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A Novel Organic Intercalation System with Layered Polymer Crystals as the Host Compounds Derived from 1,3-Diene Carboxylic Acids

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Received June 21, 2002

Abstract: A new type of organic intercalation system using poly(muconic acid) and poly(sorbic acid) crystals as the host compounds is described. The layered polymer crystals as the host are derived from benzyl-, dodecyl-, or naphthylmethylammonium salts of (*Z*,*Z*)-muconic or (*E*,*E*)-sorbic acids by topochemical polymerization. The subsequent solid-state hydrolysis of the resulting ammonium polymer crystals provides the corresponding carboxylic acid polymer crystals. When alkylamines are reacted with poly(muconic acid) or poly(sorbic acid) crystals dispersed in methanol at room temperature for a few hours, the intercalation proceeds to give layered ammonium polymer crystals via solid-state reactions, in which the polymers maintain a layered structure throughout. The interplanar spacing value of the polymer crystals changes according to the size of the guest molecules; that is, it exactly depends on the carbon number of the alkylamines used for each reaction of poly(muconic acid) or poly(sorbic acid) crystals. The stacking structure of alkyl chains with a tilt in the intercalated alkylammonium layers exists irrespective of the chemical and crystal structures of the host polymers. The intercalation of higher alkylamines into poly(muconic acid) crystals proceeds fast and quantitatively, while the conversion is dependent on the reaction conditions such as the structure and amount of the amine and the reaction time during the intercalation with poly(sorbic acid) crystals, due to the difference in the repeating layered structures of these polymer crystals. Some functional amines are also used as the guest molecules for this organic intercalation system.

Introduction

In intercalation reactions, molecules or ions as the guest species are reversibly inserted into a layered host solid without major rearrangement of the structural features of the host.[1,2] A host compound recognizes guest species and accepts them with a reversible change using noncovalent bonding, as is typically seen in inorganic materials such as graphite, clay, and metal oxides. Intercalation chemistry is important to develop advanced materials such as heterogeneous catalysts, ionic and protonic conductors, specific adsorbents, nonlinear optics, photonic devices, and nanocomposites.[3] The mechanism of intercalation reactions and the properties of the obtained layered products have intensively been investigated for systems consisting of inorganic layered solids as the host in combination with various kinds of inorganic and organic components as the guest species. In contrast to a variety of intercalation hosts made of inorganic compounds and inorganic−organic hybrids, very few examples of intercalation systems using organic compounds as both the host and the guest are known except for the one-dimensional intercalation of double-strand DNA helices. A limited number of organic crystals have been reported as the organic mimics of clay. For example, sodium calix[4]arenesulfonate complexes with water or water/acetone closely mimic the structural behavior of clays.[4] The structure is divided into organic and inorganic layers, the former of which is formed by interlocking

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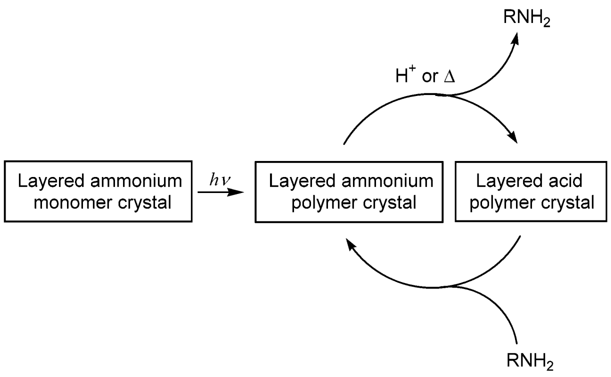
10.1021/ja020869c CCC: $22.00 © 2002 American Chemical Society

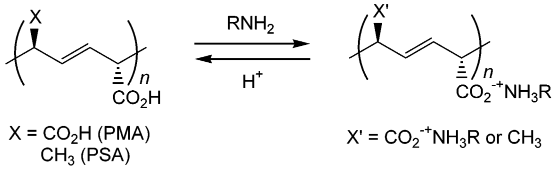
Scheme 1



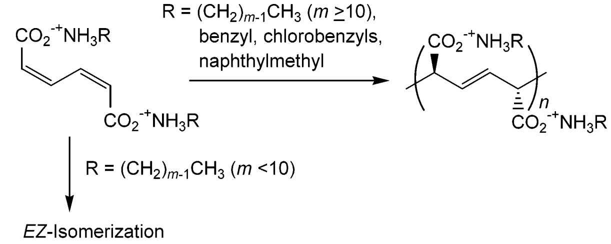
calixarenes in an up−down fashion. Cholic acid was revealed to form inclusion compounds with a variety of organic substances.[5] The added guest molecules were removed or exchanged without intervention of an amorphous state. Organic laminates were developed as a new class of clay mimics with affinity for aromatic guests.[6] Several kinds of organic salts have also been reported for lamellar architecture with soft and resilient hydrogen-bonded frameworks based on the molecular hosts.[7] There is much interest in solid organic hosts, of which guest-binding properties are reminiscent of traditional zeolites.[8] A network structure is built up on a basic design strategy using hydrogen bonding and coordination and is controlled by the geometric and topological properties of the building blocks.

Recently, we reported that layered polymer crystals are obtained by the topochemical polymerization of alkylammonium muconates as the 1,3-diene dicarboxylic acid monomer under photoirradiation in the crystalline state and that they function as an intercalation compound.[9,10] The ammonium muconate polymer crystals are converted into poly(muconic acid) (PMA) crystals by hydrolysis with HCl in an aqueous methanol or by thermolysis in the solid state, and the process is reversible. Alkylamine molecules are intercalated into the PMA crystals dispersed in a methanol solution of the amine with stirring at room temperature within a few hours. The ammonium layers can be removed and inserted in the polymer crystals, as shown in Scheme 1. These transformations are heterogeneous because both the polymer crystals as the acid and as the ammonium salts are insoluble in methanol as the dispersant. Nevertheless, intercalation proceeds with a high efficiency to achieve a high conversion (94−96%) when an *n*-alkylamine is used as the guest molecule. Repeated cycles of the ammonium-acid transformation provide similar polymer crystals without serious damage or collapse of the layer structure despite a drastic change in the chemical and crystallographic structures during the reactions. More recently, we have revealed that similar intercalation occurs when the crystals of poly(sorbic acid) (PSA) are used in place of PMA (Scheme 2).[9] Here, PSA and PMA are 2,5-*trans*-polymers with a similar main chain structure and tacticity but a different side chain. They are obtained from 1,3-diene mono- and dicarboxylic acid derivatives as the starting monomers via similar polymerization conditions and mechanism.

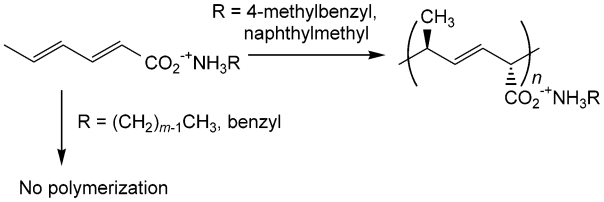
Scheme 2



Scheme 3



Scheme 4



For the topochemical polymerization of 1,3-diene monomers, the packing structure of the monomers in the crystals is important to control the polymerization reactivity.[9] The arrangement of monomer molecules in a column structure with a stacking distance of 5 Å results in a successful topochemical polymerization, and the monomer packing structure importantly depends on the chemical structure of the monomers.[11] Actually, limited monomers induce the topochemical polymerization in the crystalline state; for example, *n*-alkyl-, benzyl-, chlorobenzyl-, and naphthylmethylammonium groups as the countercation of muconates are valid for the polymerization, but short alkylammoniums favor *EZ*-isomerization (Scheme 3).[12−14] For the polymerization of sorbates, naphthylmethyl- or 4-methylbenzylammoniums are successfully used, but *n*-alkyl or unsubstituted benzylammonium derivatives provide no polymer (Scheme 4).[15]

Modifying the polymer crystals by the introduction of functional groups is necessary for constructing an advanced organic material. Because of the structural limit for the topochemical polymerization, however, it is not a steady strategy

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Table 1. Conversion for Intercalation of *n*-Alkylamines with Various Alkyl Chain Lengths into PMA and PSA and Interlayer Spacing of the Resulting Alkylammonium Polymer Crystals[a]

	host = PMA				host = PSA	
	$[-NH_2]/[-CO_2H] = 1$		$[-NH_2]/[-CO_2H] = 10$		$[-NH_2]/[-CO_2H] = 10$	
m[b]	conversion (%)	*d* (Å)	conversion (%)	*d* (Å)	conversion (%)	*d* (Å)
2	36.9		85.8		60.2 (87.0[c])	18.0[c]
3	49.6		92.2	15.4		
4	54.1	16.9	85.5	16.5	61.0 (89.6[c])	23.9[c]
5			93.7	18.3	70.0	27.0
6	71.4	20.5	89.3	20.5	83.1	27.3
7			95.4	21.9	84.1	30.1
8	85.9	24.5	91.0	24.4	80.0	31.1
10	77.0	28.4	93.6	27.1	78.7	35.2
12	81.9	32.6	94.7	32.6	88.0	39.8
14	79.6	36.1	95.1	36.2	84.9	43.4
16	79.9	40.8	95.3	40.5	79.3	46.6
18	91.6	45.0	96.4	45.5	77.8	53.2

[a] Reaction conditions: PMA or PSA 50 mg, methanol 20 mL, stirred for 1 h for PMA or 2 h for PSA at room temperature. Conversion was determined from the fraction of the alkylammonium carboxylate in the polymer crystals after the unreacted alkylamine was removed. Interlayer spacing (*d*) was determined from 2θ value from the peak observed at a low-angle region in powder X-ray diffraction profiles. [b] Number of the carbon atom of *n*-alkylamine. [c] $[-NH_2]/[-CO_2H] = 50$.

to design the monomer crystals with a specific functional group without losing its topochemical polymerization ability. In contrast, intercalation has great potential for the introduction of various functional groups to induce not only a change in crystal structure but also chemical reactions, molecular recognition, separation, and physical interactions. Here, we describe the intercalation of alkylamines as well as some functional amines into the organic polymer crystals under various conditions to discuss the fundamental features and the reaction mechanism of the organic intercalation system using PMA and PSA as the crystalline host compounds.

Results and Discussion

Intercalation of Alkylamines with PMA and PSA. First, we examined the effects of the chain length of *n*-alkylamines on intercalation efficiency and the structure of the resulting ammonium polymer crystals. An intercalation reaction was carried out with PMA or PSA crystals as the host compounds, which are dispersed in a methanol solution of the corresponding amine with stirring at room temperature. The results are summarized in Table 1. The conversion was determined from the fraction of the alkylammonium carboxylate in the polymer crystals.

The conversion increased with an increase in the carbon atom number (*m*) and the molar ratio of the used *n*-alkylamines ($[-NH_2]/[-CO_2H]$). The intercalation into PMA was performed at a high efficiency of more than 95% when a large excess of the amines including a long-alkyl chain was used (10-fold equivalent and $m > 12$). Figure 1a shows the effect of the ratio of the amine used to the carboxylic acid of the polymers on the conversion for the reactions of several alkylamines with a different alkyl-chain length. In the case of $m > 6$, the conversion was high and remained almost constant over the whole region of excess amines. During the reaction of *n*-butylamine, the conversion increased according to the $[-NH_2]/[-CO_2H]$ ratio in the examined range. The reaction proceeded rapidly and reached a constant conversion within several hours, irrespective of the structure of the alkylamine used. The time dependence of the conversion revealed that the intercalation of amines with a long or short *n*-alkyl group proceeded at a different rate according to the size of the alkylamine. For example, the initial slope of the time-conversion curve as well as the conversion finally achieved after 10-h reaction was much higher for the intercalation of octadecylamine, as compared to those of *n*-butylamine (Figure 1b). This indicates the accelerated intercalation by the long-alkyl chain structure of the guest molecules.

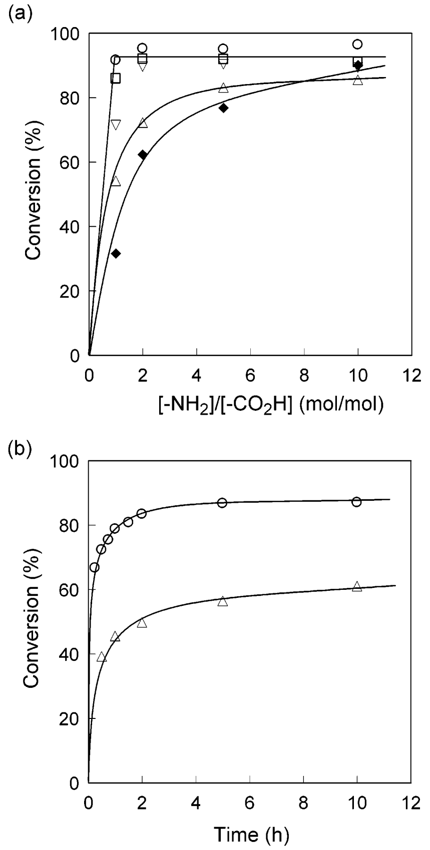

Figure 1. (a) Effect of the $[-NH_2]/[-CO_2H]$ ratio on the conversion for the intercalation of *n*-alkylamines with a different alkyl chain length using PMA as the host crystals; reaction time, 1 h: (○) octadecylamine, (□) octylamine, (▽) *n*-hexylamine, and (△) *n*-butylamine. (◆) Intercalation of dodecylamine with PSA (reaction time, 5 h). (b) Effect of the reaction time for the intercalation of *n*-alkylamines with a different alkyl chain length into PMA as the host crystals; $[-NH_2]/[-CO_2H] = 1$: (○) octadecylamine and (△) *n*-butylamine.

Similar intercalation was also examined with PSA in place of PMA. All of the *n*-alkylamines were intercalated into PSA, but the reactivity was much lower than that for PMA. In contrast to the facile intercalation with PMA, PSA as the host compound resulted in a low conversion even when a long-chain alkylamine was used. Consequently, a large excess of the guest amine was necessary to obtain a quantitative conversion for the intercalation using PSA (Table 1 and Figure 1).

Figure 2 shows a typical change in wide-angle powder X-ray diffraction profiles for PMA intercalated with different *n*-alkylamines. The value of the interlayer spacing (*d*) was determined from the 2θ value for the characteristic peaks observed at a low-angle region in the diffraction profiles, being assigned on the basis of the reported single-crystal structures of alkylammonium muconates.[11,12] The *d*-value depends on the size of the alkyl group of the used amine, from 4.8 Å for PMA to 16.5 and 32.6 Å for the polymers intercalated with *n*-butyl- and dodecylamines, respectively. The latter profile agreed well

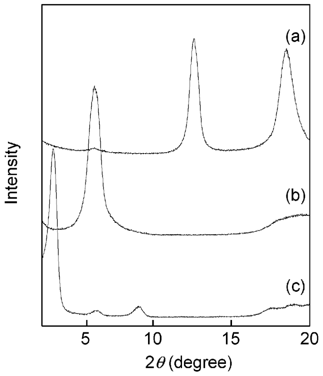

Figure 2. Wide-angle powder X-ray diffraction profiles of PMA crystals before and after intercalation of *n*-alkylamines. (a) PMA before intercalation ($d = 4.8$ Å), (b) PMA intercalated with *n*-butylamine ($d = 16.5$ Å), and (c) PMA intercalated with dodecylamine ($d = 32.6$ Å).

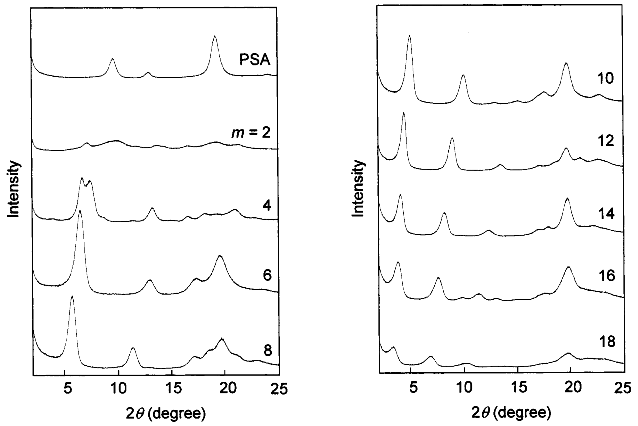

Figure 3. Wide-angle powder X-ray diffraction profiles of PSA intercalated with various *n*-alkylamines. The *m* is the carbon number of the *n*-alkylamine used as the guest for the intercalation.

with that (31.7 Å) for the polymer crystals obtained by direct topochemical polymerization of the corresponding alkylammonium monomer. Figure 3 shows the change in diffraction profiles for PSA intercalation with various *n*-alkylamines from ethyl- to octadecylamine ($2 \leq m \leq 18$). The polymer crystals obtained by the intercalation of small alkylamines ($m < 4$) into PSA provided a broad and split diffraction pattern. This suggests the formation of an incomplete layer structure during the intercalation of a short alkylamine. The incomplete layer formation is different from the facile intercalation with higher alkylamines providing layered crystals independent of the amount of the amines.

The *d*-values for PMA and PSA crystals intercalated by various *n*-alkylamines are summarized in Table 1. The *d*-value increased with an increase in the *m*-value for each series of PMA and PSA intercalation. Figure 4 shows a change in the *d*-value dependent on the size of the intercalated amines. Both of the polymer crystal series produce an exactly identical slope; the thickness of the alkylamine layer increases by 1.00 and 1.02 Å for each carbon in the *N*-alkyl substituent, for the PMA and PSA series, repectively. Accordingly, the alkyl chains of the amines stacked in the layers have a similar tilt structure, despite the differences in the polymer chain structure and also in the reaction behavior during the intercalation. When *m* is smaller than 3 for PMA, the intensity of the diffraction at a low-angle region, characterized as the layered structures, decreased due to the incomplete layered structure and molecular packing of the small amines (see Figure S1 in the Supporting Information). In the case of PSA ($m < 4$), broad or split diffraction peaks tend to disturb the determination of a precise *d*-value.

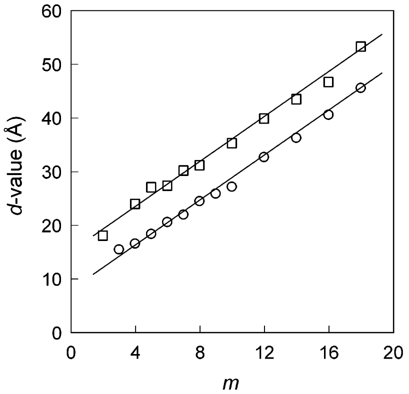

Figure 4. Change in the *d*-value for (○) PMA and (□) PSA as a function of the carbon number of the *n*-alkylamine (*m*). The slope of both of the lines is equal to 1.0 Å per an increment in the carbon number.

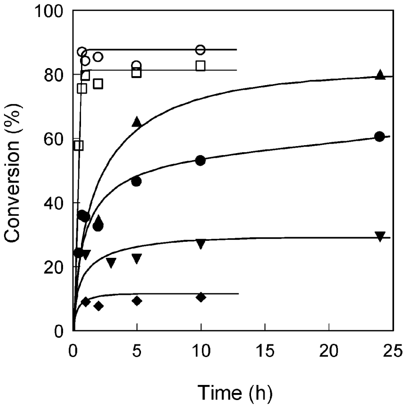

Figure 5. Effect of reaction time on conversion for the intercalation using various amounts of cyclohexylamine into PMA and PSA. For PMA: $[-NH_2]/[-CO_2H]$ = (○) 10 and (□) 1. For PSA: $[-NH_2]/[-CO_2H]$ = (▲) 50, (●) 10, (▼) 5, and (◆) 2.

Figure 5 shows the results for the intercalation of cyclohexylamine into PMA and PSA at various molar ratios of $[-NH_2]/[-CO_2H]$. A more emphasized difference in the reactivity was observed between the reactions with PMA and PSA crystals. Cyclohexylamine readily reacted with PMA, similarly to the reaction of *n*-alkylamines, at a high conversion independent of the time and the amount of the amine. In contrast, the intercalation with PSA occurred slowly, and the conversion was strongly dependent on the reaction time and the $[-NH_2]/[-CO_2H]$ ratio.

The intercalation of some branched alkylamines other than cyclohexylamine was also examined. As an example, the intercalation behavior of structural isomers for butylamines is summarized in Table 2 (for a complete table of the results of the intercalation of butylamines in various dispersants, see the Supporting Information). *n*-Butylamine was intercalated at a high yield independent of the kind of the dispersant when an excess of the amine was used. However, the use of methanol is invalid as the dispersant for the intercalation of branched butylamines due to swelling and dissolution of the polymers or a low conversion. For example, the reaction of PMA with *tert*-butylamine failed because the resulting *tert*-butylammonium salt is readily soluble in methanol. Similar results were observed for the PSA intercalation. Consequently, no appropriate solvent

Table 2. Intercalation of Butylamines into PMA and PSA as the Host Crystals[a]

host	dispersant	guest amine	conversion (%)
PMA	methanol	*n*-butylamine	85.5
		isobutylamine	62.2[b]
		sec-butylamine	64.1[b]
		tert-butylamine	soluble
	solvent-free[c]	*n*-butylamine	89.9
		isobutylamine	75.8
		sec-butylamine	90.2
		tert-butylamine	50.3 (91.3)[d]
PSA	methanol	*n*-butylamine	61.0
		isobutylamine	41.7
		sec-butylamine	30.4
		tert-butylamine	soluble

[a] Reaction conditions: $[-NH_2]/[-CO_2H] = 10$, stirred for 1 h for PMA or 2 h for PSA in methanol as the dispersant. [b] Swelling. [c] Solid-state intercalation with a neat amine ($[-NH_2]/[-CO_2H] = 10$) by grinding in a mortar for 10 min. [d] With a large excess of *tert*-butylamine, by grinding for 30 min.

Table 3. Effects of *N*-Methyl Substitution of Benzyl- and Dodecylamines on Conversion for Intercalation into PMA and PSA

guest amine	conversion (%)		
	PMA[a]		PSA
	time = 1 h	2 h	2 h
dodecylamine	88.2	86.5[b]	91.1
N,*N*-dimethyldodecylamine	28.9 (30.5)[c]		2.8
dodecylamine/ *N*,*N*-dimethyldodecylamine	82.4[d]		
tridodecylamine	0.8[e]		
benzylamine	78.9 (75.5)[b]	78.0[b]	4.8 (35.2)[f]
N-methylbenzylamine	23.4		3.9
N,*N*-dimethylbenzylamine	11.1	7.8[b]	3.5

[a] $[-NH_2]/[-CO_2H] = 10$. Benzylammonium (*Z*,*Z*)-muconate was used as the starting material for the preparation of precursor polymer crystal. The resulting PMA crystals were needles after solid-state hydrolysis. [b] Dodecylammonium (*Z*,*Z*)-muconate as the starting material to provide powdery PMA crystals by the polymerization and the subsequent hydrolysis in the solid state. [c] $[-NH_2]/[-CO_2H] = 1$; time 0.5 h, solid-state intercalation without any solvent. [d] Equimolar mixture of dodecylamine and *N*,*N*-dimethyldodecylamine was used ($[-NH_2]/[-CO_2H] = 2$; reaction time, 4 h), but only dodecylamine was incorporated into the polymer crystals (see also Figure S2 in the Supporting Information). [e] $[-NH_2]/[-CO_2H] = 10$; reaction time, 2 h; dispersant, chloroform. [f] $[-NH_2]/[-CO_2H] = 50$; reaction time, 24 h.

was found for the intercalation of *tert*-butylamine; some solvents provided insoluble products at a very low conversion, and the others resulted in a solution due to a good solubility of the product polymers. The reaction in water also induced the swelling of the host PMA or PSA during the reaction, resulting finally in a homogeneous solution. The intercalation of isobutyl- and *sec*-butylamines also resulted in a lower conversion in various dispersants, which differed from the facile intercalation of *n*-butylamine with a linear structure.

Very recently, we have found that solvent-free intercalation effectively proceeds to give the ammonium polymer crystals in a high conversion.[16] This is performed in a simple and more convenient procedure by grinding the PMA crystals in the presence of a neat amine in a mortar without any solvent. Not only *tert*-butylamine but also the other butylamines provide the intercalated ammonium polymers in a high yield via the solid-state intercalation. After the reaction, an excess amount of the unreacted amine is washed out with an appropriate solvent such as *n*-hexane. The solvent-free intercalation in the solid state is advantageous for the fabrication of layer polymer crystals reacted with sterically hindered alkylamines, when the products tend to dissolve in the solvent used as the dispersant.

Selectivity and Insertion Mechanism of Guest Amines. The intercalation of secondary and tertiary amines was also attempted, but the conversion was low despite the expectation of enhanced reactivity due to an increasing basicity (Table 3). Dodecyl- and benzylamines were intercalated into PMA, irrespective of the kind of precursor, ammonium polymers in a high yield, indicating the transformation of the ammonium polymers from the benzyl- to dodecylammonium polymer crystals and its reverse. In contrast, the corresponding *N*-methyl- and *N*,*N*-dimethyl-substituted amines showed low conversions. The solid-state intercalation was also attempted but failed. The more sterically hindered tridodecylamine was also never intercalated into PMA.

The steric requirement around the ammonium carboxylate moiety after the reaction is important rather than the basicity of the amines, resulting in the unsuccessful intercalation of sterically hindered secondary and tertiary amines. The secondary and tertiary amines form hydrogen bond networks different from those formed with primary amines, if the reaction could proceed to give ammonium carboxylate polymers. This is one of the reasons for the low reactivity. In the crystals of the primary ammonium salts of PMA and PSA, a two-dimensional hydrogen bond network is formed at the interface between the carboxylate anion and countercation layers, in which the carboxylate anion acts as a triple hydrogen bond donor, and the ammonium cation acts as a triple hydrogen bond acceptor. Whereas the construction of another type of hydrogen bond system, possibly a ladder-type hydrogen bond network or a closed-flame hydrogen bond pattern, is expected for secondary and tertiary ammonium crystals, the style of the hydrogen bond network sensitively depends on the number of hydrogens in the ammonium cation. In other words, PMA or PSA crystals memorize the crystal structure of primary ammonium polymers and recognize the structure of alkylamines. In the reaction with a suitable primary alkylamine fitting the memorized structure of the polymer crystal structure, an intercalation reaction proceeds at a greater rate and reaches a high conversion. This is also supported by a competitive experiment using dodecylamine and *N*,*N*-dimethyldodecylamine simultaneously (Table 3). After a competitive intercalation reaction in the presence of both of the amines, the incorporated amine was isolated by subsequent hydrolysis with the dueteride hydrochloric acid and methanol to prepare for an NMR measurement. Consequently, no *N*,*N*-dimethyldodecylamine was detected in the NMR spectrum.

The PMA crystals are prepared by the hydrolysis of the benzyl- or dodecylammonium polymer crystals of muconic acid, because muconic acid has no polymerization reactivity. The appearance of the crystals of the precursor ammonium polymers is the same as those of the corresponding ammonium monomer crystals because the polymerization occurs via a crystal-to-crystal process in a topochemical reaction mechanism. Therefore, the benzyl- and dodecylammonium polymer crystals are obtained as needle and powdery crystals, respectively, by the recrystallization of the ammonium monomers and the subsequent topochemical polymerization. Furthermore, the apparent crystal shape such as crystal habit has no change on a macroscopic scale except the thickness of needles (and also the volume of crystals) during the hydrolysis and intercalation in the solid state.

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(16) Odani, T.; Matsumoto, A. *Polym. J.*, in press.

A difference in the macroscopic morphology of the PMA crystals has no effect on the intercalation reactions, as is already shown in Table 3. Both the PMA crystals with apparent needles and powdery forms have an identical crystallographic structure; that is, they provide an identical powder X-ray diffraction pattern.

To examine the effects of crystallinity on the intercalation reactions, two different types of PMA host crystals were prepared. One is large needles of a few millimeters in length, which were obtained by the topochemical polymerization of benzylammonium (*Z*,*Z*)-muconate monomer crystals with a needle shape and the subsequent hydrolysis in the solid state. Another PMA sample was isolated as a white solid by precipitation during the neutralization of the methanol solution of triethylammonium salts of PMA. Consequently, it has been revealed that the reaction with the solid-type PMA obtained by the reprecipitation provides an intercalated polymer in a low conversion (24%). The crystallinity of the starting PMA as well as the resulting ammonium polymer was confirmed to be low by X-ray diffraction measurements (see the Supporting Information). This result suggests that the highly ordered and stacked layers are indispensable for successful intercalation reactions. A specific surface of the crystals acts as the entrance for the guest molecules, possibly from the sides of the stacked layers. A cooperative structural change in the stacked layers is the key to the quantitative insertion of the guests and drastic change in the crystal layer structure during the reaction. Polymer chains in the polymer crystals with a stereoregular structure are aligned with the specific axis of the crystals and linked to each other by the two-dimensional hydrogen bond network. Covalent bonds along the polymer chain as well as hydrogen bonds connecting polymer chains support the reversible solid-state transformation between the acid and ammonium polymers. The cooperative process of the insertion of the molecules and the formation of restructured layers is indispensable for quantitative transformation.

The direct exchange process of a guest alkylamine was confirmed to occur from the alkylammonium polymer crystals to other ammonium crystals. For example, the benzylammonium polymer crystals were transformed to the dodecyl derivatives during the reaction with an excess of dodecylamine. The transformation is achieved not via the formation of carboxylic acid polymer crystals. The incorporated guest amines were examined by NMR spectroscopy after the dodecylammonium muconate polymer crystals were dispersed in 100-fold molar excess of benzylamine for a week. The NMR spectrum confirmed that 95% of the amine was exchanged from the dodecyl to the benzyl one. This is also supported by a change in the powder X-ray diffraction profile (Figure 6). These results indicate that the interlayer diffusion and the direct exchange of the alkylamine molecules is possible in the polymer crystals, although the reaction proceeds in the solid state.

Despite the importance of understanding the rate and mechanism of the intercalation at a molecular level, it is difficult to directly observe the intercalation behavior of each guest molecule into a layer in the host polymer crystals. Therefore, we examined a change in the layered structure of the polymer crystals for the intercalation with a different amount of guest molecules less than an equimolar amount relative to the carboxylic acid in the polymers. The wide-angle X-ray diffraction profiles are shown in Figure 7. The intensity of the characteristic peak due to the PSA decreased due to the intercalation of dodecylamine, but it was still detected as a small shoulder in the profile of the polymer at 65% conversion. In the diffraction of the polymer at 80% conversion, the original peaks due to PSA crystals were hardly detected.[17] Simultaneously, new peaks due to the ammonium polymer crystals were also observed from the earlier stage of the reaction. These results strongly indicate that the intercalation proceeds not at random, but cooperatively over the adjacent layers. A conformational change in the polymer layers (i.e., a change in the pattern of the hydrogen bond network) possibly also induces a structural change below or in the upper layers, leading to the acceleration of the intercalation reactions in the successively stacked layers.

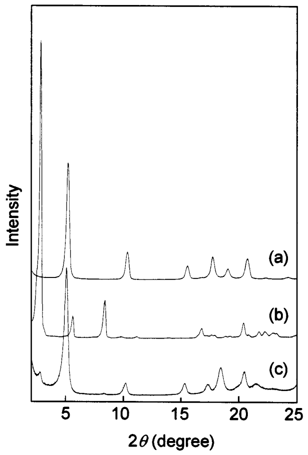

Figure 6. Wide-angle powder X-ray diffraction profiles of the polymer after the direct exchange experiment. The reaction conditions: dodecylammonium polymer crystals were dispersed in methanol in the presence of a 100-fold molar excess of benzylamine with stirring for a week at room temperature. (a) Poly(benzylammonium muconate), (b) poly(dodecylammonium muconate), and (c) after direct exchange reaction.

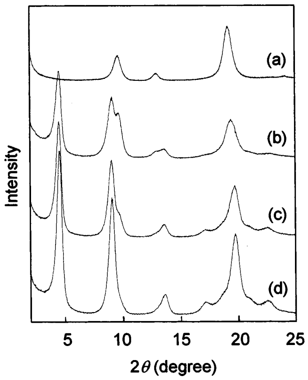

Figure 7. Change in wide-angle powder X-ray diffraction profile for the intercalation of dodecylamine into PSA at different conversion. (a) PSA (conversion 0%), (b) 36%, (c) 65%, and (d) 80%.

Layer Structure of the Polymer Crystals. The tilt angle of alkyl chains intercalated with *n*-alkylamine is determined to be 38° against the two-dimensional polymer sheet of PMA and PSA crystals. It is calculated from an increment in the *d*-values depending on the carbon number of alkyl groups in the *n*-alkylamines as the guest in the consideration of the distance

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(17) In our preliminary results reported in ref 10, a peak due to the original PMA was veiled by the other peaks due to the ammonium polymer, and, therefore, we somewhat overestimated the structural change in the intermediate conversions.

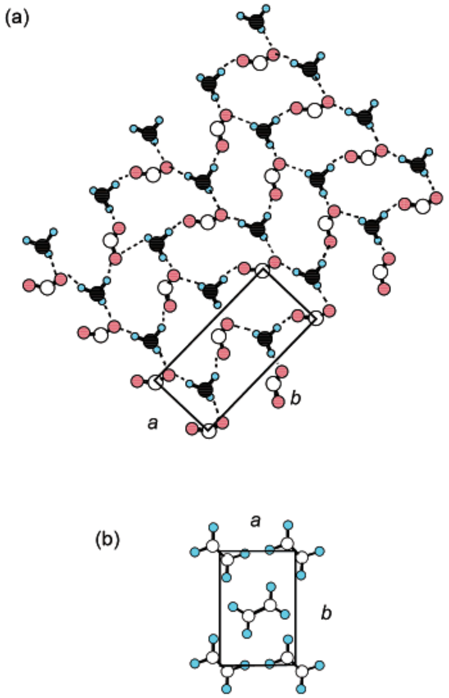

Figure 8. (a) Two-dimensional hydrogen bond network structure observed in the ammonium muconate crystals. $a = 4.9$ Å, $b = 11$ Å. (b) Unit cell of the crystals of polyethylene viewed down along the *c*-axis. $a = 4.9$ Å, $b = 7.4$ Å.

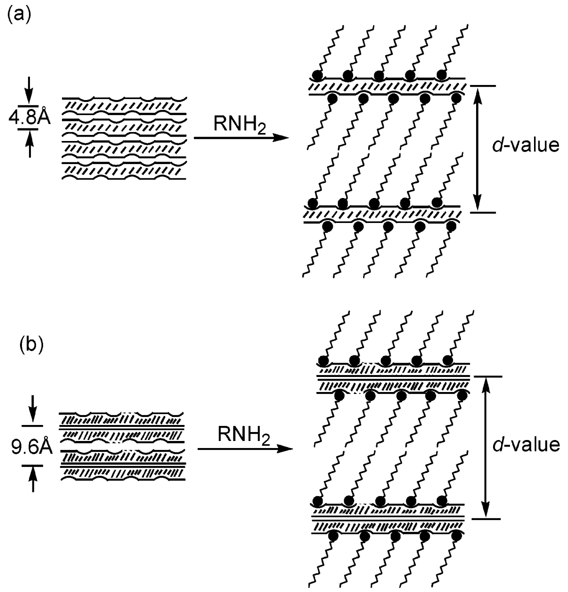

Figure 9. Model of layered polymer crystals obtained from (a) muconic and (b) sorbic acid derivatives and change in the structure during the intercalation.

of repeating units (2.54 Å) for the trans zigzag chain of alkanes. The slope of the lines in Figure 4 and the absolute *d*-values support the stacking structure of the alkylammonium counterparts with a tilt but not an interdigitation structure. Stacking structures have been reported for the inorganic layered materials intercalated with long-alkyl chain guests, being dependent on the structure of the guest molecules and the host materials, as well as the reaction conditions.[2,18]

Most layered compounds including our organic intercalation materials are isolated as a polycrystalline form. Polyethylene crystals include the typical structure of alkyl-chain stacking. The values of the *a*-, *b*-, and *c*-axes for the unit cell of polyethylene are 4.9, 7.4, and 2.54 Å, respectively.[19] Here, the *c*-axis is in the same direction as that of the extended alkyl chain and equal to the distance of one repeating unit of a trans zigzag chain. The fiber period for the crystals of PMA and PSA derivatives is approximately 4.8 Å, which has been determined by the X-ray single-crystal structure analysis of the ester polymers.[20] These facts give us an assumed structure for the tilt alkyl chains of the *n*-alkylammonium countercations; probably, the alkyl chains are tilted in a direction orthogonal to the polymer chain in the crystals, rather than in a parallel direction, on the basis of the consideration of the tilt angle of 38° in combination with the two-dimensional lattice parameters for hydrogen bond sheets (4.9 and 11 Å) and the alkyl-chain packing (4.9 and 7.4 Å) (Figure 8).

The polymer crystals of the alkylammonium muconates and sorbates have a layered structure, which is similar to that of the monomer crystals because the crystal structure is maintained during the polymerization, as well as the pattern of the hydrogen bond network. Figure 9 shows schematic models for the layered structure of PMA and PSA as well as their ammonium polymers.The muconate polymer sheet is sandwiched between two alkylammonium layers to make a BAB-type stacking unit, where A and B refer to the acid and base layers, respectively. The BAB layers stack further in the crystals. The interface between the A and B layers is tightly fixed by the electrostatic interaction due to the salt formation and by the two-dimensional hydrogen bond network. In contrast, the B layers interact with each other by the weak interaction consisting of a van der Waals force. The alkylammonium sorbate monomer crystals as well as the corresponding polymer crystals have a BAAB-type layered structure, which is different from the BAB-layered structure of the muconate derivatives. The interface between the A and B layers is similar to that in the muconate crystals. In the sorbate crystals, not only the B−B but also the A−A interfaces interact with each other by a weak van der Waals force. A difference in the stacking structures between PMA and PSA is reflected in the results of a change in the powder X-ray diffraction profile for the repeated intercalations. The broadened peaks were observed for the PSA series according to the number of the repeated cycles, but not in the PMA. We have already described the intercalation ability of PSA inferior to PMA. The incorporation efficiency for the intercalation of alkylamines into the PSA crystals was always lower than the results of PMA under similar conditions. This is accounted for by the difficulty of the interlayer transmission of the chemical and structural change.

Intercalation of Functional Amines. The organic intercalation system using the carboxylic acid polymer crystals is valid for not only alkylamines but also various amines with a functional group by the selection of the chemical structure of

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Table 4. Intercalation of Functional Amines with PMA[a]

guest amine	$[NH_2]/[CO_2H]$ (mol/mol)	time (h)	conversion (%)
$H_2N(CH_2)_2OH$	10	4	74.8
$H_2N(CH_2)_3OH$	10	2	81.4
$H_2NCH_2CH_2OCH_2CH_2OH$	10	4	90.4
$H_2NCH_2(CH_2CH_2O)_3CH_2CHCH_2NH_3$	9	2	98.2
(*RS*)-$H_2NCH_2CHOHCH_3$	2	24	82.2
(*R*)-$H_2NCH_2CHOHCH_3$	2	48	88.5
$H_2N(CH_2)_6NH_2$	10	24	83.6
(9*Z*)-$H_2N(CH_2)_8CH{=}CH(CH_2)_7CH_3$	1	1	93.7
(2*E*,4*E*)-$H_2NCH_2CH{=}CHCH{=}CH(CH_2)_8CH_3$	5	8	86.9
$H_2N(CH_2)_9C{\equiv}CC{\equiv}C(CH_2)_{11}CH_3$	2	24	76.8

[a] In methanol as the dispersant.

the guest amines and the reaction conditions. Here, we describe some preliminary results of the intercalation of functional amines. Typical examples of the results for the reaction of functional amines with PMA are shown in Table 4. Amino alcohols are incorporated in a high yield, irrespective of the position of a hydroxyl group and the absolute structure of an asymmetric center. The polymer crystals modified using optically active alcohols and oligo(oxyethylene)s would be potentially applied to the chiral separation and ionic conductor materials in the future, respectively. The reaction with α,ω-alkanediamines also provides the polymer crystals modified by an amino group. In contrast, we failed in the introduction of a carboxylic acid using α,α- and α,ω-amino acids due to the low solubility of amino acids. The use of water as the dispersant resulted in the swelling of the polymers during the reaction.

Long-chain unsaturated amines are readily intercalated, as had been expected, similarly to the reaction of saturated amines. The ammonium polymer crystals showed an interesting photoreactivity of the side groups, according to the structure of the unsaturated bonds. The oleyl derivative photoreacted to give an oligomeric product, which was isolated from the polymer crystals after reactions. The diene- and diyne-modified polymer crystals provided a new type of the polymer crystals, of which the stacking layers consist of the PMA anion layers, and the countercation layers including polydiene and polydiyn sheets. The detailed results of the intercalation of some functional amines and their applications will be separately reported.

Conclusions

We have shown the fundamental features and mechanism of the intercalation of various alkylamines with PMA and PSA as the organic host compounds. The organic intercalation system consisting of layered organic polymers and guest amines has some characteristics different from a large number of known intercalation compounds as the inorganic hosts such as clays, metal phosphonates or phosphites, graphite, metal oxides, and so on.[2] For example, montmorillonite as a typical clay mineral has negatively charged layers according to the content of Al and Mg ions. In the layer, the negative charges delocalize, and the charge density is not high. In contrast, the polymer crystals as the organic intercalation host have carboxylic acid orderly arranged along the polymer chains in a high density. This structural feature is potentially used as a new kind of intercalation material for reactions, recognition, separation, and catalysis. The intercalation chemistry dates back to the 1840's, and the field of intercalation has grown since the 1960's from the chemistry and physics of graphite to various directions of research and applications using other kinds of lamellar host compounds including clays, layered double hydroxides, phosphates, phosphonates, metal carcogenides, and perovskites.[2] We believe that our organic polymer hosts are added to the lineup of intercalation hosts as new members and are expected to develop a new field of the intercalation chemistry and material science.

Experimental Section

General Procedure. NMR spectra were recorded on a JEOL JMN A400 spectrometer in D_2O or CD_3OD at ambient temperature. IR spectra were taken with a JASCO FT/IR 430 spectrometer. Wide-angle X-ray diffraction profile was measured on a RIGAKU X-ray diffractometer RINT-Ultima 2100 with Cu K_α radiation.

Materials. (*Z*,*Z*)-Muconic acid was supplied by Mitsubishi Chemical Corp., Ltd., Tokyo. Other commercial chemicals were used as received without further purification. Benzyl- and dodecylammonium (*Z*,*Z*)-muconates were prepared from (*Z*,*Z*)-muconic acid and the corresponding amine in methanol and were quantitatively isolated by precipitation with a large amount of diethyl ether, followed by recrystallization from methanol. The photopolymerization of alkylammonium (*Z*,*Z*)-muconates in the crystalline state was carried out under UV irradiation with a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W) at a distance of 10 cm through a Pyrex filter. The polymer was isolated by removing the unreacted monomer with methanol. The hydrolysis of poly(alkylammonium muconate)s was carried out in HCl methanol solution (1 mol/L) with stirring at room temperature for 1 h. IR spectroscopy confirmed the quantitative transformation. PMA: IR (KBr) 1712 ($\nu_{C=O}$) cm^{-1}.

1-Naphthylmethylammmonium (*E*,*E*)-sorbate was prepared from (*E*,*E*)-sorbic acid and 1-naphthylmethylamine in diethyl ether. Fine colorless crystals were immediately precipitated when 1-naphthylmethylamine was added to the diethyl ether solution of (*E*,*E*)-sorbic acid, followed by recrystallization from methanol. The photopolymerization of the sorbate and the hydrolysis of the resulting polymer were carried out according to the procedures similar to those for the preparation of PMA. PSA: IR (KBr) 1715 ($\nu_{C=O}$) cm^{-1}.

Intercalation of Alkylamines. A typical procedure for the intercalation is as follows unless the conditions are noted. The PMA crystals of 50 mg were dispersed in methanol solution (20 mL) of a desired amount of alkylamine and stirred at room temperature for 2 h. The polymer crystals were isolated with a glass filter, washed with a small amount of fresh methanol (ca. 10 mL), and dried in vacuo. The conversion was gravimetrically determined. The fraction of the alkylammonium carboxylate in the polymer crystals was also confirmed by gravimetric and elemental analysis and IR spectroscopy.

^{1}H NMR Analysis of Intercalated Amine. After the intercalation of amines into PMA, the incorporated amine was isolated by the subsequent hydrolysis with the deuterium hydrochloric acid and methanol-d_4 solution (1 mol/L) with stirring at room temperature for 2 h. The methanol-d_4 solution was directly analyzed by ^{1}H NMR spectroscopy to determine the composition of amines incorporated into PMA.

Acknowledgment. This work was supported by PRESTO-JST (Conversion and Control by Advanced Chemistry) and also by a Grant-in-Aid for Scientific Research (No. 13450381) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: X-ray diffraction profiles, NMR spectra, and complete data for Table 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA020869C