Synthesis of New Stereoregular Host Polymers for Organic Intercalation by Solid-state Hydrolysis Using Layered Syndiotactic Polymer Crystals

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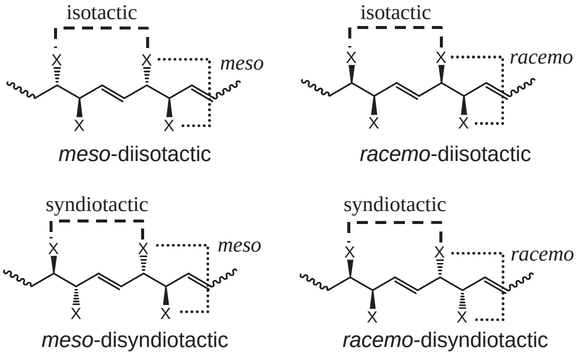
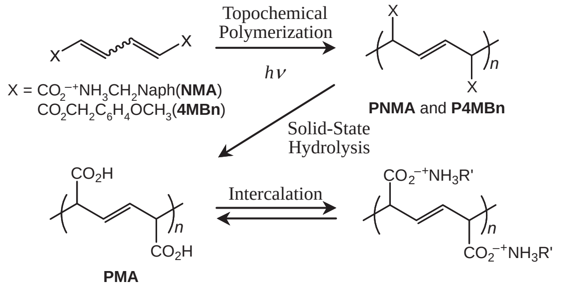
meso- and *racemo*-disyndiotactic muconate polymers, which were prepared by the solid-state polymerization of the substituted benzyl esters of muconic acid, were converted to the corresponding stereoregular poly(muconic acid)s with a layered structure by solid-state hydolysis to examine their feature as the host polymers for organic intercalation.

Solid-state organic reactions attract significant interest because of many advantages compared with conventional organic reactions in a solution.[1] A solid-state reaction often provides a target product with a high conversion and selectivity, i.e., in approximately 100% yield. When solid-state reactions include no isolation and purification processes, they are environment-friendly synthetic methods. A large number of reactions have been developed to obtain specific products during the solid-state reactions under topochemical control with the aid of supramolecular chemistry as well as modern crystal engineering.[2] We have reported supramolecular control over the stereochemistry of polymers obtained by the solid-state polymerization of 1,3-diene monomers (Scheme 1).[3] By using symmetry in monomer crystals, *meso*- and *racemo*-diisotactic 1,4-*trans*-polymers are produced by the topochemical polymerization of 1-naphthylmethylammonium muconates under photoirradiation in the crystalline state.[4] Similarly, disyndiotactic polymers were obtained by the polymerization of 4-methoxybenzyl muconates with an alternative monomer stacking in the crystals.[5] We previously reported that a diisotactic poly(muconic acid) is prepared from poly(alkylammonium muconate)s with the corresponding stereochemical structure by solid-state hydrolysis, and used as the host compounds for organic intercalation.[6] The organic intercalation system using polymer crystals as the hosts has some characteristics different from those of a large number of known intercalation compounds as inorganic hosts.[7] While the fine tuning of the structure of inorganic hosts are difficult, organic hosts enable us to design a structure and function by controlling the position and orientation of carboxylic acid as the guest-trapping site in polymer sheets via the control of the host polymer tacticity. Recently, we have found that syndiotactic ester polymers are transformed into poly(muconic acid) (**PMA**) in the form of crystals via a solid-state reaction process in a quantitative conversion as well as ammonium polymers.



Scheme 1.

In this communication, we report the solid-state transformation of muconate polymer crystals into various kinds of stereoregular **PMA**s with a layered structure, and the preliminary results of the intercalation of *n*-alkylamines using the new types stereoregular **PMA** crystals with different tacticities (Scheme 2).



Scheme 2.

Transformation from the 1-naphthylmethylammonium polymers (**PNMA**), which were obtained from 1-naphthylmethylammonium muconates (**NMA**) after UV or γ-ray irradiation in the crystalline state, to the corresponding **PMA** was achieved by hydrolysis in the solid state, dispersed in methanol containing an aqueous HCl with stirring at room temperature for 1 h. The tacticity of the polymers was maintained during the hydrolysis. For example, *meso*- and *racemo*-diisotactic muconate polymers were converted to *meso*- and *racemo*-diisotactic poly(muconic acid)s (***m*-iso-PMA** and ***r*-iso-PMA**), respectively in the form of crystalline solids. It was supported by the NMR spectra of the polymers, which were further transformed into a methanol-soluble ammonium polymer. The disyndiotactic polymers were prepared from the muconic ester derivatives, whereas all the polymerizable ammonium monomers favor translational molecular stacking leading to diisotactic polymer formation during the topochemical polymerization process. The 4-methoxybenzyl muconates (**4MBn**) provided *meso*- and *racemo*-disyndiotactic polymers. The obtained ester polymer crystals were transformed into the corresponding disyndiotactic **PMA** crystals (***m*-syn-PMA** and ***r*-syn-PMA**) by hydrolysis with concd H_2SO_4 as shown in Table 1. The hydrolysis reaction proceeded heterogeneously and the quantitative transformation from the ester to the acid was completed within 1 h at room temperature. The ester polymer crystals rapidly turned to a deep red color in concd

Table 1. Hydrolysis of stereoregular diene polymers under various conditions

Precursor polymer[a]	Acid	Time/h	Hydrolysis results[b]
***m*-iso-PNMA**	1 M HCl aq/MeOH	1	Quantitatively
***r*-iso-PNMA**	1 M HCl aq/MeOH	1	Quantitatively[c]
***m*-syn-P4MBn**	concd H_2SO_4	1	Quantitatively
***r*-syn-P4MBn**	concd H_2SO_4	1	Quantitatively
	CF_3CO_2H (neat)	168	Partly[d]
	30% HBr/CH_3CO_2H	24	No reaction
	64% H_2SO_4	24	No reaction
	concd HCl	24	No reaction
***m*-iso-P3MBn**	concd H_2SO_4	1	Quantitatively[e]
	30% HBr/CH_3CO_2H	24	No reaction
	concd HCl	24	No reaction
***m*-iso-P4ClBn**	concd H_2SO_4	1	No reaction

[a] ***m*- and *r*-iso-PNMA**: *meso*- and *racemo*-diisotactic poly(1-naphthylmethylammonium muconate), ***m*- and *r*-syn-P4MBn**: *meso*- and *racemo*-disyndiotactic poly(4-methoxybenzyl muconate), ***m*-iso-P3MBn**: *meso*-diisotactic poly(3-methoxybenzyl muconate), ***m*-iso-P4ClBn**: *meso*-diisotactic poly(4-chlorobenzyl muconate). [b] Hydrolysis proceeded in the solid state. Conversion was determined by gravimetric analysis and IR or NMR spectroscopy. [c] 51% isolated yield. [d] 41% conversion. [e] With dissolution.

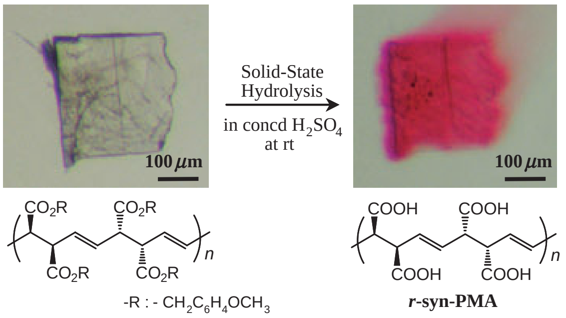


Figure 1. Change in color during the solid-state hydrolysis of *racemo*-disyndiotactic poly(4-methoxybenzyl muconate) in concd H_2SO_4 after 1 min.

H_2SO_4, and then H_2SO_4 as the medium also became colored around the crystal (Figure 1). Both the crystal and medium turned colorless when poured into water. The coloration is likely due to the formation of stable benzyl cationic species during the reaction. In contrast to the facile reaction in concd H_2SO_4, several other attempts led to no reactions or partial hydrolysis under various conditions (Table 1). For example, no reaction proceeded using hydrochloric acid in a methanol solution. A concentrated hydrochloric acid, 30% hydrogen bromide in acetic acid, and 64% sulfuric acid never hydrolyzed the ester polymer even after 24 h at room temperature. We recovered the starting ester polymer in 99, 92, and 94% yields, respectively. Trifluoroacetic acid gave a partially hydrolyzed polymer even after a 1-week reaction. The solid-state transformation in concd H_2SO_4 was available for the preparation of **syn-PMA**s, but not for the synthesis of **iso-PMA**s with a layered structure; the diisotactic ester polymers, e.g., poly(3-methoxybenzyl muconate) (**P3MBn**), were soluble in concd H_2SO_4 during the hydrolysis. Poly(4-chlorobenzyl muconate) (**P4ClBn**) was not hydrolysed at all under similar conditions. Hydrolysis behavior was dependent on their isotactic–syndiotactic structure and a substituent on a benzyl ester group, but not the *meso–racemo* structure.

When **iso-PMA** was dispersed in the methanol solution of alkylamines and stirred at room temperature for 2 h, a change in the morphology of crystals was observed during the intercalation accompanying the formation of the corresponding ammonium polymer crystals.[6a] A high crystallinity and crystal morphology were maintained during the series of reactions consisting of polymerization, hydrolysis, and intercalation, when a polymer has a diisotactic repeating structure. We also succeeded in the solid-state hydrolysis of syndiotactic ester polymers and the intercalation of alkylamines with **syn-PMA** similar to the isotactic polymers. Powder X-ray diffraction profiles confirmed the layered structure of the ammonium polymers after the intercalation of alkylamines for the both cases using **iso-** and **syn-PMA**s. However, the intercalation behavior was dependent on iso- and syndiotactic structures. This is due to the difference in the structure of the two-dimensional hydrogen-bond network formed between the carboxylate anions and the ammonium cations in the polymer sheets. Further details of the effect of the polymer tacticity on the layer structure and guest molecule arrangement are now under investigation using IR and Raman spectroscopies as well as an X-ray structural analysis.

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