

Mesoporous Zeolite as a New Catalyst for Polymerization of Lactones

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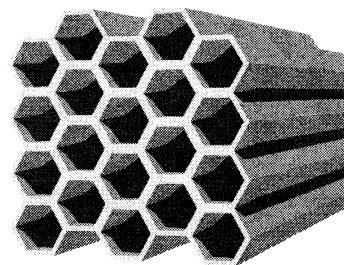
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ABSTRACT: Polymerization of lactones such as δ -valerolactone (VL) and ϵ -caprolactone (CL) with protic compounds proceeded in the presence of an aluminosilicate mesoporous zeolite Al-MCM-41 (pore diameter of 27 Å, surface area = 1,010 m² g⁻¹), to give polyesters with narrow molecular weight distribution. The polymerization is likely to proceed via the activated monomer mechanism by the cooperative function of Lewis acidic aluminum and Brønsted acidic silanol functionalities on the interior wall. With titanate-mounted MCM-41 (Ti-MCM-41), the polymerization of VL gave a polymer containing an extremely high molecular weight fraction.

KEY WORDS Mesoporous Zeolite / Polymerization of Lactone / Living Polymerization / Heterogeneous Catalyst / Block Copolymer /

In contrast to microporous zeolites having pore diameter below 15 Å, mesoporous zeolites have a porous silicate framework with a uniform, controllable pore diameter from 15 to 100 Å and an exceptionally large surface area (~1000 m²g⁻¹). In 1992, researchers of Mobil reported the first example of mesoporous zeolite MCM-41 by hydrothermal synthesis using aliphatic long-chain surfactant as template.¹ Since then, many reports on the synthesis of mesoporous materials have been made.² Mesoporous zeolites can be prepared via a liquid crystal template method using aggregates of surfactants or block copolymers as template instead of isolated molecules as used for conventional microporous materials. Various metal atoms such as Al, Ti, V, Cu, Cr, Zr, Fe, W, and Mn can be incorporated into the silicate framework of mesoporous zeolites, by addition of the metal source to a hydrothermally synthesized gel or a post-treatment of a siliceous mesoporous zeolite with the metal source. Combination of a large pore-size mesoporous zeolite with catalytically active metal ions can be used as catalysts for selective transformation of organic substrates.³ For example, a titanate-mounted MCM-41 (Ti-MCM-41) has been reported to exhibit a high catalytic activity for epoxidation of olefins such as cyclohexene.⁴ The cracking activity of MCM-41 containing aluminum atoms in the silicate framework (Al-MCM-41) has also been investigated.⁵

We have reported that Al-MCM-41 acts as a novel nanoflask for free radical polymerization of methyl methacrylate,⁶ where the hexagonal channels of the zeolite isolate the active ends of propagating polymers and prohibit their recombination and disproportionation reactions. Consequently, control of the molecular weight of poly(methyl methacrylate) can be realized over a wide range by changing the monomer-to-initiator mole ratio. In this polymerization, the aluminum atoms on the interior surface of Al-MCM-41 are expected to interact with the ester oxygen atoms of the monomer to form an inclusion complex. By taking notice of this acid-base interaction, we have more recently demonstrated that Al-MCM-41 can be applicable to the controlled ring-opening polymerization of cyclic esters



Scheme 1. Schematic Representation of Mesoporous Zeolite (MCM-41).

(lactones) to form narrow molecular-weight-distribution (MWD) polyesters.⁷

In the present paper, we report further details of the ring-opening polymerization of lactones such as δ -valerolactone (VL) and ϵ -caprolactone (CL) with MCM-41-based mesoporous materials.

RESULT AND DISCUSSION

Polymerization of δ -valerolactone (VL) in the presence of

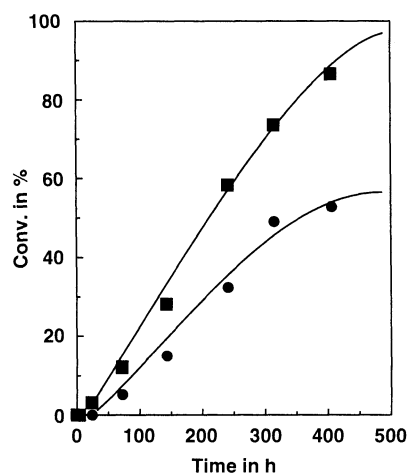


Figure 1. Polymerization of δ -valerolactone (VL) (■) and ϵ -caprolactone (CL) (●) in the presence of MCM-41 at 130 °C without solvent: VL = 4 mL; MCM-41 = 0.1 g.

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MCM-41 without solvent took place slowly at 130 °C, where a short induction period was observed at the initial stage. For example, when 4.0 mL of VL was added to 0.1 g of dry MCM-41 in a round-bottomed flask and the resulting suspension was stirred magnetically at 130 °C, the polymerization proceeded to 87% monomer conversion in 406 h (Figure 1). The molecular weight of the produced polymer was increased linearly with the monomer conversion (Figure 2). The molecular weight distribution (MWD) of the

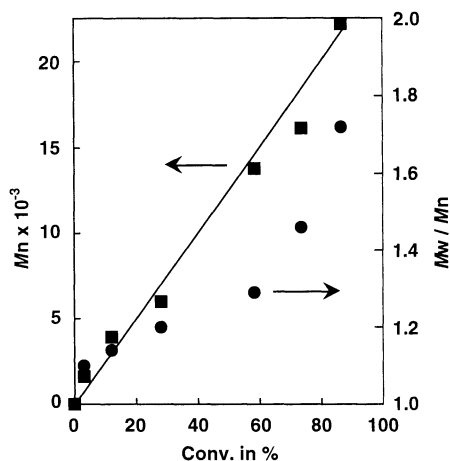


Figure 2. Polymerization of δ -valerolactone (VL) in the presence of MCM-41 at 130 °C without solvent: VL = 4 mL; MCM-41 = 0.1 g. M_n (■) (M_w/M_n) (●)-conversion relationship.

polymer was narrow at a relatively low monomer conversion ($M_w/M_n = 1.2$ at 28% monomer conversion), while it gradually became broader as the polymerization proceeded. In contrast to MCM-41, $\text{Me}_3\text{Si-MCM-41}$, derived from MCM-41 by silylation of the surface silanol functionalities with chlorotrimethylsilane, was not at all effective for the polymerization of VL, indicating that the acidity of the MCM-41 surface plays an essential role in the polymerization. With MCM-41, the polymerization of ϵ -caprolactone (CL) also took place at a high temperature such as 130 °C but more slowly than that of VL (Figure 1), affording a polymer with M_n and M_w/M_n , respectively, of 12500 and 1.6 at 53% monomer conversion.

Using Al-MCM-41 (%-Al/Si = 4) under otherwise identical conditions to the above, the polymerization of VL proceeded much faster than with MCM-41, to attain 95% monomer conversion in 72 h. This observation indicates that Lewis acidic aluminum centers on the surface of Al-MCM-41 can accelerate the polymerization by coordination to the monomer. However, unfortunately, the MWD of poly(VL) was broad throughout the polymerization ($M_w/M_n = 1.5 \sim 1.7$), possibly as the result of a trans-esterification, leading to chain reshuffling.

Along the line of this study, we found that addition of alcohol to the polymerization system with MCM-41 or Al-MCM-41 resulted in a well-controlled polymerization to give a polymer with a narrow MWD. For example, when a mixture of VL (4.0 mL) and *n*-butanol (BuOH) at a mole ratio of 10 was heated to 100 °C in the presence of MCM-41 (0.1 g), the polymerization proceeded to attain 94% monomer conversion in 99 h, to give a polymer with M_n of 1400 and $M_w/M_n = 1.15$. As shown in Figure 3, the polymerization

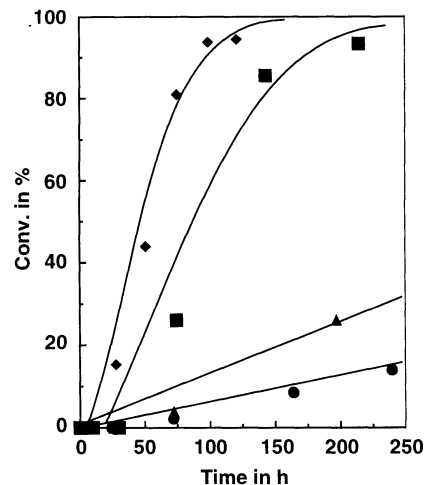


Figure 3. Polymerization of δ -valerolactone (VL) in the presence of MCM-41 at 100 °C without solvent: VL = 4 mL; MCM-41 = 0.1 g; [VL]/[BuOH] = 10 (◆), 48 (■), 157 (▲), and without BuOH (●).

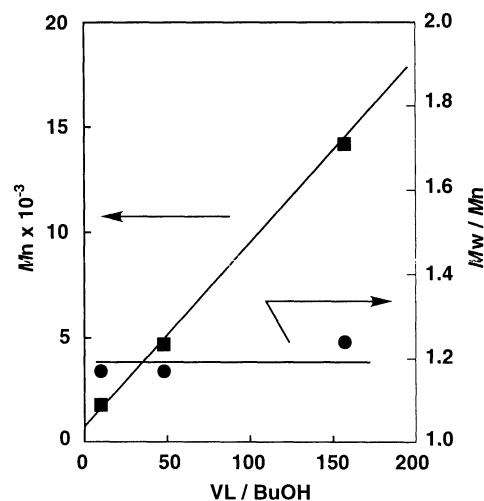


Figure 4. Polymerization of δ -valerolactone (VL) in the presence of MCM-41 at 100 °C without solvent: VL = 4 mL; MCM-41 = 0.1 g. M_n (■) (M_w/M_n) (●)-[VL]/[BuOH] relationship.

was faster as the ratio of VL/BuOH was lower. The molecular weight of the polymer could be controlled over a wide range, retaining the narrow MWD, by changing the mole ratio of VL to BuOH, (Figure 4). The degree of polymerization of the polymer was close to the feed mole ratio of VL to BuOH, indicating the formation of a polymer from every molecule of BuOH.

^1H NMR spectrum (CDCl_3) of a polymer obtained with the MCM-41/BuOH system ([VL]/[BuOH] = 50, 90% monomer conversion) (Figure 5) showed a set of signals at δ 0.94 (a) and 1.38 (b), assignable to a BuOCO- functionality, and a triplet signal at δ 3.7 (c), assignable to a hydroxyl terminal (HOCH_2 -), in addition to the signals due to the repeating monomeric units. The degree of polymerization of the polymer (45), estimated from the monomer-to-initiator mole ratio and conversion, agreed well with that calculated from the ^1H NMR end-group analysis (Figure 5), indicating that BuOH serves as initiator and chain transfer agent for the polymerization and is quantitatively incorporated into the polymer terminal.

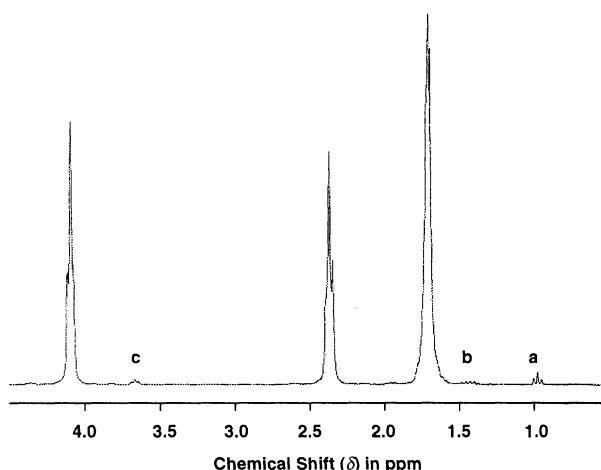


Figure 5. Polymerization of δ -valerolactone (VL) in the presence of MCM-41 at 100 °C without solvent: VL = 4 mL; MCM-41 = 0.1 g; [VL]/[BuOH] = 50; 90% monomer conversion. ^1H NMR spectrum of a polymer isolated by precipitated from MeOH.

A similar controlled chain growth has been observed in the polymerization of VL with Al-MCM-41 in the presence of BuOH, where the monomer was consumed much faster than with MCM-41, affording a polymer with a narrow MWD.⁷ For example, at a mole ratio of VL to BuOH of 100 at 100 °C in the presence of Al-MCM-41 (0.1 g) containing 4% aluminum (Figure 6, ■), the polymerization of VL proceeded to attain 90% monomer conversion in 98 h, whereas that with aluminum-undoped MCM-41 under the same conditions required 580 h to reach 90% monomer conversion (Figure 6, ◆). When the content of aluminum (%-Al/Si) in Al-MCM-41 was decreased from 4 to 2 to 1%, the rate of polymerization of VL clearly dropped (Figure 6, ● and ▲), again indicating an essential role of the Lewis acidic aluminum sites in accelerating the polymerization. Nevertheless, in all these cases, the produced polymers had a satisfactorily narrow MWD.

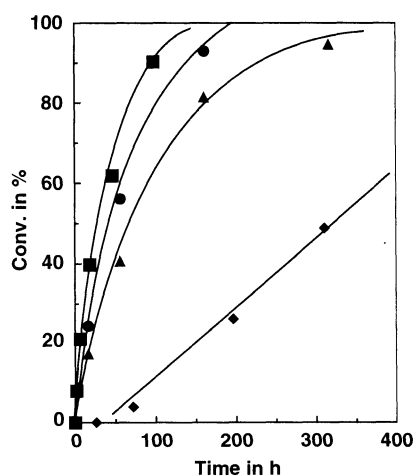
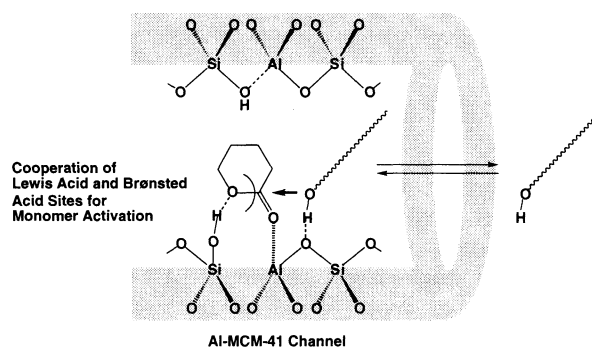


Figure 6. Polymerization of δ -valerolactone (VL) with *n*-butanol (BuOH) in the presence of Al-MCM-41 at 100 °C without solvent: VL = 4 mL; [VL]/[BuOH] = 100; Al-MCM-41 = 0.1 g; %-Al/Si in Al-MCM-41 = 4 (■), 2 (●), 1 (▲) and 0 (MCM-41) (◆).

For the polymerization of lactones with BuOH in the presence of Al-MCM-41, we propose the activated monomer mechanism by a cooperative function of Lewis acidic aluminum and Brønsted acidic silanol sites (Scheme 2),⁷ taking into account no polymerization with Me_3Si -MCM-41 (trimethylsilylated MCM-41) and a much lower activity of MCM-41 than Al-MCM-41. Cooperative functions of Lewis acidic and Brønsted acidic functionalities have been recognized for some organometallic systems and their catalyses.⁸ The role of mesoporous silicate framework here is considered to provide an exceptionally wide surface, which is beneficial for the monomer activation and the accessibility of the growing polymer molecules to the monomer activation site.



Scheme 2. Schematic Representation of the Polymerization of δ -Valerolactone (VL) within Al-MCM-41.

The above results prompted us to investigate the polymerization of VL with MCM-41 containing other metal ions. For this purpose, we chose titanate-mounted MCM-41 (Ti-MCM-41), considering a similarity of Ti-MCM-41 to Al-MCM-41 in terms of Lewis acidity. However, the polymerization profile was much different from that with Al-MCM-41. For example, when a mixture of VL (4 mL) and Ti-MCM-41 (0.25 g) was heated at 50 °C under N_2

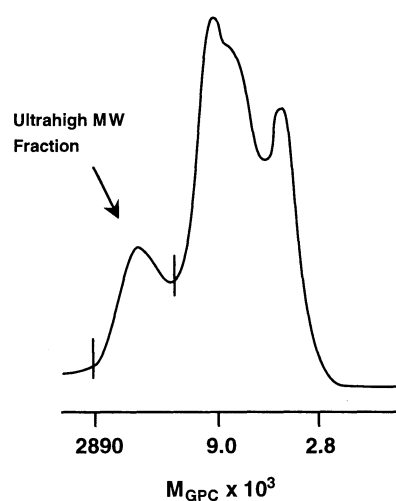


Figure 7. Polymerization of δ -valerolactone (VL) in the presence of Ti-MCM-41 at 50 °C without solvent: VL = 4 mL; Ti-MCM-41 = 0.25 g. GPC profile of the polymer (precipitated from MeOH) at 12% monomer conversion.

without solvent, the polymerization took place very slowly, to attain 12% monomer conversion in 43 h. Of interest to note here is the fact that the polymerization mixture turned into a gel even at such a low monomer conversion. When the gel was poured into THF at room temperature, a small amount of insoluble fraction precipitated. GPC analysis of the THF-insoluble fraction with chloroform as eluent showed a multimodal molecular weight distribution (Figure 7), indicating the presence of multiple active sites in Ti-MCM-41. However, to our surprise, the polymer contained an ultrahigh-molecular-weight fraction with a peak top molecular weight higher than 10^6 . Although behavior of the polymerization is not well clarified yet, formation of such a high molecular weight polyester has never been synthesized. Thus, fine-tuning of the polymerization with Ti-MCM-41 may be the subject worthy of further investigation.

EXPERIMENTAL

Materials

δ -Valerolactone (VL), ϵ -caprolactone (CL), and *n*-butanol (BuOH) were dried over calcium hydride and then distilled under reduced pressure in a nitrogen atmosphere. Cetyltrimethylammonium chloride ((CTMA)Cl) and tetraethyl orthosilicate (TEOS) were used as received. Cetyltrimethylammonium hydroxide ((CTMA)OH) and tetramethylammonium hydroxide ((TMA)OH) were obtained as 25 wt% methanolic and aqueous solutions, respectively. MCM-41 was prepared by the hydrothermal method: To an aqueous solution of (CTMA)Cl (14.4 g, 45 mmol) was added 25 wt% methanolic (CTMA)OH (54 g, 45 mmol), and the mixture was added dropwise to TEOS (31 g, 150 mmol) with vigorous stirring at 0 °C. After 30 min the reaction mixture was heated to 40 °C for 1 h, then at 80 °C for 3 h to flush out ethanol generated by the reaction. The resulting mixture was treated with aqueous (TMA)OH to adjust the pH to 11.5, loaded into a Teflon bottle, and allowed to stand at 100 °C for 8 days. The solid product was isolated from the reaction mixture by filtration, washed with distilled water, dried at room temperature, and then calcined at 540 °C for 6 h under air. The powder x-ray diffraction (XRD) pattern of the product showed peaks, which were indexed with 100 and 110, characteristic of a hexagonal symmetry with a d-spacing of 34.6 Å.

To silylate the silanol functionalities of MCM-41, a suspension of a mixture of hexamethyldisiloxane (40 mL) and chlorotrimethylsilane (23 mL, 184 mmol) containing MCM-41 (1 g) was refluxed for 16 h and filtered, and dried under reduced pressure at room temperature to leave a trimethylsilylated MCM-41 ($\text{Me}_3\text{Si-MCM-41}$). Al-MCM-41 and Ti-MCM-41 were synthesized according to the reported procedures.^{1,4a}

Polymerization Procedure

Typically, a 10-mL round-bottomed flask, attached to a three-way stopcock, containing MCM-41 (0.1 g) and a Teflon-coated magnetic stirring bar was degassed under reduced pressure at 120 °C for 3 h. After the flask was purged with dry N_2 , a mixture of VL (4.0 mL, 43 mmol) and *n*-butanol (VL/BuOH = 50) was added by a hypodermic syringe, and the resulting suspension was heated with stirring magnetically at 100 °C under N_2 . An aliquot of the

polymerization mixture was periodically taken out by a syringe from the flask, and was poured into CDCl_3 and THF, which were then filtered through a Teflon-coated porous membrane with a pore diameter of 0.5 μm . The CDCl_3 filtrate was subjected to ^1H NMR spectroscopy to determine the monomer conversion, while the THF filtrate was loaded on a gel permeation chromatograph (GPC) to evaluate the number average molecular weight (M_n) and molecular weight distribution of the polymer.

Measurements

^1H NMR measurements were performed in CDCl_3 on a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to CHCl_3 (δ 7.28) as internal standard. GPC was performed at 40 °C on a TOSOH model 8020 high-speed liquid chromatograph using THF as eluent at a flow rate of 1.0 mL min^{-1} . The column set consisted of four polystyragel columns (7.8 mm- Φ x 30 cm); TOSOH TSK_{gel} G2000H_{XL}, G3000H_{XL}, G5000H_{XL}, and GMH_{XL}. The molecular weight calibration curve was obtained by using standard polystyrenes. Powder x-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2400 diffractometer with $\text{Cu K}\alpha$ radiation (20 kV, 50 mA), 0.005 ° step size, and a scan speed of 1 ° min^{-1} .

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