

Organic Intercalation with Layered Polymer Crystals Consisting of Diisotactic and Disyndiotactic Polymer Chains

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We have investigated the intercalation reactions of alkylamines as the guest molecules into diisotactic and disyndiotactic poly(muconic acid)s as the host compounds. The intercalation behavior depends on the tacticity and hydrogen bond network structure of the polymers. When *n*-alkylamines were intercalated into diisotactic poly(muconic acid) crystals, the reaction was reversible. In contrast, a reaction with disyndiotactic poly(muconic acid) was irreversible. The stacking structure of the guest amine in the interlayer space is discussed based on the interlayer spacing values and the dependence on the carbon number of the used alkylamines. The intercalation of a functional guest amine was also carried out.

Key words: intercalation, tacticity, polymer crystal, layer structure, host-guest chemistry

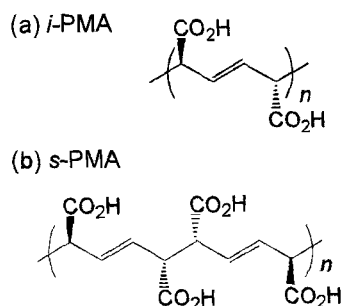
1. INTRODUCTION

Inorganic-organic hybrid materials have been attracting much attention in the field of polymer and materials chemistry. Because of the combination of two or more components with different properties implies great potential to create a novel advanced material^{2,3}. Intercalation is the system that molecules or ions as the guest species are reversibly inserted into a layered host solid^{4,5}. Various functional organic species as the guests are introduced into inorganic host materials in order to develop advanced materials for catalysis, photonic devices, nanocomposites, and so on³. Inorganic materials have structural and chemical stabilities superior to organic compounds, but structural design is hard to do. In contrast, the fine structure and properties of organic compounds are controlled by artificial molecular design. Recently, we reported a new kind of intercalation system using organic host materials⁶. Organic host crystals combined with organic guest molecules are expected to provide any specific features through not only host-to-guest but also guest-to-guest interactions. In an organic intercalation system, we can design both guest and host organic species based on their molecular structures.

We have previously reported that *meso*-diisotactic-1,4-*trans*-polymer is produced in the form of polymer crystals by the topochemical polymerization of alkylammonium (*Z,Z*)- or (*E,E*)-muconates as the 1,3-diene dicarboxylic acid monomers under photoirradiation in the crystalline state⁷. These polymer crystals are converted into diisotactic poly(muconic acid) (*i*-PMA) by hydrolysis with HCl in an aqueous methanol [Scheme 1(a)]. The reaction heterogeneously proceeds to provide *i*-PMA as the crystalline solid. *i*-PMA has a layered structure, which is available as the host compound for the intercalation of various organic guests such as

alkylamines⁶, unsaturated amines⁸, azo-containing amines⁹, and other functional amines¹⁰, as well as the alkali cations as the inorganic guest¹¹. More recently, we have revealed that similar intercalation also undergoes for the crystals of disyndiotactic poly(muconic acid) (*s*-PMA) [Scheme 1(b)], which is obtained from di(4-methoxybenzyl) muconate as the starting monomer via similar topochemical polymerization and the subsequent hydrolysis with conc. H₂SO₄ in the solid state¹².

Scheme 1



In this paper, we report the intercalation of various *n*-alkylamines using two types of host polymers, *i*-PMA and *s*-PMA, to investigate the effects of the tacticity of polymer chains on their layer structure in the crystals and intercalation properties.

2. EXPERIMENTAL

2.1 Materials

(*Z,Z*)-Muconic acid was supplied from Mitsubishi Chemical Co., Ltd., Tokyo. Other commercial chemicals were used as received without any further purification.

Dodecylammonium (*Z,Z*)-muconate was prepared from (*Z,Z*)-muconic acid and dodecylamine in methanol and were quantitatively isolated by precipitation with a

large amount of diethyl ether, followed by recrystallization from methanol. The photopolymerization of dodecylammonium (*Z,Z*)-muconate was carried out in the crystalline state under UV irradiation with a high-pressure mercury lamp (Toshiba SHL-100-2, 100W) 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(dodecylammonium muconate) was carried out in HCl methanol solution (1 mol/L) with stirring at room temperature for 1 h. IR spectroscopy confirmed the quantitative transformation. *i*-PMA: IR (KBr) 1703 ($\nu_{\text{C=O}}$), 983 ($\nu_{\text{trans-CH=CH}}$) cm^{-1} .

Di(4-methoxybenzyl) (*E,E*)-muconates were prepared by the reaction of (*E,E*)-muconic acid with 4-methoxybenzyl chloride in the presence of potassium carbonate in hexamethylphosphoramide. Photopolymerization was carried out similarly to the method for the polymerization of dodecylammonium muconate. The hydrolysis of poly(4-methoxybenzyl muconate) was carried out in conc. H_2SO_4 at room temperature for 1 h. IR spectroscopy confirmed quantitative transformation. *s*-PMA: IR (KBr) 1712 ($\nu_{\text{C=O}}$), 974 ($\nu_{\text{trans-CH=CH}}$) cm^{-1} .

2.2 Intercalation

A typical procedure for the intercalation is as follows. The *i*- or *s*-PMA crystals of 25 mg were dispersed in methanol solution (10 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 fraction of the alkylammonium carboxylate in the polymer crystals was determined gravimetrically, or by elemental analysis and IR spectroscopy.

2.3 Measurements

NMR and IR spectra were recorded on a JOEL JMN A400 and JASCO FT/IR 430 spectrometer, respectively at an ambient temperature. Wide-angle X-ray diffraction profile was recorded on a RIGAKU X-ray diffractometer RINT-Ultima 2100 with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

3. RESULTS AND DISCUSSION

3.1 Intercalation Behavior

Figure 1 shows the effect of the chain length of guest amines on the yield of the resulting ammonium polymer for the intercalation of various alkylamines using *i*-PMA and *s*-PMA as the host polymers. When *i*-PMA was used, all *n*-alkylamines were intercalated into the host acid polymer to yield the corresponding ammonium polymers in a high conversion, independent of the length of the alkyl group. On the other hand, in the case of *s*-PMA, intercalation with short alkylamines (carbon atom number (m) < 8) resulted in a low yield and the swelling of the resulting polymers was observed in methanol as the dispersant. Long alkylamines underwent intercalation into *s*-PMA in a high conversion without swelling, similarly to the intercalation into *i*-PMA.

The difference in the intercalation behaviors for *s*-PMA and *i*-PMA is possibly due to a difference in the

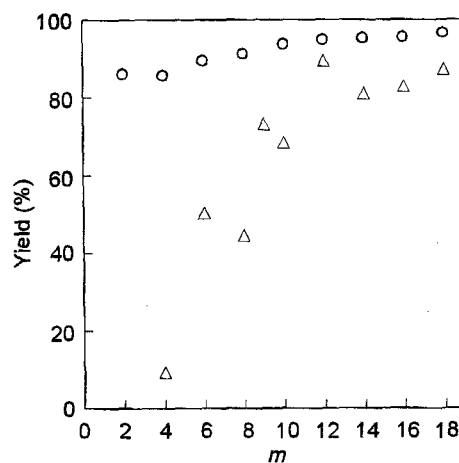


Fig. 1 Effect of the carbon number of *n*-alkylamine (m) on the yield of ammonium polymer for intercalation into (○) *i*-PMA (cited from ref. 6) and (△) *s*-PMA; $[-\text{NH}_2]/[-\text{CO}_2\text{H}] = 10$.

polymer–polymer interactions in the PMA crystals as the host. The structure of hydrogen bond networks formed in the resulting ammonium polymer crystals is different from each other. The ammonium polymer crystals obtained by the intercalation with *i*-PMA have two-dimensional hydrogen bond networks formed at an interface between the carboxylate anion and ammonium counteranion layers⁷ (Figure 2). This structure is the identical to that observed for the polymer crystals directly obtained by topochemical polymerization of the corresponding monomer.

The intercalation using *s*-PMA provides polymer crystals with a different type of hydrogen bond network. It may be zero- or one-dimensional hydrogen bond network. This is supported by the irreversibility of intercalation using *s*-PMA as the host. It has been reported that the layer structure is maintained during the intercalation with *i*-PMA. Consequently, the intercalation of dodecylamine can be done repeatedly. In contrast, *s*-PMA is once used for the intercalation of dodecylamine successfully. In the second cycle of the intercalation, the polymer crystals dissolved in methanol as the dispersant. This suggests that the ammonium polymer crystals derived from *i*-PMA have “robust” layered structure by two-dimensional hydrogen bond network, while those from *s*-PMA have “fragile” layered

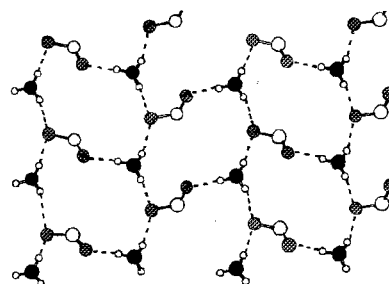


Fig. 2 Two-dimensional hydrogen bond network of ammonium polymer crystals obtained by intercalation with *i*-PMA.

structure by low-dimensional ones. The hydrogen bond network takes an important role for the organic intercalation system.

3.2 Layer Structure

Figure 3 shows the diffraction profiles of the ammonium polymer crystals obtained by the intercalation of *i*-PMA and *s*-PMA with various *n*-alkylamines. An intensive peak was observed for the polymers using *i*-PMA at $2\theta = 1.9\text{--}5.4^\circ$, depending on the alkyl-chain length. When the m value increased from 4 to 18, the interlayer spacing (d) increased from 15.4 to 45.5 Å. Here, the d -values were estimated from the 2θ values and the single crystal structures of some related muconates. In the powder X-ray diffractions in a series of the polymer obtained from *s*-PMA [Figure 3(b)], the profile changed in a different manner according to the alkyl length. When the m value was 8 and 10, single peak was observed at 3.8 and 3.0° , which are corresponding to 23.3 and 29.6 Å as the d -value, respectively. In the profiles for the polymers obtained with long alkylamines ($m = 16, 18$), several peaks were observed at a wider angle region. In the reaction with intermediate amines ($m = 12, 14$), the both series of the diffraction were detected. Namely, two kinds of characteristic peaks exist when dodecylamine and tetradecylamine are used.

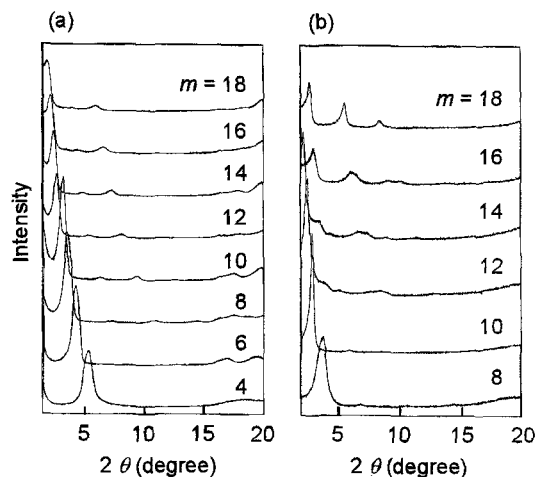


Fig.3 Wide-angle powder X-ray diffraction profiles of (a) *i*-PMA and (b) *s*-PMA intercalated with various *n*-alkylamines. The m is the carbon number of *n*-alkylamine used as the guest for intercalation.

Figure 4 shows a change in the d -values dependent on the size of the intercalated *n*-alkylamines. As has previously been reported for the *i*-PMA intercalation⁶, the d -value linearly increases with the carbon number of the guest amines and thickness of the ammonium layer increases by 1.0 Å for each carbon of *n*-alkylamine. We have also concluded that the alkyl chains of the amines are stacked in the layer with a similar tilt structure ($\omega = 38^\circ$), as shown in Figure 5. In the case of *s*-PMA, the intercalated alkylamines have two types of the stacking patterns in interlayer space between the polymer sheets. Stacking type A includes the inclined structure of the

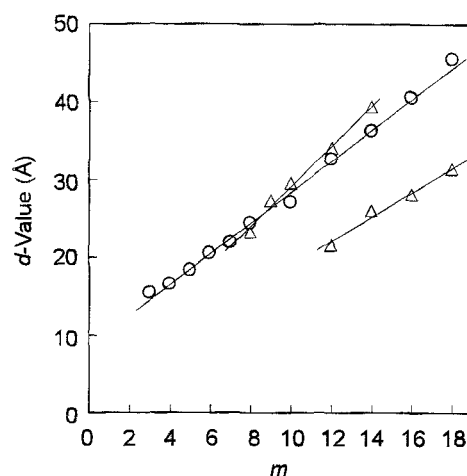


Fig.4 Change in d -value as a functional of the carbon number of *n*-alkylamine (m) for (O) *i*-PMA (cited from ref. 6) and (Δ) *s*-PMA intercalated with the corresponding *n*-alkylamine.

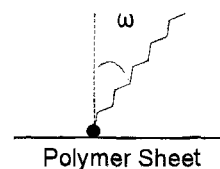


Fig.5 Tilt structure of alkylamine intercalated between polymer sheets. $\omega = 38^\circ$ for *i*-PMA as the host and ca. 50° (A type) and 0° (B type) for *s*-PMA as the host.

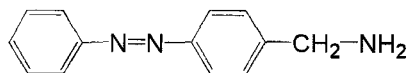
alkyl chains of the amines, which are stacked in the layer with a tilt structure (ω ca. 50°) similar to *i*-PMA. Stacking type B has a vertical structure ($\omega = 0^\circ$).

The polymer crystals obtained by the intercalation of *n*-alkylamines with $m \geq 12$ are classified into A type, while the polymer crystals obtained by the intercalation of alkylamines with $m \leq 14$ are B type. The arrangement of guest molecules is determined by the packing of alkyl chains when long alkylamines are used as the guest. When the alkyl-chain length is shorter, the guest molecules are influenced by the tacticity of the host polymer. The intermediate size in the alkyl chain length ($m = 12, 14$) results in both A and B type stacking structures, as was mentioned above. In the intercalation reaction with *i*-PMA, the packing structure is independent of the length of guest alkylamines because of the same tendency of the both interactions. Guest-to-guest and host-to-host interactions favor the A type stacking in the ammonium polymers derived from *i*-PMA due to the identical spacing of 5 Å among hydrogen bond networks and alkyl-chain packing^{10,13}. In the intercalation using *s*-PMA, the packing structure is dependent on the length of guest ones. Guest-to-guest interaction is a predominant packing factor when longer alkylamines are the guests, and host-to-guest interaction becomes important when shorter ones used.

3.3 Intercalation of Functional Amine

We also carried out the intercalation of 4-phenylazobenzylamine as the functional guest molecule (Scheme

Scheme 2



2) into *s*-PMA, similarly to *i*-PMA⁹. The absorption band due to the *trans*-azobenzene chromophore inserted into *s*-PMA shifted toward a shorter wavelength region ($\lambda_{\text{max}} = 304$ nm), compared with that of a monomeric azobenzene in a dilute ethanol solution ($\lambda_{\text{max}} = 323$ nm). This is similar to the intercalation behavior with *i*-PMA. This is explained by interaction between chromophores in the aggregates. According to the MacRae and Kasha theory¹⁴, a blue shift is observed when chromophores aggregate in head-to-head parallel orientation (H-aggregate). The H-aggregate of the azobenzene derivatives in the interlayer space of *s*-PMA suggests that 4-phenylazobenzylamine has a vertical packing structure, similarly to the structure of small *n*-alkylamines in *s*-PMA.

4. CONCLUSIONS

We have revealed the intercalation behavior of *s*-PMA and *i*-PMA as the host compounds, which have sheet structures different from each other. The hydrogen bond network between carboxylate anion and counter-cation layers is important for this organic intercalation system. A difference in the tacticity of the host polymers influences to guest-to-guest and host-to-guest interactions. A design of the host structure is important to control guest-to-guest and host-to-guest interactions for the organic intercalation system.

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