

Solvent-Free Synthesis of Layered Polymer Crystals

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ABSTRACT: A new solvent-free synthetic process of layered polymer crystals as novel organic intercalation materials from (*Z, Z*)-muconic acid is described. This process includes the monomer synthesis, topochemical polymerization, transformation to poly(muconic acid), and intercalation. Alkylammonium muconate monomers were prepared by grinding muconic acid and the corresponding alkylamines in a ceramic mortar without any solvent. Topochemical polymerization of the alkylammonium muconates in the crystalline state was carried out under UV irradiation with a high-pressure mercury lamp or sunlight. Transformation from poly(alkylammonium muconate) to poly(muconic acid) was achieved by thermolysis at 250 °C under reduced pressure with a maintenance of their crystallinity. Intercalation of alkylamines into the polymer crystals proceeded by grinding poly(muconic acid) and alkylamine similar to the monomer synthesis. This process is a new type of polymer synthesis using green and sustainable materials and reactions as the solvent-free system.

KEY WORDS Topochemical Polymerization / Polymer Crystal / Intercalation / Solvent-Free Organic Reaction / Green Chemistry / Muconic Acid /

Intercalation is an interesting phenomenon that guest molecules are reversibly inserted into a layered host compound with the maintenance of their layered structure.¹ While many kinds of organic and inorganic guest compounds have already been reported, host compounds are always inorganic materials such as graphite, clay, and metal oxides.^{2–6} Recently, we have reported that poly(muconic acid) crystals act as a novel organic intercalation host.^{7,8} The polymer crystals are obtained from the topochemical polymerization of alkylammonium muconates and the subsequent hydrolysis.⁹ All the topochemically polymerizable monomer crystals of alkylammonium salts have a layered structure; the layer of muconate dianions is sandwiched with the layers of alkylammonium cations.^{9–11} The layered structure is preserved during the polymerization and the subsequent transformation. The intercalation system is important to synthesize functional polymer crystals that cannot be obtained by the direct topochemical polymerization in the crystalline state.

In our previous study, the intercalation of alkylamine into the poly(muconic acid) crystals was carried out heterogeneously with a polar organic solvent as the dispersant. Reaction behaviors depended on the kind of used the amine and the dispersant. For the intercalation of *n*-alkylamine, a high conversion was achieved in the reaction dispersed in methanol.⁷ In contrast, the polymer crystals dissolved in methanol during an attempt to intercalate branched alkylamine. Insoluble alkylamines are not intercalated in a methanol dispersion system.

The solubility of the amines and the resulting polymers into a dispersant determines the process for the organic intercalation.

Recently, the concept of green sustainable chemistry was proposed and many approach of environmentally benign organic synthesis have been reported.^{12,13} In the twelve principles of green chemistry,¹² it is noted that the use of auxiliary substances (*e.g.*, solvents and separation agents) should be eliminated whenever possible and be innocuous when used. The reactions in the solid-state are one of the environmentally benign reactions in terms of unnecessary any solvents. Many kinds of organic reactions proceed even in the solid state similar to in solution.^{14–19}

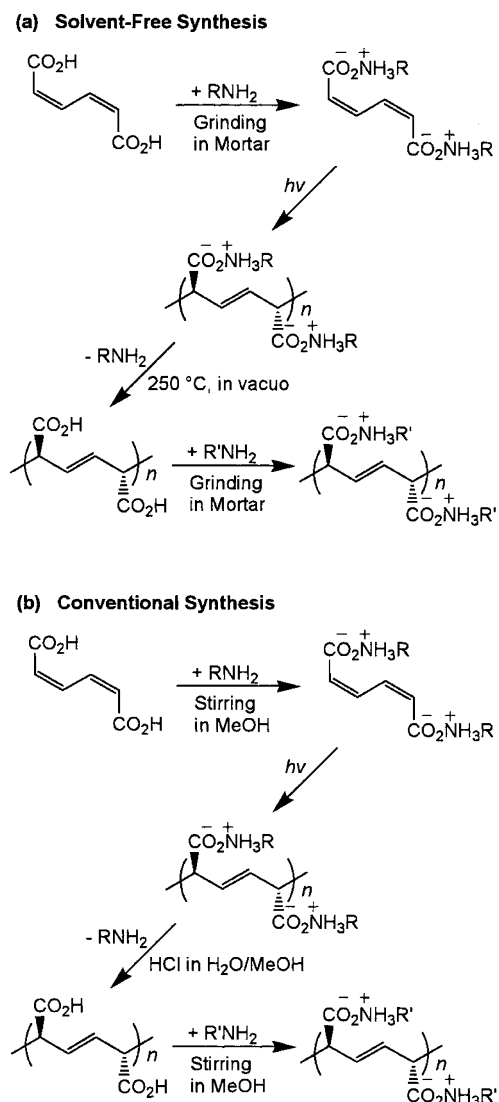
In this paper, we describe the solvent-free reactions of the polymer crystals synthesis in each step including monomer synthesis, polymerization, and transformation to poly(muconic acid) as well as the intercalation, all of which are carried out in the solid state (Scheme 1). The solvent-free reactions with several alkylamines are demonstrated as the model of the synthesis of functional polymer crystals. The results are compared with those for the previously reported conventional procedures using organic solvents.

EXPERIMENTAL

General Procedure and Measurements

(*Z, Z*)-Muconic acid was supplied by Mitsubishi Chemical Co., Ltd., Tokyo. Benzylamine and dode-

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Scheme 1. Synthesis of the organic intercalation materials of (a) solvent-free procedure and (b) conventional procedure.

ylamine were commercially available and used without further purification. The IR spectra were recorded on a JASCO FT-IR 430 spectrometer. The powder X-Ray diffraction profiles were measured on a Rigaku RINT2000 diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

Typical Procedure for Solvent-Free Synthesis with Benzylamine

Solvent-Free Synthesis of Benzylammonium (*Z,Z*)-Muconate. A mixture of 0.929 g (6.54 mmol) of (*Z,Z*)-muconic acid and 1.40 g (13.1 mmol) of benzylamine was ground in a ceramic mortar for 0.5 h. The reaction mixture changed from a slurry to a powder within a few minutes. The product was confirmed by IR spectroscopy and powder X-Ray diffraction. The isolated yield was gravimetrically determined after rapid washing with 50 mL of diethyl ether. ^1H NMR (D_2O , 400 MHz) δ 7.33 (Ar, 10 H), 6.85 (CH = CH–CH = CH,

2 H), 5.82 (CH = CH–CH = CH, 2 H), 4.05 (CH₂, 4 H); IR (KBr) 1585 ($\nu_{\text{CH}=\text{CH}-\text{CH}=\text{CH}}$) cm^{-1} , 1507 ($\nu_{\text{C}=\text{O}}$) cm^{-1} ; powder X-Ray diffraction (Cu- $K\alpha$) $2\theta = 4.82, 9.84, 17.76, 18.28, 20.00, 21.74, 23.56, 24.34, 25.32, 27.14, 27.50, 29.08, 30.48, 32.70, 33.04, 35.54^\circ$.

Photopolymerization of Benzylammonium (*Z,Z*)-Muconate. The photopolymerization was carried out using a high-pressure Hg lamp (Toshiba SHL-100-2, 100 W) at a distance of 10 cm with a Pyrex filter or under sunlight. Monomer crystals prepared by the solvent-free synthesis were used without further purification. After the polymerization, the unreacted monomer was removed using a large amount of methanol. IR (KBr) 1526 ($\nu_{\text{C}=\text{O}}$) cm^{-1} ; 995 ($\delta_{\text{trans}-\text{CH}=\text{CH}}$) cm^{-1} ; powder X-Ray diffraction (Cu- $K\alpha$) $2\theta = 5.11, 10.16, 15.38, 17.36, 18.22, 20.51, 25.80, 29.40, 31.43, 32.53^\circ$.

Thermolysis of Poly(benzylammonium muconate). Poly(benzylammonium muconate) (0.196 g) was heated at 250 °C for 2 h *in vacuo* in a glass tube oven. The transformation to poly(muconic acid) was confirmed by IR spectroscopy and powder X-Ray diffraction. IR (KBr) 1707 ($\nu_{\text{C}=\text{O}}$) cm^{-1} ; powder X-Ray diffraction $2\theta = 18.61, 26.87, 36.29^\circ$.

Intercalation of Benzylamine into Polymer Crystals. Poly(muconic acid) (0.272 g) and benzylamine (0.411 g) were mixed and ground in a ceramic mortar for 0.5 h, similar to the solvent-free synthesis of the benzylammonium muconate monomer. The intercalation into polymer crystal was confirmed by IR spectroscopy and powder X-Ray diffraction. The intercalation conversion was gravimetrically determined after removing all the unreacted amine by suction filtration with diethyl ether (50 mL). IR (KBr) 1526 ($\nu_{\text{C}=\text{O}}$) cm^{-1} ; powder X-Ray diffraction $2\theta = 5.37, 10.45, 15.61, 17.54, 18.60, 20.78, 25.90, 26.10, 32.77, 32.87, 36.30^\circ$. For the intercalation with *tert*-butylamine, *n*-hexane was used instead of diethyl ether to remove the unreacted amine.

For conventional methods for monomer synthesis, hydrolysis, and intercalation, the procedures were described in the previous paper.^{7,9}

RESULTS AND DISCUSSION

Monomer Synthesis

Benzyl- and dodecylammonium (*Z,Z*)-muconates were prepared by grinding (*Z,Z*)-muconic acid and the corresponding amines without any solvent in a ceramic mortar for 0.5 h. The products were obtained as powdery solids regardless of whether the amine is liquid or solid. Figure 1 shows the IR spectrum of the benzylammonium salts obtained by solvent-free method. A peak due to the carboxylic acid at 1684 cm^{-1} is not

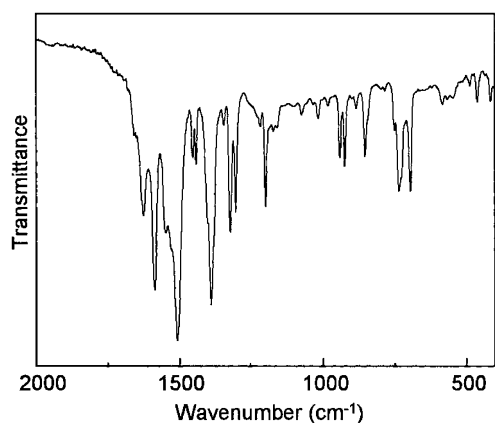


Figure 1. IR spectrum of benzylammonium (*Z,Z*)-muconate prepared by solvent-free synthesis.

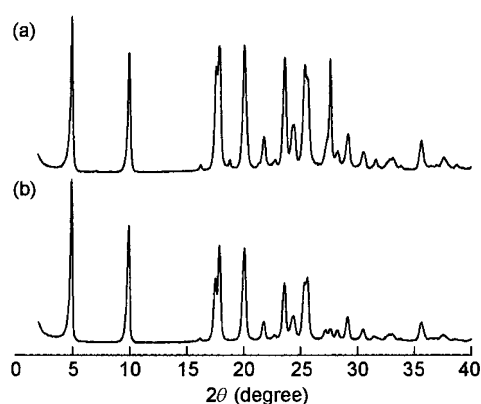


Figure 2. Powder X-Ray diffraction profiles of benzylammonium (*Z,Z*)-muconate obtained by (a) solvent-free synthesis, (b) conventional synthesis in solution.

observed and a peak based on the carboxylate appears at 1509 cm^{-1} . It suggests that the reaction proceeds quantitatively despite of a heterogeneous reaction. The powder X-Ray diffraction profile of the ammonium salts prepared by the solvent-free method was similar to that of the monomer crystals prepared by recrystallization (Figures 2a and 2b), except for a strong peak observed at $2\theta = 27.50^\circ$ due to the unreacted (*Z,Z*)-muconic acid. The powder X-Ray data indicate that the crystals of the ammonium salt and muconic acid separately exist, and that the crystals may change their crystal phase from that of the acid to that of the ammonium salts without providing solid solutions or cocrystals. Therefore, the crystals of the ammonium salts are polymerizable even if the monomer crystals include a small amount of the unreacted crystals of muconic acid. The isolated yields of the monomer crystals were determined gravimetrically after washing with diethyl ether to remove the unreacted muconic acid and amine. The results are shown in Table I. The monomer crystals were obtained in high yield by the solid-state as well as solution method.

Table I. Monomer synthesis of alkylammonium (*Z,Z*)-muconates by solvent-free and conventional solution methods

Alkyl group	Preparation method	[NH ₂]/[CO ₂ H]	Isolated yield
		mol/mol	%
Benzyl	In the solid state ^a	1.0	92
	In a solution ^b	1.1	95
Dodecyl	In the solid state ^a	1.0	94
	In a solution ^b	1.1	99

^aGrinding in a mortar for 0.5 h and then washed with diethyl ether. ^bStirring in methanol for 0.5 h and then precipitated by a large amount of diethyl ether.

Table II. Photopolymerization of alkylammonium (*Z,Z*)-muconate crystals prepared by solvent-free and conventional recrystallization methods

Alkyl group	Method ^a	Irradiation	Temp.	Time	Yield
			°C	h	%
Benzyl	Solvent-free	UV light	30	72	30
			30	144	36
	Recrystallization	Sunlight	30–40	72	30
			30–40	8	21
Dodecyl	Solvent-free	UV light	30	72	81
			30	144	87
	Recrystallization	Sunlight	30–40	72	76
			30	8	80

^aFor preparation of the monomer crystals.

Topochemical Polymerization

Topochemical polymerization of monomer crystals was carried out by photoirradiation using a high-pressure mercury lamp or sunlight. The results are shown in Table II. The formation of the polymer was confirmed by IR measurement after removing unreacted monomer with methanol, as shown in Figure 3a. The monomer prepared by the grinding method resulted in a polymer formation in a lower yield compared with that by the recrystallization method. This is due to the small crystal size. We have already reported that the polymer yield of small crystals prepared by the reprecipitation was lower than that of the larger crystals.^{20–22} The crystal size of the monomers prepared by the solvent-free grinding method was less than $20\text{ }\mu\text{m}$. In contrast, the recrystallization provides large-sized monomer crystals.

In the powder X-Ray diffraction profile of the polymer derived from the benzylammonium monomer synthesized in the solid-state, the diffraction profile was observed as the identical profile of the polymer prepared from recrystallized monomer crystal. This indicates that the polymerization proceeded *via* the topochemical reaction in the crystalline state, irrespective of the methods for the monomer preparation. For

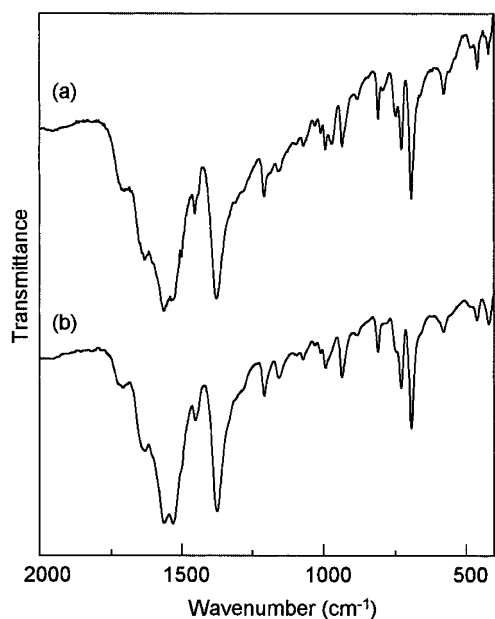


Figure 3. IR spectra of poly(benzylammonium muconate) (a) as polymerized, (b) prepared by solvent-free intercalation of benzylamine into poly(muconic acid) crystals.

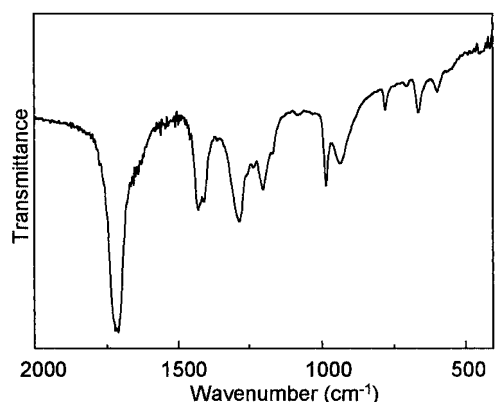


Figure 4. IR spectrum of poly(muconic acid) prepared by thermolysis of poly(benzylammonium muconate).

the dodecylammonium derivatives, the polymerization similarly proceeded to give crystalline polymers in a high yield compared with the benzylammonium derivative. The sharp peaks were observed in the powder X-Ray profile of the polymer obtained from the solvent-free monomer synthesis similar to that of the polymer prepared by the recrystallized monomer.

Transformation to Poly(muconic acid)

The transformation from the ammonium polymer to poly(muconic acid) was achieved by thermolysis at 250 °C for 2 h *in vacuo*. Figure 4 shows the IR spectrum of the ammonium polymer after heating. A peak due to the carboxylic acid at 1706 cm^{-1} appeared instead of a peak due to the carboxylate at 1526 cm^{-1} in that of ammonium polymer as shown in Figure 3a. The spectrum shown in Figure 4 was similar to the poly(muconic

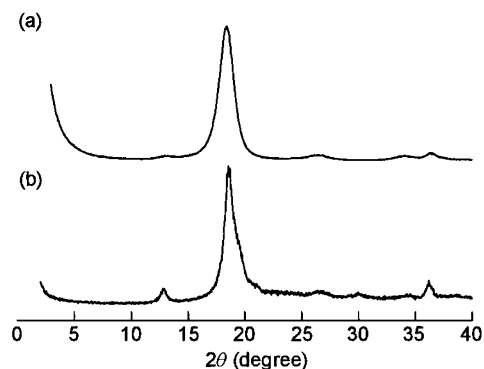


Figure 5. Powder X-Ray diffraction profiles of poly(muconic acid) obtained by (a) thermolysis, (b) conventional hydrolysis in HCl $\text{H}_2\text{O}/\text{MeOH}$ solution.

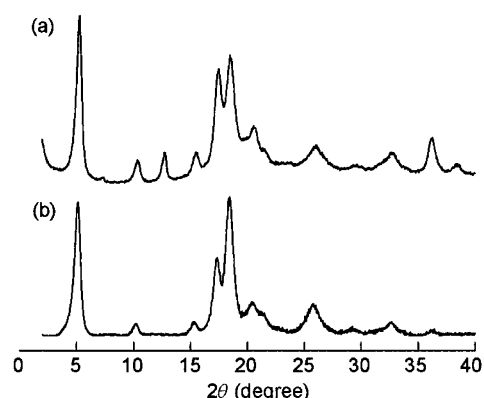


Figure 6. Powder X-Ray diffraction profiles of poly(benzylammonium muconate) obtained by (a) solvent-free intercalation, (b) conventional intercalation dispersed in MeOH solution.

acid) prepared by the treatment with hydrochloric acid in methanol: a peak due to the carboxylic acid was observed at 1710 cm^{-1} . The powder X-Ray diffraction profile of poly(muconic acid) obtained by thermolysis indicated that it is also crystalline (Figures 5a and 5b).

Intercalation into the Polymer Crystal

The intercalation of the benzyl- and dodecylamines into the acid polymer crystals was carried out by grinding in a mortar based on a method similar to the monomer synthesis. The results are shown in Table III. The intercalation proceeded regardless of the kind of the used alkylamine. The IR spectrum of the benzylammonium polymer obtained by the solid-state intercalation was identical to that of the polymer directly obtained by the topochemical polymerization of the monomer (Figure 3b). The X-Ray diffraction profile of the polymer crystal of the benzyl ammonium salt obtained by the solid-state intercalation agreed with the results from the conventional solvent-using system as shown in Figures 6a and 6b. The solid-state intercalation readily proceeded as well as the previous method in which methanol was used as the dispersant. When the poly(muconic acid) crystals were dispersed

Table III. Intercalation of alkylamines into poly(muconic acid) crystals by solvent-free and conventional dispersion methods

Alkylamine	Method	$[\text{NH}_2]/[\text{CO}_2\text{H}]$	Conversion ^a
		mol/mol	%
Benzylamine	Solvent-free ^b	1	84
	Dispersion ^c	1	67
		10	79
	Neat ^d	Large excess	15
Dodecylamine	Solvent-free	1	79
	Dispersion	1	91
		10	50
<i>tert</i> -Butylamine		Large excess	91
	Dispersion	1	— ^e
<i>tert</i> -Octylamine	Solvent-free	1	56
	Dispersion	1	— ^e
4-Amino-TEMPO ^f	Solvent-free	1	47
	Dispersion	1	— ^e

^aDetermined gravimetrically. ^bSolvent-free method: grinding in a mortar for 0.5 h. ^cDispersion method: Stirring in methanol as a dispersant for 1 h. ^dNeat method: Reaction in a excess amount of neat benzylamine without any dispersant. Poly(muconic acid) crystals were dispersed and magnetically stirred in benzylamine without methanol. ^eThe resulting polymer was soluble in methanol. ^f4-Amino-2,2,6,6-tetramethylpiperidine-1-oxyl.

and magnetically stirred in excess benzylamine without methanol, the intercalation hardly proceeded despite of the similar solvent-free reaction. This indicates that severe mechanical mixing is indispensable for high conversion of solvent-free intercalation.

Furthermore, the solid-state intercalation method enables to intercalate sterically hindered amines that cannot intercalate by the conventional method in methanol because the resulting polymer crystals were soluble. In the case of *tert*-butylamine, a high conversion over 90% was achieved using excess amines. We also introduced 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) as a counter amine into the layered polymer crystals using the solvent-free intercalation. The properties of the layered polymer crystals with containing stable radicals are now under investigation.

CONCLUSION

We have demonstrated the totally solvent-free process for the synthesis of polymer crystals using (*Z*, *Z*)-muconic acid as the starting material. All the reactions in four steps of the process, *i.e.*, monomer synthesis, polymerization, transformation to poly(muconic acid), and intercalation, proceeded in the solid state as well as in conventional method using solvents and dispersants.

The starting muconic acid is a metabolite of benzene and related aromatic compounds. Recently, the environmentally benign synthesis of the starting muconic acid from D-glucose using an engineered microbe was reported.^{23,24} The system described in this paper is a new type of polymer synthesis using a green material as the starting compound and the solvent-free process. The solid-state intercalation method can be applied to the synthesis of new kinds of advanced materials using functional amines. The polymer crystals obtained by organic intercalation are expected to be used as functional organic materials in various fields.

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