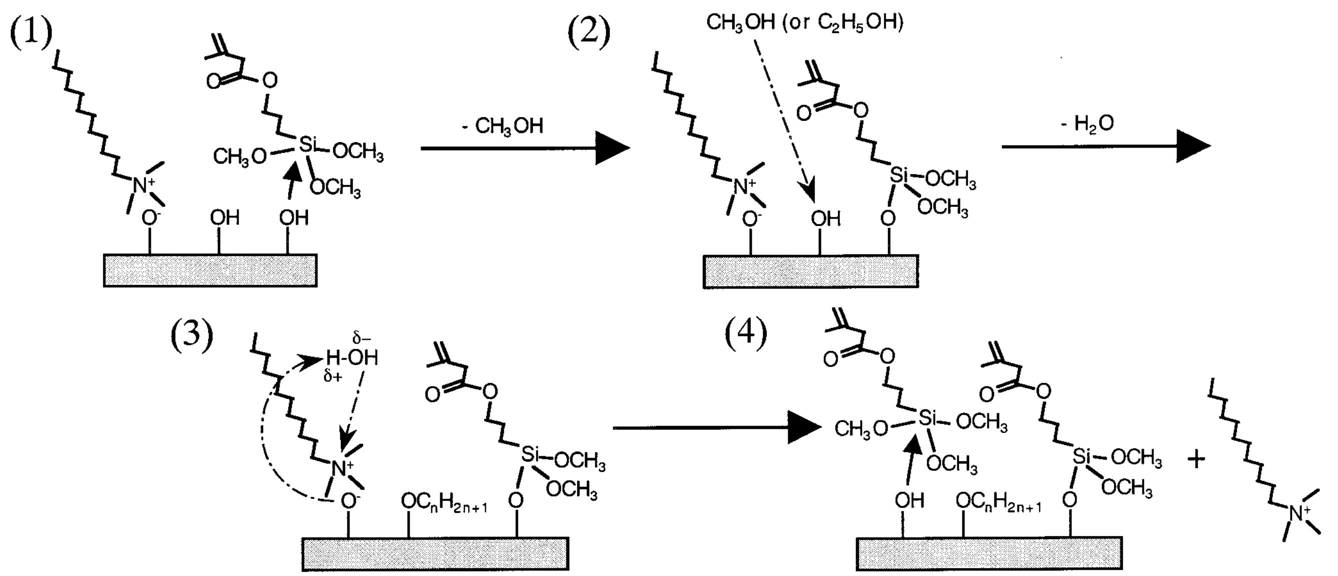

Figure 5. Grafting of γ-MPS groups to the interlamellar surfaces of magadiite.

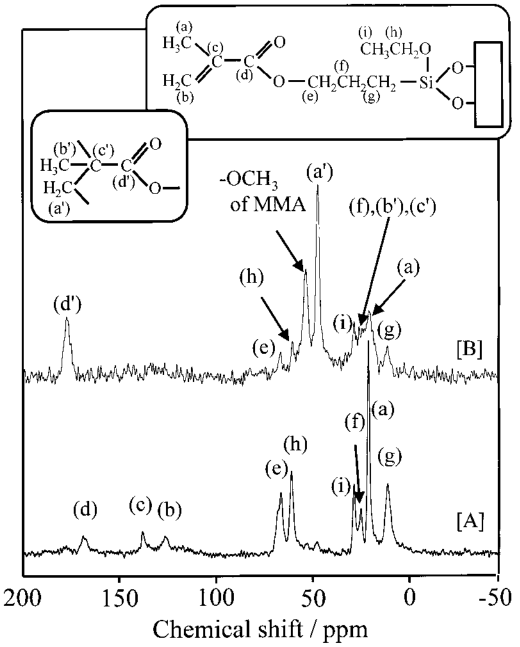

Figure 6. ^{13}C CP/MAS NMR spectra of (A) γ-MPS−magadiite and (B) PMMA−γ-MPS−magadiite (with total suppression of spinning sidebands).

TMAOSi≡ sites to form $C_{12}TMA$ hydroxide and silanol groups. (4) Newly formed free silanol groups (step 3) react with the organoalkoxysilane as in the step 1). When ethanol was replaced by acetonitrile, the grafting proceeded in a similar manner. In this case water is only generated by the reaction of methanol (from step 1) with silanol groups.

γ-Methacryloxypropyldichloromethylsilane was also used as the grafting agent.[36] The basal spacing of this product was 2.10 nm. However, the ^{13}C CP/MAS NMR spectrum of the product exhibited peaks due to chloropropylsilyl groups. HCl formed during silylation decomposes methacryloxy groups:

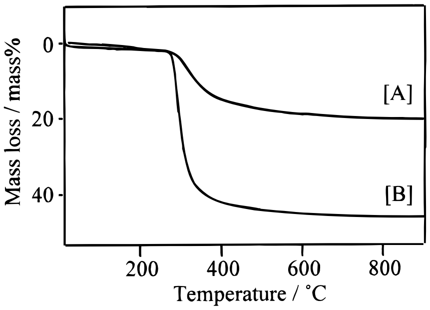

Figure 7. TG curves of (A) γ-MPS−magadiite and (B) PMMA−γ-MPS−magadiite.

$$CH_2{=}C(CH_3)COOCH_2CH_2CH_2Si(CH_3)(OSi{\equiv})_2 + HCl \rightarrow CH_2{=}C(CH_3)COOH + ClCH_2CH_2CH_2Si(CH_3)(OSi{\equiv})_2$$

Thus, the use of γ-methacryloxypropyldichloromethylsilane is less appropriate for further copolymerization reactions.

PMMA-γ-MPS-Magadiite. After the intercalative copolymerization of MMA, the basal spacing increased from 2.15 to 2.66 nm (Figure 2D). Considering the size of MMA molecule of 0.3−0.6 nm, the increase of the basal spacing is in agreement with the insertion of PMMA into the interlayer space. Even after washing the product in a Soxhlet extractor, the basal spacing did not change, although the carbon content of the product was considerably reduced. This strongly indicates that the copolymerized chains are immobilized onto the interlayer surface.

The carbon content (Table 1) is twice of that of γ-MPS−magadiite. If the increase in the carbon content is ascribed to the incorporation of the polymer, the amount of the polymer incorporated is 4.9 MMA/$Si_{14}O_{29}$ unit. Because the amount of γ-MPS is 1.2/$Si_{14}O_{29}$ unit, MMA molecules are attached at the γ-MPS groups but also polymerized with other MMA molecules. Because the copolymers are bound to the silicate layers, the molecular mass could not be determined.

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(36) $C_{12}TMA$−magadiite (1 g) treated at 100 °C for 2 h under reduced pressure was mixed with 30 mL of distilled toluene and 2.18 mL of γ-methacryloxypropyldichloromethylsilane (Chisso Co.), and the mixture was refluxed for 48 h under nitrogen atmosphere. The product was washed several times with toluene and acetone and dried in air for 2 days.

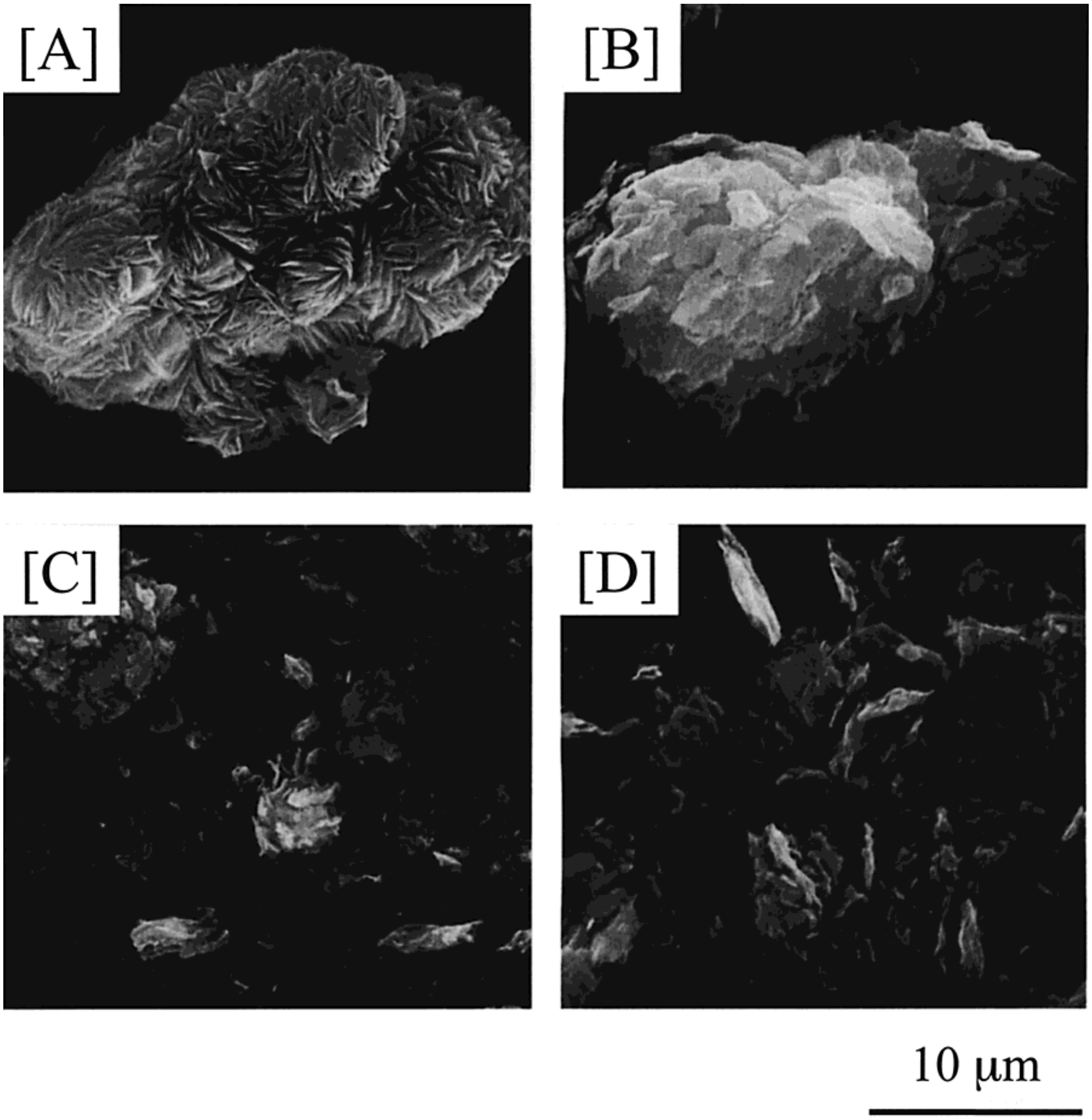

Figure 8. Scanning electron micrographs of (A) Na−magadiite, (B) C_{12}TMA−magadiite, (C) γ-MPS−magadiite, and (D) PMMA−γ-MPS−magadiite.

In the ^{13}C CP/MAS NMR spectrum (Figure 6B) a new intense peak appeared at 45 ppm (a′) due to the carbon atoms of methylene groups in the polymerized chains. The peaks for the carbon atoms of the C═C double bonds at 125 and 137 ppm disappeared almost completely, confirming the polymerization of γ-MPS groups. The signal at 168 ppm due to *C*═O groups shifted to 176 ppm.

In the IR spectrum (not shown), the peak due to C═O stretching mode at 1720 cm^{-1} shifted to 1730 cm^{-1}. In a previous paper, a similar shift was observed for amorphous silica-based composites in which the silica surfaces were modified with γ-MPS groups and copolymerized with MMA.[30,31,37] The reason of the shift is the disappearance of the conjugated double bonds of the methacryloxy groups.

The TG curves of γ-MPS−magadiite and PMMA−γ-MPS−magadiite are displayed in Figure 7. The weight loss of both samples starts at 260−290 °C. The decomposition temperature is common for these systems; for example, inorganic−organic nanocomposites derived from organoalkoxysilane and methyl methacrylate by a sol−gel process show a similar behavior.[38]

Na−magadiite shows aggregates composed of thin flaky crystals (Figure 8) as observed before.[8] The plates of C_{12}TMA−magadiite are more loosely packed. The platy crystallites of γ-MPS−magadiite are dispersed. Also, for PMMA−γ-MPS−magadiite, the platey crystal morphology was clearly observed. Thus the basic layer structure of magadiite is retained even after the interlamellar polymerization.

Conclusions

γ-MPS−magadiite was prepared by reacting C_{12}TMA exchanged magadiite with γ-methacryloxypropyltri-

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methoxysilane. The intercalated γ-MPS groups were copolymerized with methyl methacrylate monomers to form a novel magadiite−polymer nanocomposite. This nanocomposite overcomes side reactions such as liberation and decomposition of organoammonium cations in conventional clay−polymer nanocomposites where organoammonium cations must be introduced into the interlayer space for hydrophobization. The present nanocompopsite, in which intercalated polymers are covalently bound to the silicate layers, is unique and has a potential for future design of silicate based inorganic−organic nanocomposites.

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