Macromolecules **1998,** *31,* 4069−4073

Mesoporous Zeolite as a New Class of Catalyst for Controlled Polymerization of Lactones

Keisuke Kageyama, Shin-ichi Ogino,[†] and Takuzo Aida*,[‡]

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Takashi Tatsumi

Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

Received February 23, 1998; Revised Manuscript Received April 14, 1998

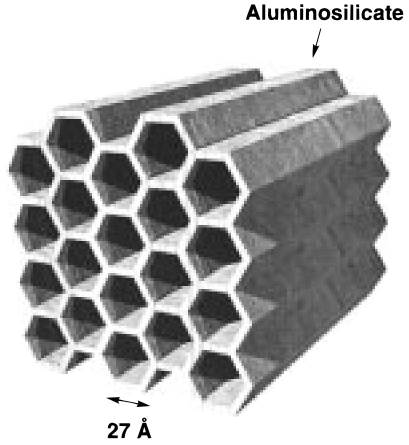
ABSTRACT: Polymerization of lactones such as δ-valerolactone (VL) and ϵ-caprolactone (CL) with protic compounds proceeded in the presence of an aluminosilicate mesoporous zeolite Al−MCM-41 (pore diameter of 27 Å, surface area = 1010 $m^2\ g^{-1}$, and Si/Al = 17), to give polyesters with a narrow molecular weight distribution. A sequential two-stage polymerization of VL and CL with Al−MCM-41/butanol gave a block copolymer. NMR and GPC studies showed that the produced polymer carries a terminal group originating from the protic compound. In contrast with Al−MCM-41, pure silicate MCM-41, an MCM-41 with masked SiOH functionalities, and a "microporous" aluminosilicate with much narrower pores (zeolite-Y; pore diameter = 8 Å) were not effective for the polymerization under similar conditions. Infrared spectroscopy of an inclusion adduct of Al−MCM-41 with VL suggested a possible interaction of the monomer onto the aluminosilicate surface. Al−MCM-41, isolated from the polymerization mixture, could be used again for the polymerization.

Introduction

Synthesis of polymers of controlled molecular weight with narrow polydispersity is of both fundamental interest and practical importance. "Living" polymerization with a rapid initiation along with the absence of chain transfer and termination reactions provides a method to achieve this purpose.[1] In the present paper, we report results of the ring-opening polymerization of lactones with protic compounds in the presence of a porous inorganic crystal called "mesoporous zeolite".

Polylactones are of industrial importance, and a variety of initiators and catalysts have been reported for the ring-opening polymerization of lactones.[2] The representative examples include aluminum alkoxides,[3] aluminum porphyrins,[4] aluminum porphyrins/bulky organoaluminum diaryl oxides,[5] and organolanthanide complexes,[6] which are capable of initiating the living polymerization of lactones and/or lactide to give polyesters with narrow molecular weight distribution (MWD). Recently, we have found that the living polymerization of six- and seven-membered lactones and a six-membered cyclic carbonate is initiated by alcohol in the presence of a bulky Lewis acid such as methylaluminum bis(2,6-diphenylphenoxide).[7] The basic concept of this polymerization comes from "immortal" polymerization,[8] which originally makes use of aluminum porphyrin as the initiator coupled with alcohol as the chain transfer agent.[9] Similar to "living" polymerization, immortal polymerization can also produce a polymer with narrow MWD, but it has an advantage over living polymerization in that the number of polymer molecules exceeds that of the initiator molecules by virtue of a rapid, reversible chain transfer reaction.[8,10] Thus, "immortal" polymerization is a catalytic version of "living" polymerization, and it is therefore important to develop very simple, easy-to-handle initiators or catalysts for this type of polymerization.

Scheme 1. Schematic Representation of an Aluminosilicate Mesoporous Zeolite (Al−MCM-41).



Mesoporous zeolite Al−MCM-41 (Scheme 1) has a porous aluminosilicate framework with a uniform, controllable pore diameter from 15 to 100 Å and an exceptionally large surface area (∼1000 $m^2\ g^{-1}$).[11] Very recently, we have reported that Al−MCM-41 acts as a novel nanoflask for free radical polymerization of methyl methacrylate, where the hexagonal channels of the zeolite isolate the active ends of propagating polymers and suppress their recombination and disproportionation reactions, thereby enabling a wide range of control of the polymer molecular weight by changing the monomer-to-initiator mole ratio.[12] In the present study, we took notice of the acidity of the large aluminosilicate Al−MCM-41 surface, which is expected to coordinate to and to activate monomer and chain transfer agent

---

[†] On leave from Technical Research Laboratory, Kansai Paint Co. Ltd., Higashi Yawata, Hiratsuka 254-0016, Japan.

[‡] Fax: +81-3-5802-3363. E-mail: aida@macro.t.u-tokyo.ac.jp.

S0024-9297(98)00270-8 CCC: $15.00 © 1998 American Chemical Society
Published on Web 05/29/1998

Table 1. Polymerization of δ-Valerolactone (VL) with Protic Compounds (ROH) in the Presence of Zeolites[a]

run	ROH	$[VL]_0/[ROH]_0$	zeolite	temp/°C	time/h	conv/%	M_n	M_w/M_n
1	BuOH	10	Al−MCM-41[b]	20	498	86.6	1000	1.07
2	BuOH	11	Al−MCM-41[b]	50	237	96.4	1200	1.07
3	BuOH	55	Al−MCM-41[b]	50	1416	94.4	5700	1.15
4	BuOH	106	Al−MCM-41[b]	50	2440	93.2	8200	1.22
5	BuOH	223	Al−MCM-41[b]	50	3333	92.2	18000	1.28
6	BuOH	11	Al−MCM-41[b]	100	5	73.5	1300	1.09
7	BuOH	11	Al−MCM-41[b]	100	73	94.0	2100	1.26
8	MeOH	56	Al−MCM-41[b]	50	1416	96.5	5400	1.22
9	BnOH	11	Al−MCM-41[b]	20	666	80.4	1500	1.08
10	H_2O	37	Al−MCM-41[b]	50	237	97.4	2900	1.13
11	BuOH	54	MCM-41[c]	50	93	0		
12	BuOH	48	MCM-41[c]	100	580	90.0	4200	1.17
13	MeOH	35	Al−MCM-41(SiOMe)[d]	50	430	0		
14	BuOH	10	silica−alumina[e]	20	770	80.3	1200	1.16
15	BuOH	50	Zeolite-Y[f]	50	450	0		

[a] Monomer/zeolite = 4 mL/0.1 g. [b] Aluminosilicate; Si/Al = 17; pore diameter = 27 Å; surface area = 1010 $m^2\ g^{-1}$. [c] Pure silicate; pore diameter = 27 Å; surface area = 1010 $m^2\ g^{-1}$. [d] Al−MCM-41 with SiOH functionalities methylated. [e] Si/Al = 6.8; surface area = ~300 $m^2\ g^{-1}$. [f] Si/Al = 2.6; pore diameter = 8 Å; surface area = ~500 $m^2\ g^{-1}$.

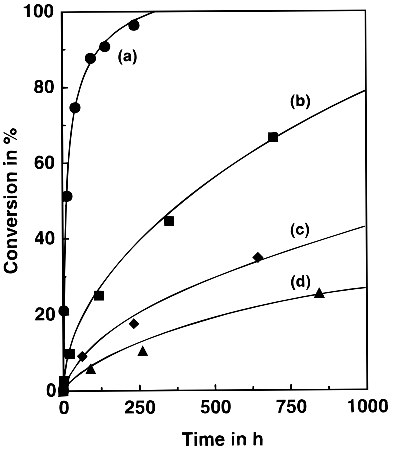


Figure 1. Polymerization of δ-valerolactone (VL) with butanol (BuOH) in the presence of Al−MCM-41 (Si/Al = 17) at 50 °C without solvent: VL = 4 mL; Al−MCM-41 = 0.1 g; $[VL]_0/[BuOH]_0$ = 11 (a), 55 (b), 106 (c), and 223 (d).

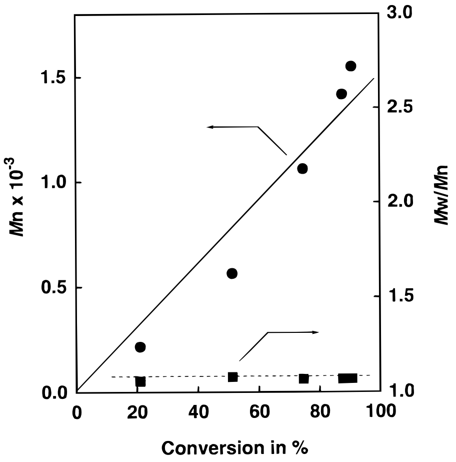


Figure 2. Polymerization of δ-valerolactone (VL) with butanol (BuOH) in the presence of Al−MCM-41 (Si/Al = 17) at 50 °C without solvent: VL = 4 mL; Al−MCM-41 = 0.1 g; $[VL]_0/[BuOH]_0$ = 11. M_n (●) (M_w/M_n (■)) − conversion relationship.

for “immortal” polymerization. Thus, we explored the possibility of “immortal” ring-opening polymerization of lactones such as δ-valerolactone (VL) and ϵ-caprolactone (CL)[10] with protic chain transfer agents in the presence of Al−MCM-41 and some related inorganic crystals.

Results and Discussion

The polymerization of δ-valerolactone (VL) with butanol (BuOH) in the presence of Al−MCM-41 proceeded at 50 °C without solvent to give a polymer with narrow molecular weight distribution (MWD). For example, when a mixture of VL (4.0 mL) and BuOH at a mole ratio of 11 was added under N_2 to a round-bottomed flask containing Al−MCM-41 (Si/Al = 17, 0.1 g) and the resulting suspension was stirred magnetically at 50 °C (run 2, Table 1), the polymerization proceeded to attain 51.3 and 96.4% monomer conversion in 15 and 237 h, respectively (Figure 1a), and gave a narrow MWD polymer with M_n of 1200 (M_w/M_n = 1.07). The degree of polymerization of the polymer (12) is close to the feed mole ratio of VL to BuOH (11). The molecular weight of the polymer was observed to increase almost linearly with monomer conversion, while retaining the narrow polydispersity (M_w/M_n = 1.06−1.07) (Figure 2). When the temperature was elevated to 100 °C under otherwise identical conditions to those given above, the polymerization was accelerated to attain 73.5% monomer conversion in only 5 h to give a polymer with narrow MWD (M_w/M_n = 1.09, run 6), while the MWD became a little broader at the final stage (run 7). On the other hand, at a lower temperature such as 20 °C, the polymerization did also take place, but extremely slowly, to reach 86.6% monomer conversion in 498 h, where the polymer formed had a much narrower MWD (M_w/M_n = 1.07) (run 1).

In the polymerization of VL with Al−MCM-41/BuOH at 50 °C, the molecular weight of the polymer was controlled over a wide range by changing the mole ratio of VL to BuOH (VL/BuOH) (runs 2−5), where the M_n increased from 1200 to 18 000 almost proportionally to VL/BuOH, while the ratio M_w/M_n stayed in the range 1.07−1.28 (Figure 3). No oligomeric products were detected by GPC. Thus, the polymerization is considered to involve a rapid, reversible chain transfer reaction with BuOH, as in the case of the immortal polymerization with protic chain transfer agents initiated by aluminum porphyrins.[10] However, it should be also noted that the polymerization became considerably slower as the ratio VL/BuOH was higher (Figure 1b−d). This trend may be characteristic of the chain growth in a confined space of the zeolite channel, where access of the reactants to the interior active sites is considered

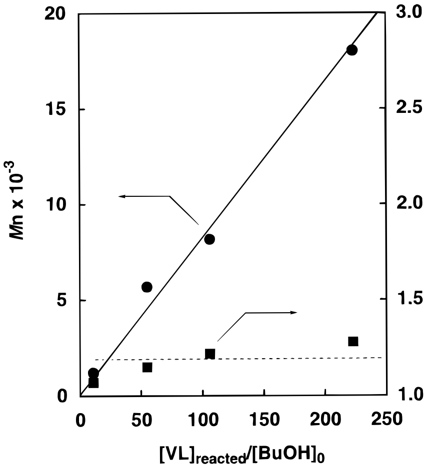


Figure 3. Polymerization of δ-valerolactone (VL) with butanol (BuOH) in the presence of Al−MCM-41 (Si/Al = 17) at 50 °C without solvent: VL = 4 mL; Al−MCM-41 = 0.1 g. M_n (●) (M_w/M_n (■))−$[VL]_{reacted}/[BuOH]_0$ relationship.

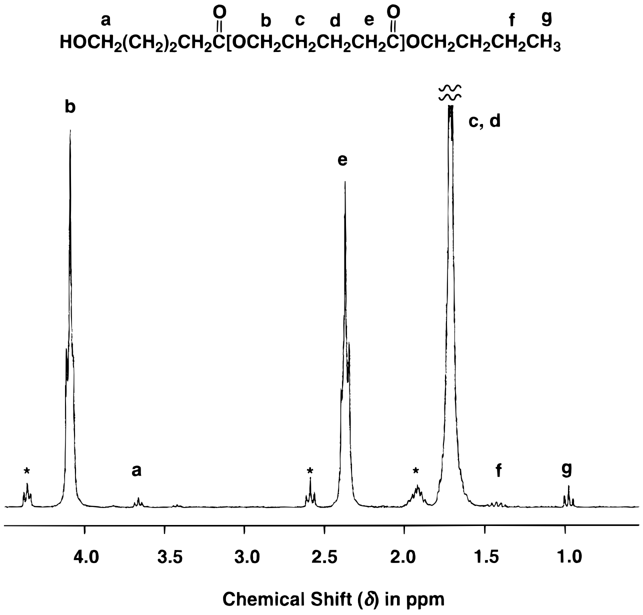


Figure 4. Polymerization of δ-valerolactone (VL) with butanol (BuOH) in the presence of Al−MCM-41 (Si/Al = 17) at 50 °C without solvent: VL = 4 mL; Al−MCM-41 = 0.1 g; 94.4% monomer conversion. ^{1}H NMR spectrum of the polymerization mixture in $CDCl_3$ at 25 °C after filtering off inorganic fractions.

to be diffusion-controlled particularly when the molecular weight of the growing polymer is relatively high.

End-group analysis of a polymer formed at $[VL]_0/[BuOH]_0$ of 55 (94.4% conversion) in the presence of Al−MCM-41 (run 3) was carried out by means of ^{1}H NMR in $CDCl_3$ at 25 °C (Figure 4), where a set of weak signals assignable to BuO_2C (δ 0.94 [g, CH_3], 1.38 [f, $MeCH_2$]) and $HOCH_2$ (a, δ 3.66) were observed along with other signals due to the repeating $-C(O)(CH_2)_4O-$ units (b−e) and unreacted VL (asterisked). No olefinic proton signals, as a result of possible dehydration of the terminal hydroxyl group, were observed.[13] The relative intensity of the signals a to g was 2:3, while that of the signals b to g was 51,[14] which nicely meets the degree of polymerization of the polymer, as estimated by GPC, of 57. Thus, the polymer carries a BuO_2C functionality at one of the terminals and a hydroxyl functionality on the other end, indicating the participation of BuOH as initiating and chain transfer agents for the polymerization of VL with Al−MCM-41.

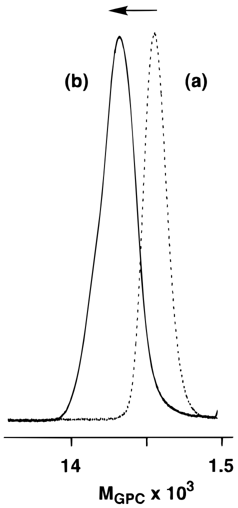
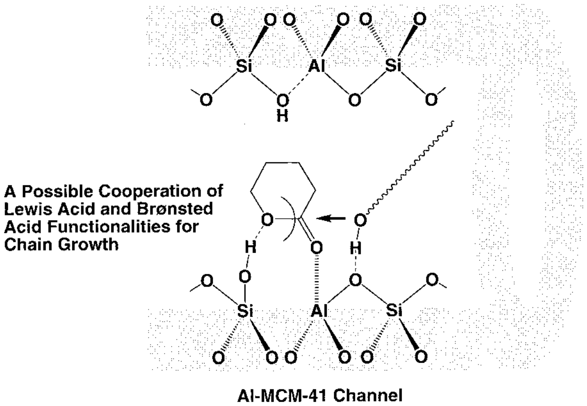


Figure 5. Sequential two-stage polymerization of δ-valerolactone (VL) and ϵ-caprolactone (CL) with butanol (BuOH) in the presence of Al−MCM-41 (Si/Al = 17, 0.1 g) without solvent: GPC profiles of (a) the first-stage (VL = 4 mL; $[VL]_0/[BuOH]_0 = 11$, 50 °C) and (b) second-stage ($[CL]_0/[VL]_0 = 1.5$, 100 °C) polymerizations.

In addition to BuOH, other alcohols such as methanol (MeOH) and benzyl alcohol (BnOH) and even water could be used as initiator/chain transfer agents for the polymerization of VL with Al−MCM-41 (runs 8−10). When BnOH was used in place of BuOH (run 9), the GPC trace of the resulting polymer, monitored by a UV detector at 254 nm,[15] displayed a unimodal peak, which was superimposable with the chromatogram monitored by an RI detector. This observation indicates the presence of a benzyl ether end functionality in the polymer chain. On the other hand, with water as initiating/chain transfer agent (run 10), a polyester carrying hydroxyl and carboxylic acid end groups was formed, as observed by ^{13}C NMR (δ 175.9 [CO_2H] and 61.9 [CH_2OH]).

To investigate the living character of the polymerization, a sequential two-stage polymerization of VL and CL was attempted with Al−MCM-41/BuOH. At the first stage, the polymerization of VL was carried out at 50 °C without solvent at $[VL]_0/[BuOH]_0 = 11$ (4 mL of VL, 0.1 g of Al−MCM-41), to prepare a prepolymer (M_n = 1,200, $M_w/M_n = 1.07$) (Figure 5a). After VL was completely polymerized, CL (4 mL, $[CL]_0/[VL]_0 = 1.5$) was added at 100 °C to the system, whereupon the second-stage polymerization of CL started to attain 100% monomer conversion in 170 h. The GPC analysis of the polymerization mixture showed a unimodal, sharp chromatogram at a higher molecular weight region (M_n = 3200, $M_w/M_n = 1.20$) (Figure 5b) than the prepolymer of VL. The ^{13}C NMR spectrum of the product was a superimposed image of those of homopolymers of VL and CL, indicating the formation of a block copolymer without any reshuffled units[16] as a result of trans esterification. The composition of the block copolymer (VL:CL = 1:1.5), as evaluated from the intensities of the ^{1}H NMR signals due to CO_2CH_2 (δ 4.09 [polyVL and polyCL]) and $CO_2CH_2CH_2CH_2$ (δ 1.38 [polyCL]), was in excellent agreement with the feed mole ratio of VL to CL. These observations indicate that the polymerization of lactones with the Al−MCM-41/ROH system is of a living character.

Scheme 2. Proposed Mechanism for the Polymerization of δ-Valerolactone (VL) with Alcohol in the Presence of an Aluminosilicate Mesoporous Zeolite (Al−MCM-41).



In the polymerization of lactones catalyzed by Al−MCM-41, the acidity of the zeolite surface appears to play an important role. In fact, an attempted polymerization of VL with BuOH ($[VL]_0/[BuOH]_0 = 54$) in the presence of MCM-41, consisting of a pure silicate framework without Al component,[17] did not proceed at 50 °C throughout the observation for 93 h (run 11). At a higher temperature such as 100 °C, the polymerization proceeded but only very slowly to attain 100% monomer conversion in 580 h (run 12). Nevertheless, the resulting polymer had a narrow MWD ($M_w/M_n = 1.17$) with M_n of 4200, which is close to the theoretical M_n (4300) as expected from the feed mole ratio of VL to BuOH. On the other hand, upon methylation of the SiOH functionalities on the Al−MCM-41 surface (Al−MCM-41 (SiOMe)),[18] no polymerization of VL occurred at 50 °C (run 13). In addition to the chemical properties of the zeolite surface, the surface area or the pore diameter of the catalyst is also an important factor. Thus, an attempted polymerization of VL ($[VL]_0/[BuOH]_0 = 10$) using a macroporous aluminosilicate (silica−alumina catalyst; Si/Al of 6.8) with a smaller surface area (300 $m^2\ g^{-1}$)[19] than Al−MCM-41[11] proceeded very slowly (run 14) despite the much higher aluminum content. Furthermore, use of a microporous aluminosilicate called zeolite-Y (Si/Al = 2.6, pore diameter = 8 Å) for the polymerization ($[VL]_0/[BuOH]_0 = 50$) at 50 °C resulted in no consumption of VL (run 15). These contrasting results demonstrate a high potential of mesoporous Al−MCM-41 for the controlled polymerization of lactones with protic compounds.

The overall surface area of Al−MCM-41, as evaluated from the nitrogen adsorption isotherm profile by the BET method, was 1010 $m^2\ g^{-1}$, while the exterior surface area was estimated to be only 49 $m^2\ g^{-1}$,[20] indicating that the surface of the interior wall occupies the majority of the overall surface (∼95%). Therefore, the polymerization is considered to have occurred within the interior of the channels. As can be seen from Figure 1a, the polymerization at the initial stage proceeds fairly rapidly but slows down when the monomer conversion exceeds 70%. This tendency is apparently due to a diffusion control, as also suggested by the significant drop of the polymerization rate at a high VL/BuOH ratio (Figure 1a−d). For the mechanism of the polymerization, we assume the "activated monomer mechanism" (Scheme 2), where the monomer is activated through interaction with a Lewis acidic aluminum atom and a Brønsted acidic SiOH functionality, since neither pure silicate MCM-41 (runs 11, 12) nor Al−MCM-41 (SiOMe) with masked SiOH functionalities (run 13) is effective for the polymerization (Table 1). Such an interaction between the monomer and the mesopore surface is suggested by the infrared spectral profile of an inclusion adduct of Al−MCM-41 with VL, where the carbonyl absorption of VL was clearly lowered from 1732 to 1718 cm^{-1}. Cooperative functions of Lewis acidic and Brønsted acidic functionalities have been recognized for some organometallic systems and their catalyses.[21] Although the "activated monomer mechanism" involving a protonated monomer[22,23] is also a candidate, the Al−MCM-41/ROH system is better behaved than the reported combinations of protonic acids and alcohols for the polymerization of lactones,[24] for which a broadening of the polymer MWD together with a concomitant formation of cyclic oligomers has been reported to occur at a high monomer-to-alcohol mole ratio such as 100.

One of the advantages of crystalline catalysts is their potential of recycling for repeated usage. In fact, Al−MCM-41 was easily separated from the polymerization mixture by filtration and washing with THF and could be used again for the controlled polymerization of VL with BuOH. By powder X-ray diffraction (XRD) studies, the isolated Al−MCM-41 was found to retain the original hexagonal channels though with a little disordering.

Conclusion

We have demonstrated that an aluminosilicate mesoporous zeolite (Al−MCM-41) is a novel, versatile catalyst for the controlled polymerization of lactones. Al−MCM-41 is a stable compound, which can be stored over a long period of time and can be recycled for repeated usage. Compared with microporous zeolites, mesoporous Al−MCM-41 provides a larger surface area and more accessible reaction sites for the polymerization. Mesoporous zeolites also have a potential advantage, since fine-tuning of their chemical properties is possible by incorporation of various transition metals on the surface or in the framework.[25,26] Further studies using mesopores of much larger pores and/or with transition metals in the channels are now in progress to enhance catalytic activities and to realize chemoselectivities.

Experimental Section

Materials. δ-Valerolactone (VL), ε-caprolactone (CL), and butanol (BuOH) were dried over calcium hydride and then distilled under reduced pressure in a nitrogen atmosphere. Methanol (MeOH) was distilled over magnesium treated with iodine under N_2. Cetyltrimethylammonium chloride ((CTMA)Cl), tetraethyl orthosilicate (TEOS), aluminum sulfate, silica−alumina catalyst, and zeolite-Y 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 and Al−MCM-41 were prepared by the hydrothermal method.[11] A representative example is shown by the synthesis of Al−MCM-41 (Si/Al = 17): To an aqueous solution of a mixture of aluminum sulfate (0.88 g, 1.8 mmol) and (CTMA)Cl (5.76 g, 15.2 mmol) were successively added 25 wt % aqueous (TMA)OH (17 g) and 25 wt % methanolic (CTMA)OH (32.57 g, 27.0 mmol), and the mixture was added dropwise to TEOS (19.5 g, 93.8 mmol) with vigorous stirring at 0 °C. After 30 min, the reaction mixture was heated at 40 °C for 1 h, then at 70 °C for 1 h, and finally 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 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 pattern of the product showed peaks which were indexed with 100, 110, 200, and 210, characteristic of a hexagonal symmetry with a *d*-spacing of 34.6 Å. The Si/Al ratio was determined by means of inductively coupled plasma spectrometer (ICP) to be 17. The overall surface area of Al−MCM-41 was evaluated by the nitrogen adsorption isotherm by the BET method. The external surface area was estimated from *t*-plots of nitrogen adsorption isotherms by the method developed by Mikhail et al.[20]

To methylate the SiOH functionalities of Al−MCM-41, a MeOH suspension of the zeolite was refluxed for 5 h and filtered, and the wet solid isolated was dried under reduced pressure at room temperature to leave Al−MCM-41 (SiOMe).[18]

Procedures. Polymerization. Typically, a 10-mL round-bottomed flask, attached to a three-way stopcock, containing Al−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 butanol (VL/BuOH = 50) was added by a hypodermic syringe, and the resulting suspension was heated with stirring magnetically at 50 °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 ^{1}H NMR spectroscopy to determine the monomer conversion, while the THF filtrate was loaded on a gel permeation chromatograph (GPC) to evaluate the average molecular weights (M_n, M_w) and MWD of the polymer.

Preparation of an Inclusion Adduct of Al−MCM-41 with VL. To a 10-mL round-bottomed flask containing VL (4.0 mL) was added Al−MCM-41 (0.1 g), and the resulting suspension was filtered after repeated freeze-to-thaw cycles. The Al−MCM-41/VL inclusion adduct, thus isolated, was dried at room temperature under reduced pressure and ground with KBr to prepare a pellet, which was subjected to infrared spectroscopy.

Measurement. ^{1}H and ^{13}C 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 for ^{1}H and δ 77.1 for ^{13}C) as internal standard. Gel permeation chromatography (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 o.d. × 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. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2400 diffractometer with Cu Kα radiation (20 kV, 50 mA), 0.005° step size, and a scan speed of 1° min^{-1}. ICP measurements for the elemental analysis of zeolites were performed on a Shimadzu ICPS-7500 sequential plasma spectrometer. Nitrogen adsorption/desorption isotherm measurements were performed on a Japan Bel Belsorp 28SA analyzer. Infrared spectroscopy was performed on a Jasco FT/IR-5300 infrared spectrometer.

Acknowledgment. The present work was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 08246102, "*New Polymers and Their Nano-Organized Systems*"), from the Ministry of Education, Science, Sports, and Culture, Japan. T.A. thanks the *Kanagawa Academy of Science and Technology Research Grants* for financial support. The authors also thank Ms. S. M. Ng for her active collaboration.

References and Notes

(1) For recent reviews, see: (a) Webster, O. W. *Science* **1991**, *251*, 887. (b) Aida, T. *Prog. Polym. Sci.* **1994**, *19*, 469.

(2) Jedlinski, Z. J, *Handbook of Polymer Synthesis*; Kricheldorf, H. A., Ed.; Marcel Dekker: New York, 1992; Part A, Chapter 11, p 645.

(3) (a) Hamitou, A.; Ouhadi, T.; Jerome, R.; Teyssié, P. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 865. (b) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640. (c) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286. (d) Kohn, F. E.; Ommen, J. G.; Feijen, J. *Eur. Polym. J.* **1983**, *19*, 1081.

(4) (a) Shimasaki, K.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 3076. (b) Trofimoff, L. R.; Aida, T.; Inoue, S. *Chem. Lett.* 1987, 991. (c) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1983**, *16*, 1792. (d) Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1990**, *23*, 2869.

(5) Isoda, M.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1997**, *30*, 57.

(6) (a) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097. (b) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115. (c) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798.

(7) Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1995**, *28*, 1320.

(8) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39.

(9) (a) Asano, S.; Aida, T.; Inoue, S. *Chem. Commun.* 1985, 1148. (b) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. *Macromolecules* **1988**, *21*, 1195.

(10) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982.

(11) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(12) Ng, S. M.; Ogino, S.; Aida, T. *Macromol. Rapid Commun.* **1997**, *18*, 991.

(13) Trombetta, M.; Busca, G.; Rossini, S.; Piccoli, V.; Cornaro, U. *J. Catal.* **1997**, *168*, 349.

(14) ^{1}H NMR end-group analysis of a polymer, isolated by reprecipitation from $CHCl_3$/MeOH, gave virtually the same result.

(15) The wavelength was selected on the basis of the absorption of anisole in THF.

(16) Imasaka, K.; Nagai, T.; Yoshida, M.; Fukuzaki, H.; Asano, M.; Kumakura, M. *Eur. Polym. J.* **1990**, *26*, 831.

(17) Luan, Z.; Cheng, C.-F.; Zhou, W.; Klinowski, J. *J. Phys. Chem.* **1995**, *99*, 1018.

(18) Ishikawa, T.; Matsuda, M.; Yasukawa, A.; Kandori, K.; Inagaki, S.; Fukushima, T.; Kondo, S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1985.

(19) Corma, A.; Fonés, V.; Pérez-Pariente, J. *J. Catal.* **1994**, *148*, 569.

(20) Mikhail, R. S.; Brunauer, S.; Boder, E. E. *J. Colloid Interface Sci.* **1968**, *26*, 45.

(21) (a) Ishihara, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 1561. (b) Ishihara, K.; Miyata, M.; Hattori, K.; Tada, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 10520. (c) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 3049.

(22) (a) Wojtania, M.; Kubisa, P.; Penczek, S. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 201. (b) Penczek, S.; Kubisa, P.; Szymanski, R. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 203.

(23) For cationic polymerization of tetrahydrofuran with zeolites, see: Hsia Chen, C. S.; Schramm, S. E.; Wentzek, S. E. *Microporous Mater.* **1996**, *6*, 205.

(24) (a) Okamoto, Y. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 117. (b) Rozenberg, B. A. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 177.

(25) For recent reviews, see: (a) Syari, A. *Chem. Mater.* **1996**, *8*, 1840. (b) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.

(26) (a) Koyano, K. A.; Tatsumi, T. *Chem. Commun.* 1996, 145. (b) Koyano, K. A.; Tatsumi, T. *Microporous Mater.* **1997**, *10*, 259. (c) Tatsumi, T.; Koyano, K. A.; Igarashi, N. *Chem. Commun.* 1998, 325.

MA980270Q