Synthesis of 2 : 1 Type 3-(Methacryloxy)propyl Magnesium (Nickel) Phyllosilicate

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New organic/inorganic hybrid polymers, 2 : 1 type 3-(methacryloxy)propyl magnesium phyllosilicate and 2 : 1 type 3-(methacryloxy)propyl nickel phyllosilicate, were synthesized at room temperature by the copolymerization reaction of [3-(methacryloxy)propyl]trimethoxysilane to metal chloride hexahydrate. These polymers were studied by X-ray diffraction, Fourier-transformed infrared spectroscopy, and nuclear magnetic resonance measurements. The polymers have an inorganic part of phyllosilicate-like structure such as mica or smectite, and organic side chains linked to the inorganic framework through an –Si–C– covalent bond. The layered inorganic parts were considered consistent with well-ordered octahedral sheets and disordered –C–SiO_3 tetrahedral sheets. The tendency of magnesium or nickel ions to form octahedral sheets played major part in the formation of the layered structure.

Formation of an organic–inorganic composite material has attracted much attention, and many studies have been carried out. One of the approaches is a sol–gel process. For example, the sol–gel reaction of metal alkoxides and organosubstituted trialkoxyslanes builds up inorganic networks in the presence of organics at low temperatures.[1] Another approach is intercalation. It is well known that polar organic molecules penetrate into interlayer spaces of phyllosilicates such as montmorillonite, and form intercalated compounds. The intercalated compounds of clay minerals with poly(methyl methacrylate), polystyrene and polyacrylonitrile have been reported.[2—5] These compounds have two-dimensional inorganic frameworks of the host minerals, and organic chains linked to an inorganic framework through an ionic interaction.

The copolymerization reaction of metal ions including Mg and Ni to the silicic acid under alkalines condition formed a phyllosilicate structure.[6] We found that the copolymerization reaction of metal ions to organosubstituted trialkoxysilane also formed a phyllosilicate structure.[7] We concluded that this 3-(methacryloxy)propyl magnesium (nickel) phyllosilicate was composed of the inorganic crystalline framework controlled to form a 2 : 1 type lamellar structure, and organic chains with methacryloyl group arranged in two-dimensional order on that framework (Fig. 1). As silicon atoms at the center of the tetrahedron link to the organic chain by an –Si–C– covalent bond, they could not form hexagonal networks as tetrahedral sheets in the usual phyllosilicate. In this paper, we discuss the conformation and forming mechanism of 3-(methacryloxy)propyl magnesium (nickel) phyllosilicate in detail with studies using X-ray diffraction, Fourier transformed infrared spectroscopy, and nuclear magnetic resonance measurements.

Experimental

Materials. [3-(methacryloxy)propyl]trimethoxysilane (MPTS); $H_2C{=}CH(CH_3){-}CO{-}O{-}(CH_2)_3{-}Si{-}(OCH_3)_3$ was obtained from Shinetsu Chemical. Methanol, magnesium chloride hexahydrate, nickel chloride hexahydrate, and a 1 mol dm^{-3} sodium hydroxide solution were purchased Wako Pure Chemical Industries, Ltd. These materials were used without any further purification.

Synthesis of 3-(methacryloxy)propyl Magnesium Phyllosilicate. Magnesium chloride hexahydrate (1.68 g) was dissolved in 200 ml of deionized water. This solution was mixed with a 50 ml methanol solution with 2.73 g of MPTS at room temperature to form a compound in the molar ratio Si/Mg = 4/3. The solution was stirred for 30 min, and mixed slowly with 16.5 ml of the 1 mol dm^{-3} sodium hydroxide solution. The amount of the Na^+ ions in an aqueous solution was equivalent to that of Cl^- ions in the mixture. The addition of the NaOH aqueous solution changed the pH value to 10.5. The obtained suspension was aged for 24 h at room temperature, followed by filtration and washing with the distilled water. The product was dried in a vacuum at room temperture for 24 h.

Synthesis of 3-(Methacryloxy)propyl Nickel Phyllosilicate. Nickel chloride hexahydrate (1.96 g) was dissolved in 200 ml of the deionized water. This solution was mixed with a 50 ml methanol solution with 2.73 g of MPTS at room temperature to form a compound in the molar ratio Si/Ni = 4/3. The solution was stirred for 30 minutes, and mixed slowly with 16.5 ml of the 1 mol dm^{-3} sodium hydroxide solution. The addition of the NaOH aqueous solution changed the pH value to 9.0. The obtained suspension was aged for 24 h at room temperature, followed by filtration and washing with the distilled water. The product was dried in a vacuum at room temperature for 24 h. We also tried to synthesize 3-(methacryloxy)propyl phyllosilicate with 10 ml of a 1 mol dm^{-3} sodium hydroxide solution (pH = 8) or 22.5 ml (pH = 13)

Characterizations. X-Ray powder diffraction measurements were taken using Rigaku RAD-B diffractometer with Cu $K\alpha$ radiation at 30 kV and 30 mA.

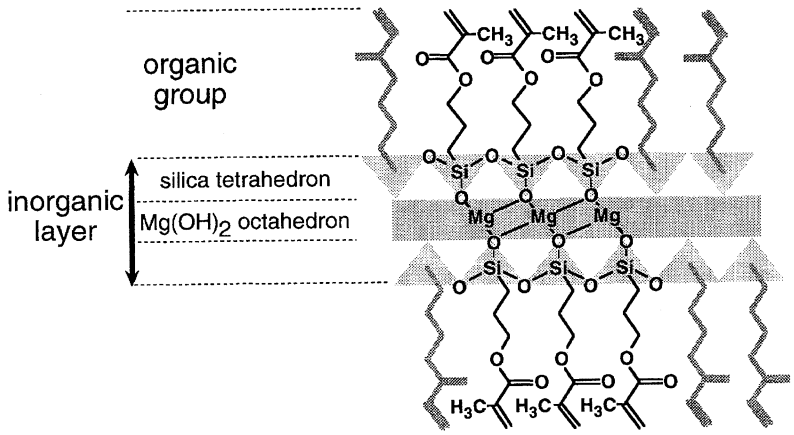

Fig. 1. A schematic sketch of 3-(methacryloxy)propyl magnesium phyllosilicate.

The FT-IR measurements were carried out on JASCO FT/IR-5M by the potassium bromide disk method.

^{29}Si magic-angle-spinning (MAS) and dipole-decoupling (DD)/MAS NMR spectra were obtained on a Bruker MSL-300 spectrometer at 59.620 MHz using 6.0 μs pulses, a 60 s recycle decay, 400 scans and a 3.5 kHz spinning rate. Chemical shifts are given in ppm from external tetramethylsilane.

The contents of magnesium and nickel were determined by ICP emission spectral analysis, while the content of silicon was determined by alkali fusion and the weight measurement. We also measured the weight contents of inorganic parts in the products by thermogravimetory at 800 °C in air using Seiko TG/DTA-580.

Results

We obtained white powder of 3-(methacryloxy)propyl magnesium phyllosilicate and green powder of 3-(methacryloxy)propyl nickel phyllosilicate.

The molar ratio of silicon/metal was 1.320 for 3-(methacryloxy)propyl magnesium phyllosilicate and 1.269 for 3-(methacryloxy)propyl nickel phyllosilicate. These ratios were nearly equal to these of MPTS and metal chloride (=4/3) in synthesis (and the stoichiometric ratio of 2 : 1 type clay minerals).

XRD patterns of 3-(methacryloxy)propyl magnesium phyllosilicate and 3-(methacryloxy)propyl nickel phyllosilicate are shown in Fig. 2A and Fig. 2B, respectively. We could not observe the peaks due to magnesium or nickel hydroxides in Fig. 2. We think that almost all magnesium or nickel ions combined with Si. This result and the Si/metal ratio suggested there were few Si compounds without Mg or Ni, besides the copolymerization product. Although peaks in the patterns of the methacrylate phyllosilicates are broad due to the lack of hydrothermal treatments, they are similar to that of 2 : 1 type phyllosilicate. As listed in Table 1, peaks of about 60° were indexed as 06, 33 for the tri-octahedral type smectite structure, and *d*-values of asymmetrical peaks around $2\theta = 40°$ agree well with those of 13, 20 for the smectite.[8] The *d*-value at 06 of magnesium phyllosilicate is larger than that of nickel, which exhibits the size difference of an octahedron due to the difference of ionic radii between Mg and Ni. This difference is also observed in synthetic clay minerals.[9] The peaks at $2\theta \approx 7°$, indexed as 001, indicate their layered

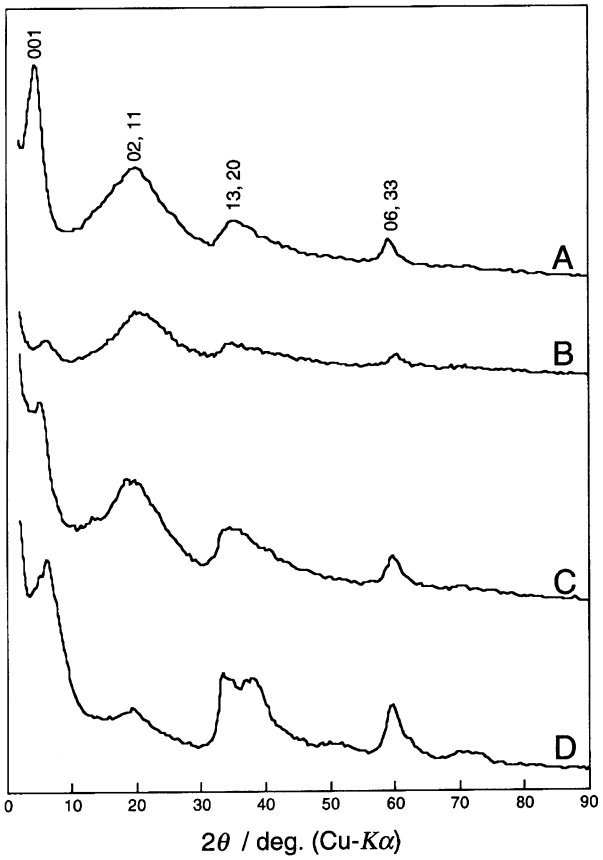

Fig. 2. X-Ray powder diffraction patterns (Cu $K\alpha$) of (A) 3-(methacryloxy)propyl magnesium phyllosilicate, (B) 3-(methacryloxy)propyl nickel phyllosilicate, (C) 3-(methacryloxy)propyl phyllosilicate synthesized with insufficient (10 ml) 1 mol dm^{-3} sodium hydroxide solution (pH = 8) and (D) 3-(methacryloxy)propyl phyllosilicate with excess (22.5 ml) 1 mol dm^{-3} sodium hydroxide solution (pH = 13).

structure with 19.62 nm (magnesium) or 16.98 nm (nickel) of the basal spacing. The basal spacing of ordinary 2 : 1 type clay minerals is about 1 nm. The basal spacing value larger than ordinary 2 : 1 type clay minerals shows the existence of organic chains in their interlayer spaces. The length of organic substituted structure; 3-(methacryloxy)propyl, is es-

Table 1. Non-Basal Diffractions from Smectites[2] and Methacrylate Phyllosilicates; Spacings in nm

h k	Saponite	Methacrylate/Ni phyllosilicate	Methacrylate/Mg phyllosilicate
indices	d	d	d
02,11	0.451	0.45	0.45
13,20	0.258	0.26	0.26
06,33	0.152	0.155	0.157

timated at 0.5 nm. The d-value of 1.7—2.0 nm is reasonable for the basal spacing of methacrylate phyllosilicates that have smectite-like structures with 3-(methacryloxy)propyl chains. The broad peaks observed at 20° are considered to have their origin in both 13, 20 diffractions of the phyllosilicate and reflections from organic chains.

An XRD pattern of the product synthesized from MPTS and nickel chloride hexahydrate with 10ml of a 1 mol dm^{-3} sodium hydroxide solution (pH = 8) is shown in Fig. 2C. Figure 2D is a pattern of product with 22.5 ml (pH = 13). A small 001 peak in Fig. 2C indicates that the shortage of OH^- in the solution leads to insufficient growth of layered structure. In Fig. 2D, no broad peak is observed at 20° and the d value of 001 (= 13.80 nm) is smaller. These results suggest that an ester connection C–O–C in the 3-(methacryloxy)propyl structure was cut during synthesis under high pH conditions. The results of the TG measurement in Table 2 support this idea. The content of inorganic fraction in the product synthesized with excessive NaOH condition is larger than that of the product in condition Na/Cl = 1.

IR spectra of 3-(methacryloxy)propyl magnesium phyllosilicate (A) and 3-(methacryloxy)propyl nickel phyllosilicate (B) are shown in Fig. 3. Absorption bands at 2950 cm^{-1} ($-CH_2-$), 1720 cm^{-1} (C=O), 1640 cm^{-1} (C=C), and 1180 cm^{-1} (Si–C)[10] in the spectra for these methacrylate phyllosilicates indicate that the methacryloyl group in the organic chains linked to Si atoms were kept in the polymer without any chemical changes during the synthesis. Bands at 1040 cm^{-1} and 1014 cm^{-1} due to the vibration of $(Si_2O_5)_n$ layer in phyllosilicates[11] show the existence of a layered silicate framework. The Mg–O vibration band at 535 cm^{-1} in Fig. 3A, which was also observed for talc,[12] indicates that there is a magnesium phyllosilicate like structure in the hybrid polymer.

An IR spectrum of the product synthesized with excessive NaOH condition is shown in Fig. 4. Little absorption bands at 2950 cm^{-1} ($-CH_2-$), 1720 cm^{-1} (C=O), 1640 cm^{-1} (C=C) and 1180 cm^{-1} suggest decomposition of organic structures

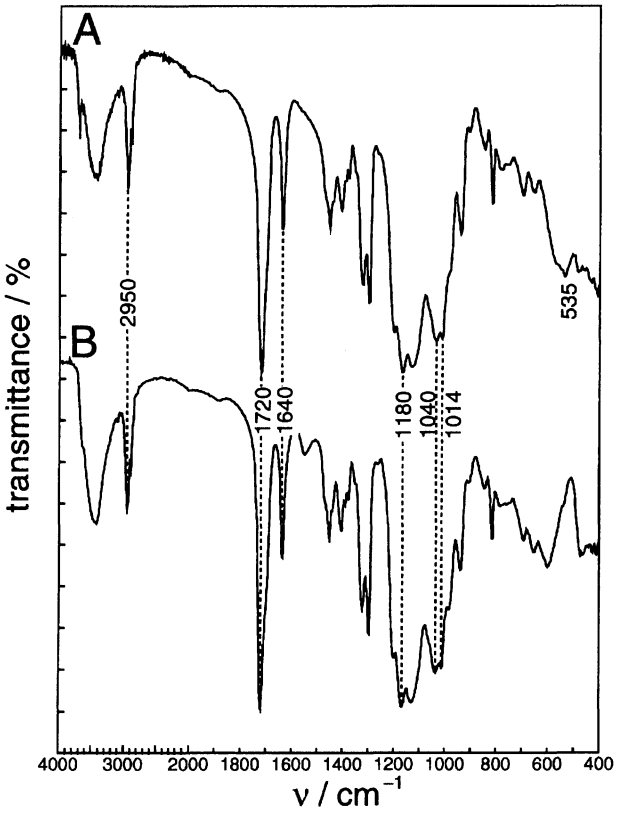

Fig. 3. Infrared spectra of (A) 3-(methacryloxy)propyl magnesium phyllosilicate and (B) 3-(methacryloxy)propyl nickel phyllosilicate (pH = 9).

in a high pH condition.

^{29}Si MAS NMR and ^{29}Si DD/MAS NMR spectra of 3-(methacryloxy)propyl magnesium phyllosilicate are shown in Fig. 5. In the ^{29}Si MAS NMR spectrum of methacrylate/magnesium phyllosilicate (Fig. 4A), three peaks range between −48 and −68 ppm. Signals from silicon atoms with four Si–O– connections in the ordinary clay minerals have appeared between −70 and −100 ppm.[13] The value of the chemical shift to tetramethylsilane (0 ppm) having four Si–C– closer than that of natural clay show that silicon atoms in methacrylate/magnesium phyllosilicate have an Si–C– bond. Two of these peaks were emphasized by the dipole decoupling technique (Fig. 5B). This fact suggests that these two peaks indicate the state of silicon atoms combining with –OH. We used MPTS as the silicon source of these methacrylate phyllosilicates; here silicon atoms have an Si–C, one Si–O–Mg, and two Si–O– bonds. Therefore, three peaks were assigned to two Si–O–Si bonds (T_2'), two

Table 2. Weight Contents of Inorganic Part in the Products Measured by Thermogravimetry at 800°C in Air

Volume of the 1 mol dm^{-3} NaOH aqueous solution (ml)	Contents of inorganic in the methacrylate/Ni phyllosilicate (wt%)	Contents of inorganic in the methacrylate/Mg phyllosilicate (wt%)
10	44.9	—
16.5	48.6	43.4
22.5	62.1	—

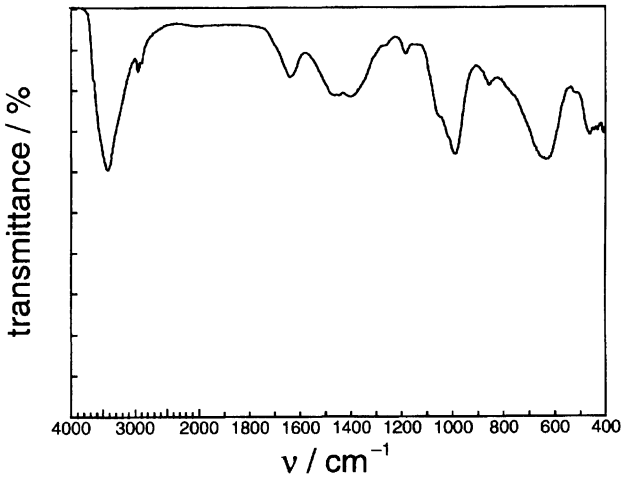

Fig. 4. Infrared spectrum of methacrylate/nickel phyllosilicate synthesized with 22.5 ml of 1 mol dm^{-3} sodium hydroxide solution (pH = 13).

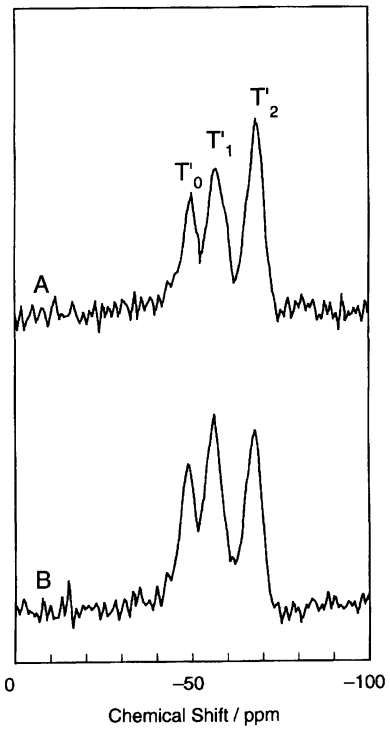

Fig. 5. ^{29}Si magic-angle-spinning (MAS) NMR (A) and ^{29}Si dipole-decoupling (DD)/MAS NMR (B) spectra of 3-(methacryloxy)propyl magnesium phyllosilicate.

Si–OH bonds (T'_0), or one Si–O–Si and one Si–OH bond (T'_1), respectively. Most of Si was T'_2, but there was a considerable amount of T'_1 and T'_0.

Discussion

These results confirm that the 2 : 1 type 3-(methacryloxy)propyl magnesium phyllosilicate and the 2 : 1 type 3-(methacryloxy)propyl nickel phyllosilicate have an inorganic part of phyllosilicate-like structure such as mica or smectite, and organic side chains of 3-(methacryloxy)propyl linked to the phyllosilicate-like framework through an –Si–C– covalent bond. Due to the existence of the Si–C bond on the silicon atom, the tetrahedral sheet must be imperfect compared with that of the natural clay minerals, and some –O–Si–O– connections are terminated by –OH. Therefore, it was considered that the polymers consist of a well-ordered octahedral sheet and –C–SiO_3 tetrahedral sheets in slight disorder (Fig. 6B).

This suggested that the formation of the tetrahedral sheets was not essential to growth of a smectite-type phyllosilicate crystal and that the growth of the octahedral sheet ruled the formation of the silicate with layered structure.

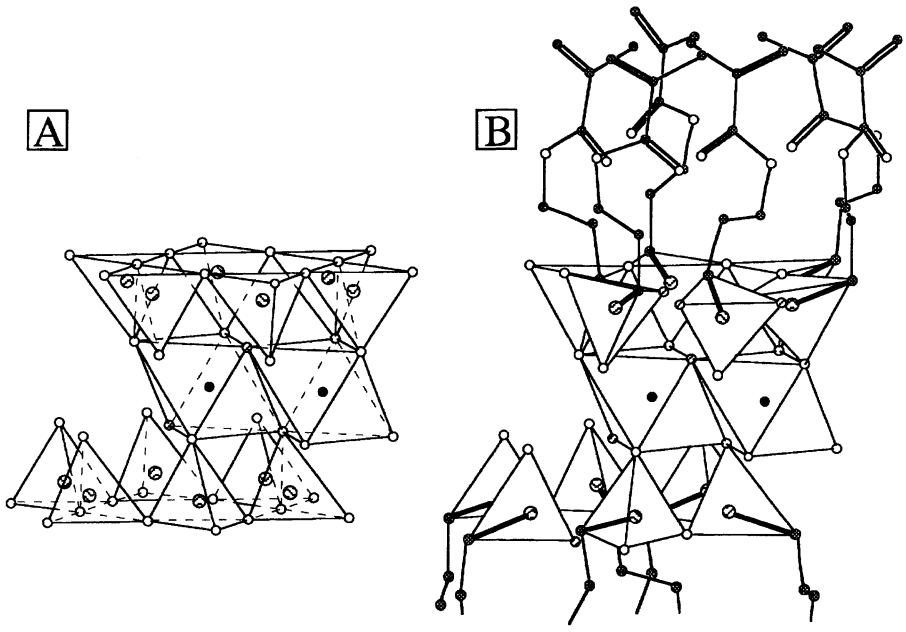

Fig. 6. Models for structures of (A) smectite and (B) a new layered polymer: 3-(methacryloxy)propyl magnesium (nickel) phyllosilicate. ◍Si, ●Mg (or Ni), ○O, ⊘OH, ◉C.

Since our synthesis method produced polymers with crystalline phyllosilicate structure without any hydrothermal treatment, it is hard to assume the existence of amorphous precursor and the rearrangement process of atoms in the synthesis. Thus we concluded the following copolymerization mechanism of trialkoxysilane and metal ion.

Hydrated MPTS molecules and magnesium (or nickel) hydroxide are first condensed together with dehydration and make a unit

$$2R\text{–}Si\text{–}(OH)_3 + Mg(OH)_2 \rightarrow R\text{–}(HO)_2Si\text{–}O\text{–}Mg\text{–}O\text{–}Si\text{–}(OH)_2\text{–}R + 2H_2O,$$

$$R : H_2C{=}CH(CH_3)COO(CH_2)_3\text{–}.$$

Since magnesium or nickel ions have a tendency to make an octahedral coordination with six oxygens, these units are polymerized with each other at an –O–Mg–O– connection and form octahedral sheets. The growth of the octahedral sheets leads the formation of the smectite-type phyllosilicate crystal. The arrangement of the organic group caused by hydrophobic interaction might also promote the formation of the two-dimensional crystal.

Conclusions.

We synthesized new polymers; 3-(methacryloxy)propyl magnesium phyllosilicate and 3-(methacryloxy)propyl nickel phyllosilicate. XRD, FT-IR, and NMR observations suggested that these polymers had an inorganic part of smectite-like structure, and organic side chains linked to the inorganic framework through an –Si–C– covalent bond.

These new polymers, 3-(methacryloxy)propyl magnesium phyllosilicate and 3-(methacryloxy)propyl nickel phyllosilicate, point in a new direction of hybrid polymer science, and are also suggestive of the need for study on the defect structure in silicate and inorganic layered crystal growth. The role of the organic chains in forming the ordered structure would be an interesting subject but a pending factor.

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