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Orientational Control of Guest Molecules in an Organic Intercalation System by Host Polymer Tacticity

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Abstract: Four kinds of stereoregular poly(muconic acid)s, which are synthesized by topochemical polymerization and subsequent solid-state hydrolysis, are used as the organic host materials for intercalation. We describe the reaction behavior and layered structure of intercalation compounds using stereoregular poly(muconic acid)s and *n*-alkylamines as host and guest, respectively. The packing structure of the guest alkylamines was determined by X-ray diffractions as well as IR and Raman spectroscopies. We have found that the orientation of the guest molecules is controlled by the host polymer tacticity, depending on the structure of the two-dimensional hydrogen-bonding network formed in the polymer sheets of the crystals.

Keywords: crystal engineering · host–guest systems · hydrogen bonds · intercalations · solid-state reactions

Introduction

During intercalation, a host compound recognizes guest species and reversibly accepts them, as is typically seen in inorganic materials with a layered structure, such as graphite, clays, metal phosphonates or phosphites, and metal oxides.[1] The reaction mechanism for intercalation, as well as the properties of the layered composites obtained, has been investigated for systems using inorganic host materials in combination with various kinds of organic and inorganic guest species.[2] In intercalation chemistry, the two-dimensional interlayer space of host compounds controls the topology of guest molecules or ions. When the layers bear an electric change, a layer charge density is one of the most important characteristics of inorganic layered solids. Staging behavior during intercalation has intensively been investigated for the control of a layer stacking structure. However, it is difficult to precisely control the in-layer position of guests using traditional inorganic host materials, because negative charges delocalize and the charge density is not high in the inorganic layers.

We previously reported the features and mechanism of the intercalation of various alkylamines with poly(muconic acid) (PMA) as the host compounds (Scheme 1).[3,4] This organic intercalation system consisting of layered organic host polymers and organic guest molecules has some characteristics different from those for a large number of known and previously reported intercalation materials. The organic crystals as the host compounds include the guest-trapping sites such as carboxylic acids that are regularly arranged along the organic crystals in a high density, in contrast to inorganic host materials. The organic intercalation enables us to control position and orientation of guest molecules by the design of a host crystal structure. However, a limited number of examples have been reported as the intercalation systems consisting of only organic compounds.[5] We have already demonstrated that a layered PMA is available as the host compound for the intercalation of various organic guests such as alkylamines,[4] unsaturated amines,[6] azo-containing amines,[7] and other functional amines,[4] as well as the metal cations as the inorganic guests.[8]

The stereochemistry of polymers can be controlled during solid-state polymerization by the crystal design of monomers on the basis of supramolecular chemistry and crystal engineering.[9,10] In our previous papers, we reported on the synthesis of a *meso*-diisotactic- (*m*-iso-)[11,12] and *racemo*-disyndiotactic- (*r*-syn-)[13] polymers through topochemical polymerization of (*Z*,*Z*)- or (*E*,*E*)-muconic derivatives using translational and alternate stacking structure, respectively. We also prepared new types of stereoregular polymers, *racemo*-diisotactic- (*r*-iso-) and *meso*-disyndiotactic (*m*-syn-)

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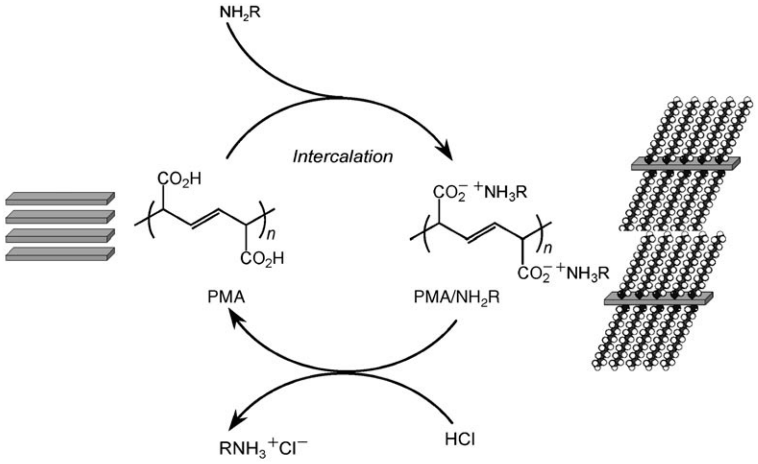
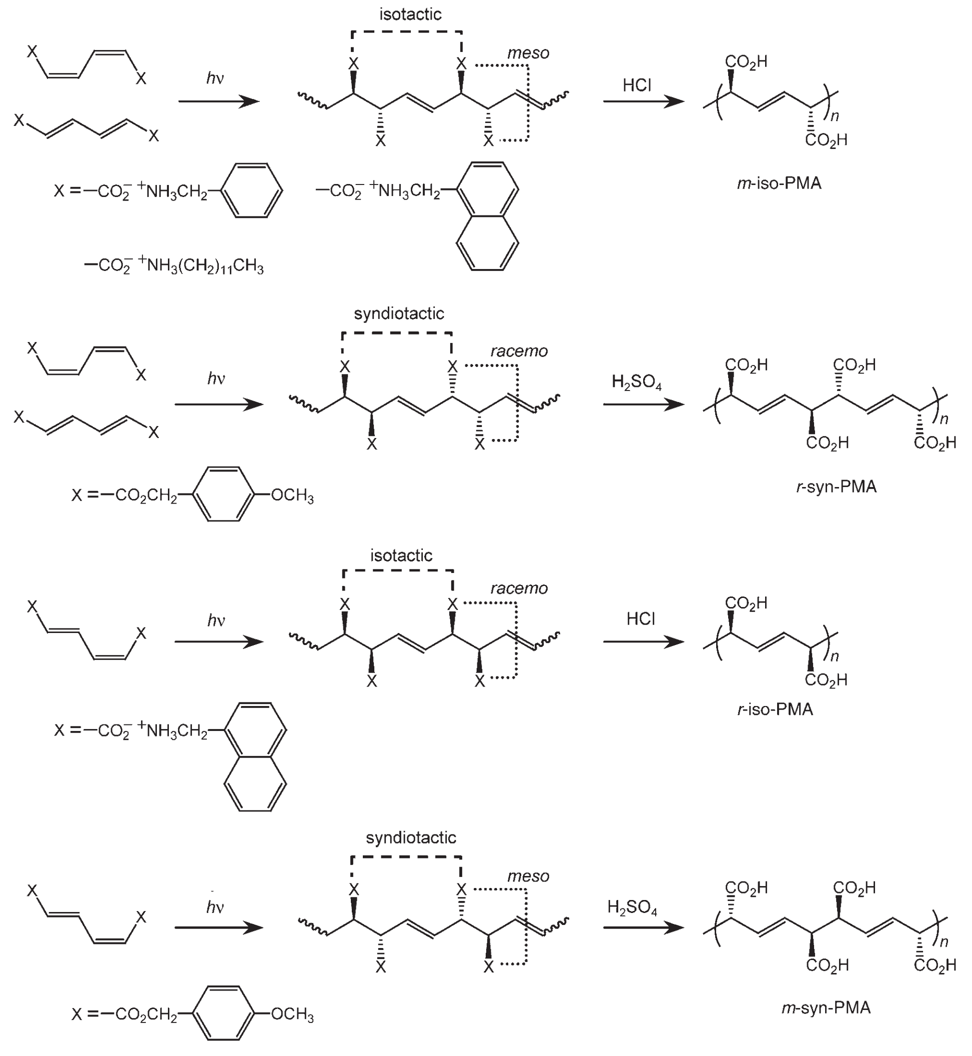


Scheme 1.

polymers using (*E*,*Z*)-muconic derivatives as the third isomer.[14] Furthermore, we found that stereoregular ammonium and ester polymer crystals are converted into the corresponding PMAs by hydrolysis in the solid state. Polymer transformation with HCl in aqueous methanol and concentrated H_2SO_4 provides various stereoregular PMAs in the form of a layered crystalline solid.[4,15] The tacticity of the polymers was maintained during the hydrolysis under acidic conditions (Scheme 2). The four kinds of host compounds have the alignment of carboxylic acids as the guest-trapping sites different from one another.

In the present study, we carried out the intercalation reactions of *n*-alkylamines using various stereoregular PMAs as the host. We revealed the reaction behavior of the intercalation, the lamellar structure of the obtained ammonium polymer crystals after intercalation, and the orientation of the guest amines inserted between the PMA sheets. The packing and conformational structures of the alkyl chains of the guest were clarified by wide-angle powder X-ray diffraction as well as IR and Raman spectroscopies. These spectroscopic measurements with a polarized or unpolarized light are often used for determining the structure of long-alkyl chain compounds, for example, *n*-alkanes, saturated and unsaturated fatty acids.[16–18] The position, line width, and splitting of each vibration mode (such as stretching, bending, and wagging) of the methylene groups provides much information about the conformation of the alkyl chains in the solid state. Because we can obtain intercalated ammonium polymers as plate- or needle-like crystals, microscopic IR spectroscopy with polarized light is useful for determining the arrangement of the methylene chains in the intercalated polymer crystals.



Scheme 2.

Results and Discussion

Intercalation with PMAs: *m*-iso-PMA acts as the host compound for an organic intercalation system as was reported previously.[4] In the present study, three other kinds of stereoregular PMAs, that is, *r*-syn-PMA, *m*-syn-PMA, and *r*-iso-PMA were tested by using various alkylamines as the guests. The PMAs were dispersed in the methanol solution of the corresponding alkylamine and stirred at room temperature for 2 h. As a result, various *n*-alkylamines were intercalated into all PMAs, similar to the intercalation with *m*-iso-PMA. The isolated yield and solubility of the products depended on the length of the alkyl group of the amines. The effect of the tacticity of the host polymers on the intercalation behavior was also determined (Table 1). When the carbon number of the alkylamines increased, the conversion to the intercalated ammonium polymers increased. The partial swelling or dissolution of the resulting polymers was observed when short-chain alkylamines less than octylamine ($x<8$) were intercalated into the PMAs except for *m*-iso-PMA. The syn-PMA crystals readily collapsed during the repeated intercalation reactions. They can be used once as the host for the intercalation, but the polymer crystals dissolve in methanol as the dispersant in the second cycle of the intercalation.

Table 1. Conversion for intercalation of *n*-alkylamines with various alkyl chain lengths into four types of PMAs.[a]

x[b]	*r*-syn-PMA	*m*-syn-PMA	*r*-iso-PMA	*m*-iso-PMA[c]
2				85.8
3				92.2
4	9.3[d]	–[d]	37.2[d]	85.5
5				93.7
6	50.3[d]	25.8[d]		89.6
7		44.9[d]		95.4
8	44.6[d]	67.7	59.6	91.0
9	73.0	92.4		
10	68.3	85.5		93.6
12	89.4	85.1	75.6	94.7
14	81.0	91.5		95.1
16	82.9	83.7		95.3
18	87.2	86.7	73.4	96.4

[a] Reaction conditions: PMA 25 mg, methanol 10 mL, $[\text{-NH}_2]/[\text{-CO}_2\text{H}]=10$, stirred for 2 h at room temperature. Conversion was determined from the fraction of the alkylammonium carboxylate in the polymer crystals after the unreacted alkylamine was removed. [b] Number of carbon atoms of *n*-alkylamine. [c] PMA 50 mg, methanol 20 mL, stirred for 1 h (ref. [4]). [d] Partial swelling.

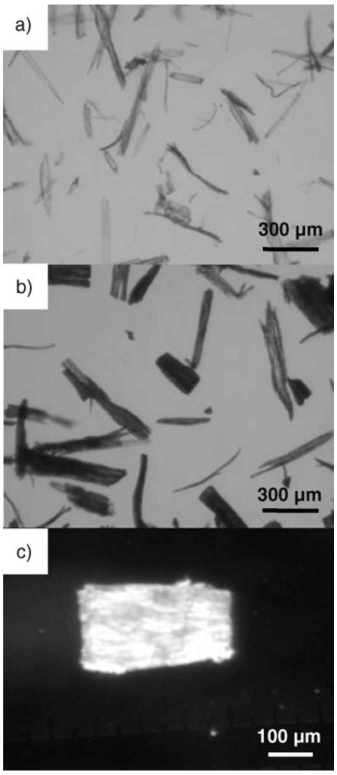
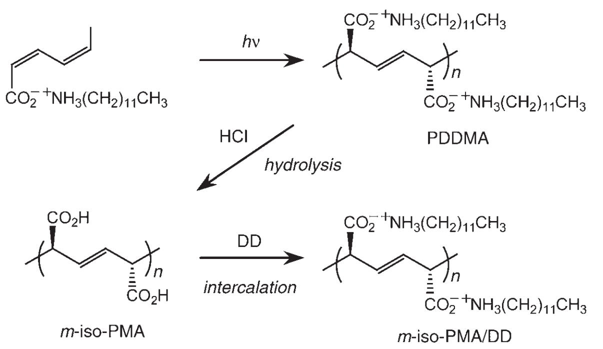


Figure 1. Microphotographs of a) *m*-iso-PMA as the host and b) *m*-iso-PMA/DD after intercalation; c) expanded photograph of *m*-iso-PMA/DD observed with polarized light.

By contrast, the crystal shape and habit of iso-PMA were maintained during the intercalation. Large platelet *m*-iso-PMA crystals that are derived from *m*-iso-poly(benzylammonium muconate) enable us to directly observe a visual change in morphology. The polymer crystals grew during the intercalation of dodecylamine (DD) as the guest amines, and the short axis of the platelet crystals increased along a layer-stacking direction to approximately 200% of the original size on average, while another axis of the crystal along the fiber direction had no change (Figure 1). A photograph under a polarizing microscope indicates the high crystallinity of the dodecylammonium polymer after intercalation (*m*-iso-PMA/DD), although the transmittance partly deteriorated.

Layered structure of intercalated compounds: Figure 2 shows the X-ray diffraction profiles for the polymers intercalated with various alkylamines from *n*-butylamine to octadecylamine (OD). The value of the interlayer spacing (d) was determined from the 2θ value for the characteristic peaks in a low-angle region in the diffraction profile, being assigned on the basis of the reported single-crystal structure for the related muconate derivatives.[10,11] Similar 2θ values were obtained for each polymer crystal after the intercalation of an alkylamine, independent of the stereoregularity of the host polymers. Furthermore, they are assigned as the (100) plane, which corresponds to the d value of 34.1, 33.9, 32.5, and 32.6 Å for *r*-syn-PMA/DD, *m*-syn-PMA/DD, *r*-iso-PMA/DD, and *m*-iso-PMA/DD, respectively. These d values for the intercalated polymers agreed well with the value ($d=31.7$ Å) for poly[di(dodecylammonium) (*Z*,*Z*)-muconate] (PDDMA) as the as-polymerized ammonium polymer crystals (Scheme 3).[3] This indicates that all the intercalations provide polymers with a similar layered structure, leading to the similar d values. The diisotactic polymer provided a simple diffraction profile, which is characterized by a series of peaks due to the (100), (200), and (300) planes as shown in Figure 2a, while another series of diffraction peaks were additionally observed in the case of the disyndiotactic



Scheme 3.

polymers (Figure 2b). In contrast to a simple increase in the *d* value (decrease in the 2*θ* values) with an increase in the carbon number (*x*) of the *n*-alkylamines for the polymer obtained from *m*-iso-PMA, the structural change in the polymers with *r*-syn-PMA was more complicated. *m*-iso-PMA/DD and *r*-iso-PMA/DD have a similar structure to each other, and *m*-syn-PMA/DD and *r*-syn-PMA/DD also have another structure, independent of the *meso–racemo* structure.

Table 2 summarizes the *d* values of the obtained ammonium polymer crystals. Figure 3 shows plots for a change in the *d* value according to the *x* value for each stereoregular polymer. Both the *m*-iso-PMA and *r*-iso-PMA crystals provided an identical slope (line a). The *d* value increases by 1.0 Å for each carbon in the alkylamines for the *m*-iso-PMA series, and that the alkyl chains of the amines are stacked in a layer with a similar tilt angle of 38°.[4] On the other hand, the X-ray powder diffraction profiles consisted of two kinds of structures for the intercalated polymers obtained from the *m*- and *r*-syn-PMAs. One of them is just the same as those for the iso-PMAs (line a), while another is a different layer structure due to the different stacking structure of the alkylammonium groups (line b).

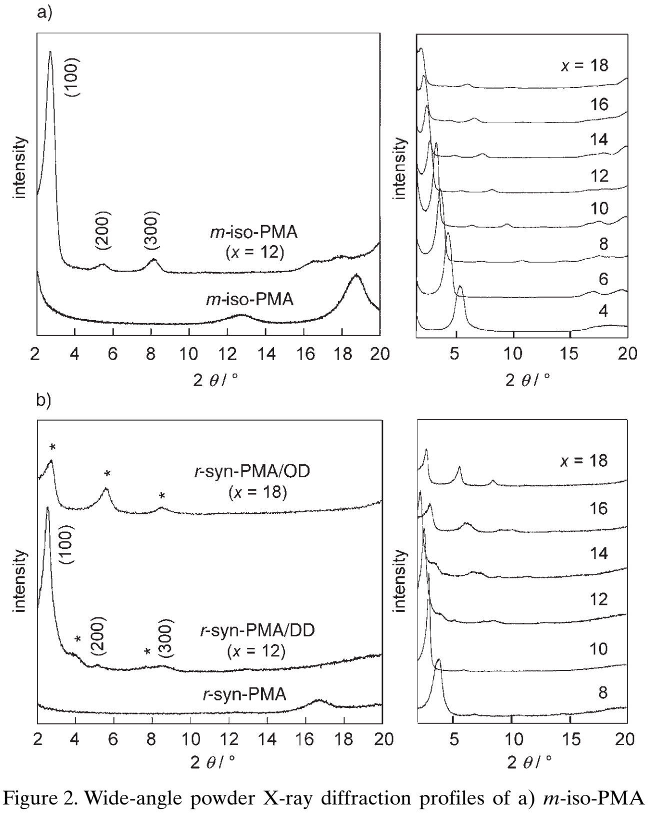


Figure 2. Wide-angle powder X-ray diffraction profiles of a) *m*-iso-PMA and b) *r*-syn-PMA intercalated with various *n*-alkylamines. *x* is the carbon number of the *n*-alkylamine used as the guest for the intercalation. The asterisk indicates another series of diffraction peaks different from those observed for *m*-iso-PMA/DD.

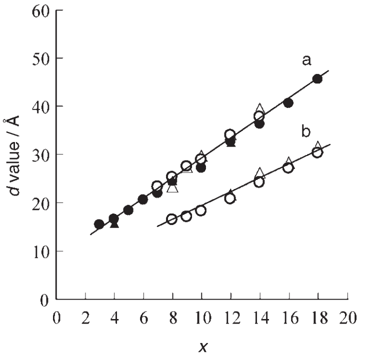


Figure 3. Change in *d* value as a function of the carbon number of *n*-alkylamines (*x*). Closed and open symbols indicate isotactic and syndiotactic polymers, respectively. Circles and triangles are *meso* and *racemo* polymers, respectively.

Table 2. *d* Values of the alkylammonium polymer crystals after intercalation of *n*-alkylamines with various alkyl chain lengths into four types of PMAs.[a]

$x^{[b]}$	*r*-syn-PMA	*m*-syn-PMA	*r*-iso-PMA	*m*-iso-PMA[c]
3				15.4
4			15.7	16.5
5				18.3
6				20.5
7		23.2		21.9
8	23.3	25.2 (16.4)	24.6	24.4
9	27.3	27.4 (17.0)		
10	29.6	28.8 (18.2)		27.1
12	34.1 (21.6)	33.9 (20.7)	32.5	32.6
14	39.4 (26.1)	37.7 (24.1)		36.2
16	(28.2)	(27.0)		40.5
18	(31.5)	(30.2)		45.5

[a] *d* Value was determined from 2*θ* value from the peak observed in a low-angle region in powder X-ray diffraction profiles. [b] Number of carbon atoms of *n*-alkylamine. [c] Ref. [4]. Values in parentheses indicate *d* value for line b in Figure 3.

The layer structure of the polymers obtained by intercalation with various PMAs is discussed on the basis of the single-crystal structure of the precursor polymer crystals. Figure 4 shows the polymer sheet structure for the *m*-iso-poly(diethyl muconate) and *r*-syn-poly[di(4-methoxybenzyl) muconate]. Two side chains that are related to the isotactic or syndiotactic relationship in vicinal repeating units are located on the same side against a polymer sheet. Another combination of the side chains assigned as the *meso*- or *racemo*-relation has a different position against a polymer sheet; they are divided into the upper and lower sides of the sheet. Namely, it is concluded that isotactic/syndiotactic and meso/racemo relationships lead to the location of the side chains at the same and different sides of the polymer sheet, respectively. The intercalation behavior is related to the in-plane location of the side chain of the polymer in the isotactic/syndiotactic relationships.

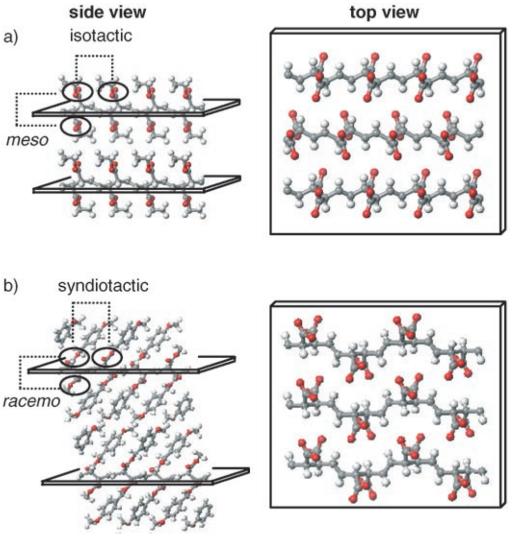


Figure 4. Position and orientation of carboxylate substituents in the side chain of stereoregular polymers. a) Side and top views of polymer sheets for *m*-iso-poly(diethyl muconate) and b) *r*-syn-poly[di(4-methoxybenzyl) muconate]. In the top views, ethyl and methoxybenzyl moieties are omitted for clarity.

Two-dimensional hydrogen bond network (HBN) and packing of guest molecules: Figure 5a, b shows each side of the 2D polymer sheets of iso-PMA and syn-PMA as well as the 2D-HBN structures for isotactic and syndiotactic ammonium polymers after intercalation. The positions and orientations of the carboxylate groups in the iso-PMA and syn-PMA crystals are similar to each other except the direction of rectangles and the sizes of each side. The rectangular areas of the 2D unit cell were 52.0 and 54.1 Å^2 for iso-PMA and syn-PMA, respectively. The similar areas result in a similar structure for the closed packing of the alkyl-chain groups with a tilt angle (38°) in the alkylammonium layer (line a in Figure 3). This inclined packing structure is suitable for the closed packing of alkyl chains similar to the typical packing structure for *n*-alkanes, fatty acids, and lipids. The direction of 2D-HBN determines the orientation of guest molecules. When iso-PMA is used as the host compounds, the guest alkyl chains are tilted in a direction orthogonal to the polymer chains. On the other hand, in the case of the syn-PMA sheet, guest alkylamines are considered to tilt in a direction parallel to the polymer chain direction by the 2D-HBN structure (Figure 5c). In the case of the syn-PMAs, an alkyl-to-alkyl interaction determines the intercalation behavior and the resulting layer structure when long alkyl-chain guests are used. Whereas, HBN is a dominant factor to determine its structure when small guests are used. The slope of line b in Figure 3 suggests a more inclined structure of the alkyl chains, but such a stacking structure is too close for the alkyl chain packing with these polymer sheets. We cannot show the exact structure of the alkyl packing in the form according to line b at the present time.

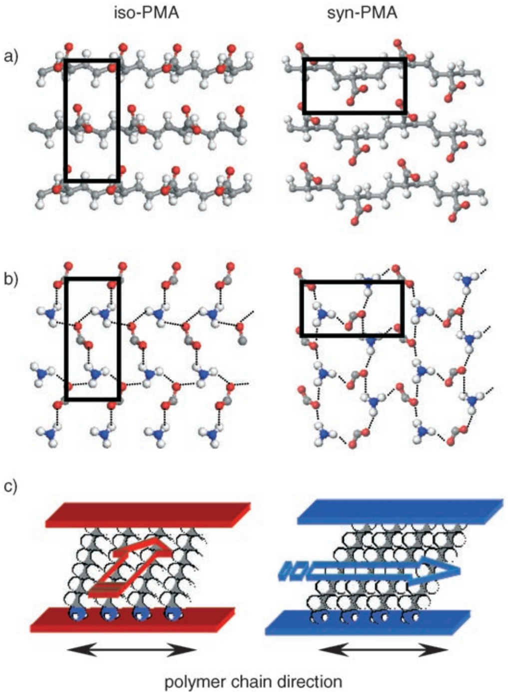


Figure 5. a) Arrangement of carboxylates on each side of the 2D polymer sheet of iso-PMA and syn-PMA as well as b) 2D-HBN structure formed in the ammonium polymers. The structure of iso-PMA was determined by the single crystal structure of isotactic ammonium polymers as the precursor, and the structure of syn-PMA was also assumed from single-crystal structure of the precursor ester polymer. c) Schematic models for the orientational structure of guest alkyl amines into the interlayer space.

Raman spectroscopic analysis: Figure 6 shows the Raman spectra for *m*-iso-PMA/DD and *r*-syn-PMA/OD, together with that for PDDMA. Both intercalated compounds have several absorption bonds due to the *trans*-zigzag structure of the alkyl chains. Bands observed at 2883 and 2848 cm^{-1} are assigned to the antisymmetric and symmetric stretching modes of the methylene groups, respectively. Peaks at 1457 and 1440 cm^{-1} are due to a methylene scissoring mode, while that observed at 1297 cm^{-1} to a twisting mode. The symmetric and antisymmetric skeletal bands of a C–C bond are seen at 1126 and 1061 cm^{-1}, respectively, being specific to the packing of the *trans*-zigzag chains. When alkyl chains take an irregular packing structure like those in a solution or melt, other broad bands are observed at different positions. Actually, however, no broad bands were observed in this study. These bands provide further information about the conformational structure of the alkyl chains.

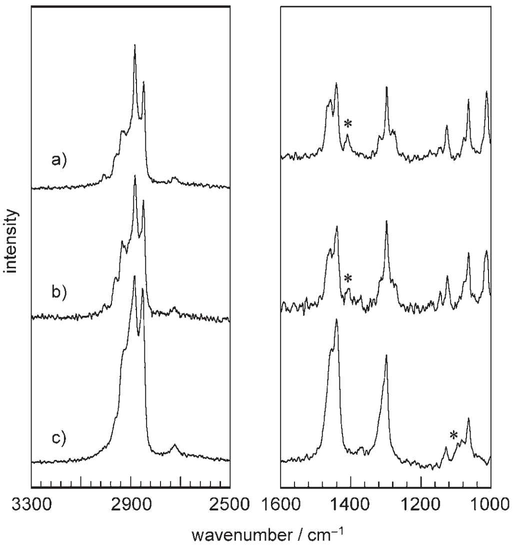


Figure 6. Raman spectra of a) PDDMA, b) *m*-iso-PMA/DD, and c) *r*-syn-PMA/OD.

First, in general, a random chain conformation containing *gauche*-type conformers has a new band around 1090 cm^{-1}, which is usually observed between bonds due to a C–C stretching at 1126 and 1061 cm^{-1}.[19] No band due to a random chain was detected in the spectra of *m*-iso-PMA/DD and PDDMA, which include all-*trans* alkyl chains. While, a weak band was observed at 1090 cm^{-1} in the spectrum of *r*-syn-PMA/OD. This suggests that the alkyl chain includes a *gauche* conformer when the guest alkylamines are introduced into the layers of the syndiotactic polymer.

Second, peaks at 1400 to 1460 cm^{-1}, attributed to a methylene scissor band, provide more intimate information regarding a conformational structure. The spectrum of *m*-iso-PMA/DD clearly showed split peaks (1457 and 1440 cm^{-1}) as well as the characteristic peak due to the $O_\perp$ subcell structure (1407 cm^{-1}). The weak and irregular lateral interaction of the guest alkyl moieties with *gauche* conformers in the *r*-syn-PMA/OD results in the broadening and disappearance of the subcell characteristic peaks.[16] The similar spectra of PDDMA and *m*-iso-PMA/DD suggest that the conformational structure of the alkyl side chains is maintained during the repetition of the intercalation and de-intercalation processes. Briefly, the host polymer sheets memorize the position of the carboxylic acids in the crystalline state, and highly control not only the position, but also the conformation of the guest molecules during the reversible reactions.

Finally, the methylene stretching regions (2800–2950 cm^{-1}) related to the intermolecular packing interaction of long-alkyl chains were investigated. The intensity ratio of the methylene antisymmetric stretch (~2880 cm^{-1}) and symmetric stretch (~2850 cm^{-1}) are widely used for the determination of the conformational disorder and packing structure.[19,20] Generally, the intensity of the antisymmetric stretching mode relative to the symmetric mode decreases when the chains have fewer lateral interactions, as is the case when the chains are dissolved or melted. Snyder et al. reported that the ratio of the intensity of the peaks at 2880 and 2850 cm^{-1} (I2880/I2850) for *n*-alkanes varied from approximately 2 in the crystalline state to 0.7 in a disordered state such as a liquid.[19,20] In this study, the I2880/I2850 ratio for PDDMA, *m*-iso-PMA/DD, and *r*-syn-PMA/OD were 1.34, 1.24, and 1.07, respectively. Similar values were obtained when other alkylamines were used as the guest molecule. The side-chain assembly in *m*-iso-PMA/DD is similar to that of PDDMA, but *r*-syn-PMA/OD implies a more disordered structure. The differences of molecular packing and conformation of the guest alkylamines result in a difference in their intercalation behavior and layered structure, depending on the structure of iso- and syn-PMA as the host.

Microscopic IR analysis with polarized light: The IR spectrum of *m*-iso-PMA/DD has peaks at around 720 cm^{-1} due to the methylene rocking mode [$r_b(CH_2)$] of the orthorhombic subcell. Generally, the $O_\perp$ subcell structure has IR bands at both 720 and 730 cm^{-1} due to the methylene rocking mode, while the characteristic absorption band at 730 cm^{-1} is very sensitive to the subcell structure and it disappears when a structure is disordered. In the spectrum of *m*-iso-PMA/DD, no peaks was observed of 730 cm^{-1} (Figure 7). Recently, Sada et al. revealed the X-ray single-crystal structure and the packing structure of the methylene chain for a series of 1-naphthylmethylammonium carboxylates with various alkyl substituents, which have a 2D-HBN similar to that observed during the intercalation of alkylamines with PMAs.[21] They confirmed the distorted orthorhombic type subcell structure of the methylene chains by X-ray structural analysis. Therefore, it is concluded that *m*-iso-PMA/DD also has similar a distorted orthorhombic type subcell structure.

The orientation of guest molecules was determined by microscopic IR spectroscopy with polarized light using an anisotropic crystalline sample of the intercalated materials. In the spectra of *m*-iso-PMA/DD, peaks due to the CH_2 rocking mode and an OCO scissoring mode around 650–750 cm^{-1} showed clear polarization properties, as shown in Figure 7. The polarization properties and polymer chain direction provide important clues for the conformational sequence of the alkyl chain. In the previous section, we described investigated that the long-chain alkylamine as the guest in the iso-PMA sheets are tilted in a direction orthogonal to the polymer chains. The result of this IR experiment with polarized light is quite consistent with the conclusion obtained from the 2D-HBN structure in Figure 5.

Conclusion

We have determined intercalation behaviors using various stereoregular polymer hosts and the lamellar structure of the obtained layered ammonium polymer crystals, as well as the conformational structure of the alkyl chains in the am-

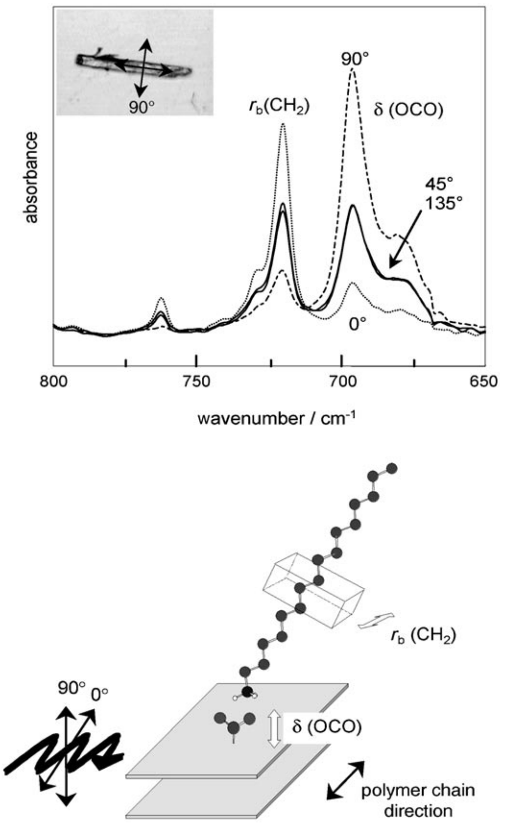


Figure 7. Polarized microscopic infrared spectrum change of *m*-iso-PMA/DD and schematic model of guest orientational structure.

monium layer by X-ray diffractions and IR or Raman spectroscopy. Powder X-ray diffractions and Raman spectroscopy provide useful information about the molecular packing structure and the conformation of guest alkylamines introduced into layered host polymer crystals. Microscopic IR spectroscopy with polarized light also provides important information about the orientational structure of guest alkylamines. Finally, we have found that the alkyl-chain guests have a regular structure consisting of an all-*trans*-planar conformation or partly containing *gauche* conformers. The difference in the conformation of the guest is due to a difference in the position of the carboxylate groups in the polymer sheets, that is, a difference in the 2D-HBN structure of the intercalated ammonium polymers. The difference in the tacticity of the host polymers provided variation in the guest orientation, that is, they are tilted in a direction orthogonal and parallel to the polymer chains in the isotactic and syndiotactic polymer sheets, respectively. Thus, we have revealed that host polymer tacticity can control the orientation of the guest alkylamines in the polymer crystals. The orientational control of guest molecules during organic intercalation will open to a way for the design of finely tunable layered materials with novel functions.

Experimental Section

Materials: (*Z*,*Z*)-Muconic acid was obtained from Mitsubishi Chemical Co., Ltd., Tokyo, or purchased from Across Co., Ltd. All the other commercial chemicals were used as received without further purification.

***meso*-Diisotactic poly(muconic acid) (*m*-iso-PMA)**: Di(dodecylammonium) (*Z*,*Z*)-muconate was prepared from (*Z*,*Z*)-muconic acid (2.45 g, 17.2 mmol) and dodecylamine (DD) (6.69 g, 36.1 mmol) in methanol (250 mL) and was quantitatively isolated by precipitation in a large amount of diethyl ether, followed by recrystallization from methanol. The photopolymerization of di(dodecylammonium) (*Z*,*Z*)-muconate (7.78 g, 15.2 mmol) was carried out in the crystalline state under UV irradiation using a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W) at a distance of 10 cm. The resulting polymer was isolated by removing the unreacted monomer with methanol. Polymer yield: 80 %. Poly[di(dodecylammonium) (*Z*,*Z*)-muconate] (PDDMA) (6.22 g) was quantitatively hydrolyzed by stirring in aqueous methanol (500 mL) containing 1 M HCl for 1 h at room temperature, resulting in the *m*-iso-PMA (1.69 g, 98 %). Poly[di(benzylammonium) (*Z*,*Z*)-muconate] and poly[di(1-naphthylmethylammonium) (*Z*,*Z*)- or (*E*,*E*)-muconate] were similarly obtained and used for the solid-state hydrolysis.

***racemo*-Diisotactic poly(muconic acid) (*r*-iso-PMA)**: Di(1-naphthylmethylammonium) (*E*,*Z*)-muconate (1.35 g, 3.0 mmol) was prepared similar to the method used for the preparation of di(dodecylammonium) (*Z*,*Z*)-muconate except for the use of (*E*,*Z*)-muconic acid, which was obtained by the thermal isomerization of (*Z*,*Z*)-muconic acid.[22] For the polymerization of the (*E*,*Z*)-muconates, the monomer crystals were placed in a Pyrex tube, which was then degassed and sealed. γ Irradiation was carried out with ^{60}Co at Osaka Prefecture University. The irradiation dose was 200 kGy at a dose rate of 48.6 kGy h^{-1}. The polymer was isolated by removal of any unreacted monomer with methanol. Polymer yield: 61 %. Hydrolysis of the resulting polymers was similarly carried out, leading to the formation of the *r*-iso-PMA (0.10 g, 39 %).

***racemo*-Disyndiotactic poly(muconic acid) (*r*-syn-PMA)**: The di(4-methoxybenzyl) (*E*,*E*)-muconates were prepared from (*E*,*E*)-muconic acid (0.52 g, 3.7 mmol), 4-methoxybenzyl chloride (1.56 g, 10.0 mmol), and potassium carbonate (0.68 g, 4.9 mmol) in *N*-methyl-2-pyrrolidone (6 mL). (*E*,*E*)-muconic acid was prepared by photoisomerization of (*Z*,*Z*)-muconic acid in the presence of iodine.[22] The suspension was stirred at room temperature for 3 d in the dark, and the reaction mixture was poured into a large amount of water. A white precipitate was filtered, dried, and then purified by silica gel column chromatography with chloroform as the eluent. Recrystallization from chloroform gave the pure di(4-methoxybenzyl) (*E*,*E*)-muconate (1.23 g, 3.2 mmol, 87 %). Photopolymerization provided *racemo*-disyndiotactic poly[di(4-methoxybenzyl) (*E*,*E*)-muconate]. Polymer yield: 81 %. The solid-state hydrolysis of the polymer resulted in the *r*-syn-PMA using conc. H_2SO_4. The obtained red suspension was filtered and washed several times with a large amount of water. *r*-syn-PMA was quantitatively isolated as a white solid (0.37 g, 100 %).

***meso*-Disyndiotactic poly(muconic acid) (*m*-syn-PMA)**: The di(4-methoxybenzyl) (*E*,*Z*)-muconates were prepared similar to the method for the preparation of the di(4-methoxybenzyl) (*E*,*E*)-muconates. γ-Radiation polymerization and the solid-state hydrolysis was carried out according to the methods similar to those for the di(1-naphthylmethylammonium) (*E*,*Z*)-muconate and poly[di(4-methoxybenzyl) (*E*,*E*)-muconate], respectively.

Intercalation: PMA crystals (25 mg) were dispersed in a methanol solution (10 mL) containing the 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 fraction of the alkylammonium carboxylate in the polymer crystals was gravimetrically determined, or by elemental analysis and IR spectroscopy.

Measurements: The NMR and IR spectra were recorded on Joel JMN A400 and Jasco FT/IR 430 spectrometers, respectively, at ambient temperature. The wide-angle X-ray diffraction profile was recorded on a

Rigaku X-ray diffractometer Rint-Ultima 2100 with $Cu_{K\alpha}$ radiation (λ = 1.5418 Å). The Raman spectra were recorded on a Nicolet Magna 750/Raman spectrometer equipped with a Nd/YAG (wavelength 1064 nm) laser for the excitation radiation at the Osaka Municipal Technical Research Institute. The polarized IR spectra were recorded using a JASCO FT/IR 430 spectrometer and IRT-30 infrared microscope system equipped with a polarizer accessory. The specimens were directly measured by a transmission or reflection adsorption method, or put between KBr plates, pressed, and then measured.

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