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# Macromolecular Synthesis Using Mesoporous Zeolites

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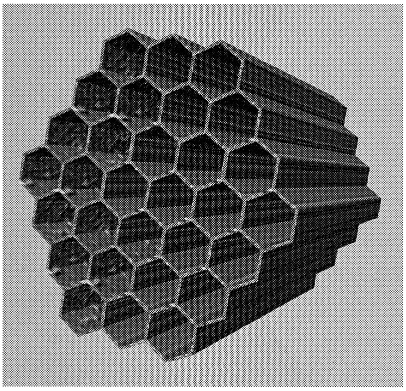
SUMMARY: Mesoporous zeolites such as MCM-41 were found to serve as nano-flasks for free radical polymerization of methyl methacrylate (MMA), where the formation of long-lived propagating radicals was observed. Al-MCM-41 with a Lewis-acidic aluminosilicate framework catalyzed living ring-opening polymerization of cyclic esters such as $\delta$-valerolactone and $\varepsilon$-caprolactone, to give narrow molecular-weight-distribution polyesters. With Ti-MCM-41, a titanate-containing mesoporous silica, ring-opening polymerization of $\delta$-valerolactone also took place to give a high molecular-weight polyester. On the other hand, with Ti-MCM-41 in the presence of methylaluminoxane (MAO), ethylene was polymerized to give a high molecular-weight, linear polyethylene.

## Introduction

Mesoporous zeolites consist of a porous silicate framework with a regular hexagonal array of uniformly sized channels in nanoscopic diameter (15–100 Å), and are characterized by an exceptionally large surface area (~1000 $m^2g^{-1}$).[1)] We were interested in utilization of mesoporous zeolites as inorganic nano-flasks for controlled polymerizations, as they could serve as restricted but adequately large spaces for the synthesis of macromolecular compounds. The present paper reports some results of our recent study on utilization of mesoporous zeolites for (1) free radical polymerization of vinylic monomers, (2) ring-opening polymerization of lactones, and (3) coordination polymerization of ethylene.



Scheme 1: Schematic structure of mesoporous zeolite (MCM-41).

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## Free Radical Polymerization of Methyl Methacrylate

In free radical polymerization, the propagation reaction is generally more difficult to control than in ionic polymerizations, due to the irreversible termination of the growing polymer radicals through recombination and disproportionation. In order to control free radical polymerization, elegant methods by utilization of transition metals for the stabilization of growing polymer radicals have been developed.2) On the other hand, in addition to such "chemical approaches", so-called "physical approaches" have also been investigated by using some confined spaces such as organic micelles3) and inclusion crystals for spatial isolation of each growing polymer radical. We have been exploring the potential of a mesoporous zeolite such as MCM-41 as a nano-flask for free radical polymerization of methyl methacrylate.4)

The free radical polymerization of methyl methacrylate (MMA) within the mesoscopic channels of MCM-41 at 100 °C proceeded to give a high molecular-weight polymer under appropriate conditions. Typically, a mixture of MMA, 2,2'-azoisobutyronitrile (AIBN) (mole ratio MMA/AIBN of 200), and thermally degassed MCM-41 powder was subjected to several freeze-to-thaw cycles. Then, the resulting "guest-including MCM-41 powder" was isolated by filtration from the suspension, and put into a polymerization tube. The tube was heated at 100 °C under $N_2$ to initiate the polymerization. After 2 h, the contents of the tube were transferred into tetrahydrofuran containing hydroquinone as a radical scavenger, and the resulting suspension was refluxed for 3 days to extract polymeric fractions from the channels.

The polymer obtained under the above conditions (71 % yield based on the amount of MMA) had a high molecular weight ($M$n = 360,000, $M$w/$M$n = 1.7), as observed by gel permeation chromatography (GPC). On the other hand, without MCM-41 under otherwise identical conditions to the above, a polymer with a much lower molecular weight ($M$n = 36,000, $M$w/$M$n = 2.8) was obtained. These results suggest a

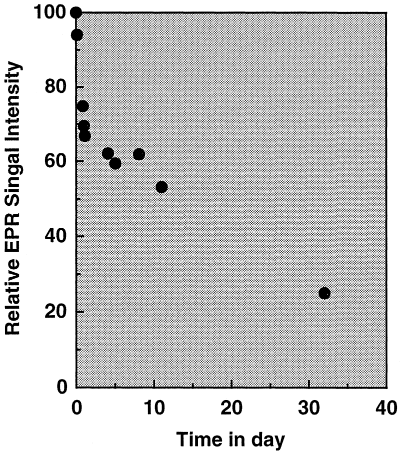


Fig. 1: Polymerization of MMA initiated with 2,2'-azoisobutyronitrile (AIBN) at a mole ratio $[MMA]_0/[AIBN]_0$ of 200 within the MCM-41 channels. Change in intensity of the EPR signal of the polymerization mixture after heating at 100 °C for 2 h.

possible elongation of the propagating polymer radical within the mesoporous channel. Accordingly, electron paramagnetic resonance (EPR) spectroscopy showed a signal due to the propagating polymer radical, which decayed slowly as shown in Fig. 1, where about 30% of the initial intensity remained even after a month.

Taking the above results into account, we explored the possibility of molecular weight control by changing the monomer-to-initiator mole ratio within the MCM-41 channels. The polymerizations of MMA within the MCM-41 channels initiated by benzoyl peroxide (BPO) at three different mole ratios of 100, 150, and 200 proceeded to attain about 25% monomer conversion in 6 days. The molecular weights of the resulting PMMAs showed a linear correlation to the mole ratio $[\mathrm{MMA}]_0/[\mathrm{BPO}]_0$ (Fig. 2).

These observations indicate a potential utility of the confined channels of MCM-41 for controlled free radical polymerization.

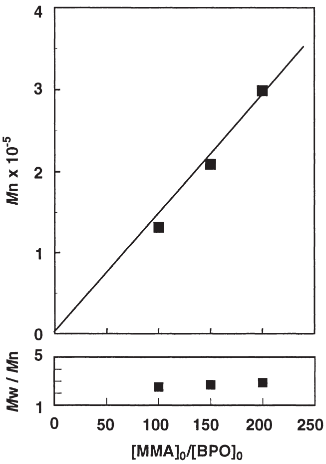


Fig. 2: Polymerization of MMA initiated with benzoyl peroxide (BPO) within the MCM-41 channels. *M*n (■) (*M*w/*M*n (●)) –$[\mathrm{MMA}]_0/[\mathrm{BPO}]_0$ relationship.

## Ring-Opening Polymerization of Lactones

Polyesters from lactones are important precursors for several polymeric materials and also have attracted attention as biodegradable polymers. We have reported that ring-opening polymerization of lactones proceeds with bulky Lewis acids in the presence of alcohols in a living manner.5) Along this line, mesoporous zeolites with a Lewis acidic surface are expected to serve as new class of inorganic polymerization catalysts. In fact, Al-MCM-41, which consists of Lewis acidic aluminosilicate framework, catalyzed controlled ring-opening polymerization of lactones such as $\delta$-valerolactone (VL) and $\varepsilon$-caprolactone (CL) initiated with alcohols, to give narrow molecular-weight-distribution (MWD) polyesters.6)

For example, when a mixture of VL and BuOH at a mole ratio of 11 was added under $N_2$ to a flask containing Al-MCM-41 (Si/Al = 17, 0.1 g), and the resulting suspension was stirred magnetically at 50 °C, the polymerization proceeded to attain 96.4% monomer conversion in 237 h, and gave a narrow MWD polymer with *M*n of 1,200 (*M*w/*M*n = 1.07). The molecular weight of the polymer could be controlled over a wide range by changing the feed molar ratio of the monomer to the alcohol, while the MWD stayed in a narrow range (Fig. 3).

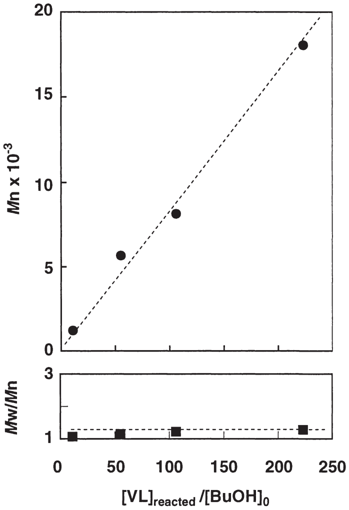
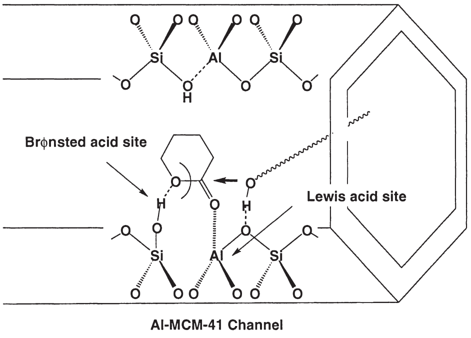


Fig. 3: Polymerization of $\delta$-valerolactone (VL) initiated with BuOH in the presence of Al-MCM-41. *M*n (●) (*M*w/*M*n (■)) –$[VL]_{reacted}/[BuOH]_0$ relationship.

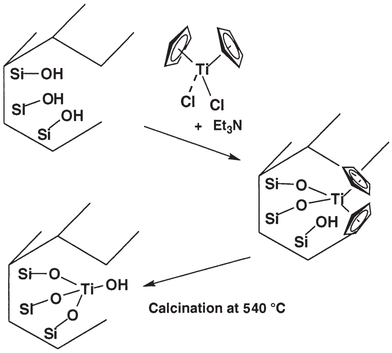
To investigate the living character of the polymerization, a sequential two-stage polymerization of VL and CL was attempted. The first-stage polymerization of VL with Al-MCM-41/BuOH was carried out at 50 °C to produce a prepolymer (*M*n = 1,200, *M*w/*M*n = 1.07). After the complete consumption of VL, CL was added at 100 °C to the system, then the second-stage polymerization of CL took place to attain 100% monomer conversion. The GPC profile of the polymerization mixture showed a unimodal, sharp chromatogram at a higher molecular weight region (*M*n = 3,200, *M*w/*M*n = 1.20), indicating the formation of a block copolymer of VL and CL. Thus, the polymerization of lactones with the Al-MCM-41/ROH has a living character. In contrast to Al-MCM-41, a microporous zeolite (zeolite-Y) with much narrower pores (pore diameter = 8 Å) was not effective for the polymerization of VL at 50 °C. This result indicates an importance of the large surface area and a wide pore width of Al-MCM-41 for the accessibility of the monomer and the polymer to the propagating site.

For the mechanism of the polymerization, we propose the "activated monomer mechanism" (Scheme 2), where the monomer is activated through a cooperative interaction with the Lewis acidic aluminum atom and the Brϕnsted acidic SiOH functionality, since neither pure silicate MCM-41 nor Al–MCM-41 having masked SiOH functionalities with methyl groups was effective for the polymerization.



Scheme 2: Proposed mechanism for the polymerization of $\delta$-valerolactone (VL) with alcohol within the aluminosilicate channels of Al-MCM-41.

The above results prompted us to investigate the polymerization of VL with MCM-41 containing other Lewis-acidic metal ions. Thus, a titanate-containing MCM-41 (Ti-MCM-41), prepared by mounting $Cp_2TiCl_2$ on the MCM-41 surface, followed by calcination (Scheme 3),[7] was chosen. Interestingly, the polymerization profile was much different from that with Al-MCM-41.[8] For example, when a mixture of VL (4 mL) and Ti-MCM-41 (0.25 g) was heated at 50 °C under $N_2$ without solvent, the polymerization took place very slowly to attain 12% monomer conversion in 43 h. It should be noted 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 polymeric materials formed and precipitated. GPC analysis of the THF-insoluble fraction with chloroform as eluent showed a multimodal MWD, suggesting 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 $10^6$. Fine-tuning of the polymerization with Ti-MCM-41 may be the subject worthy of further investigation.



Scheme 3: Method for the preparation of Ti-MCM-41.

## Polymerization of Ethylene

Polymerization of olefins by supported catalysts have been of interest from an industrial point of view. We have found that Ti-MCM-41 in the presence of methylaluminoxane (MAO) initiates polymerization of ethylene, to give a high molecular-weight, linear polyethylene.

Typical polymerization procedure is as follows: A toluene solution of MAO (Al/Ti = 100) was added to a glass autoclave (100 mL) containing dried Ti-MCM-41 powder (0.05 g). To this autoclave was introduced ethylene gas at an initial pressure of 10 atm with stirring at room temperature. The pressure was observed to drop gradually as the polymerization proceeded, where a complete consumption of ethylene was attained in 70 h. Then, a small amount of methanolic HCl was added to the polymerization mixture, and an insoluble fraction was isolated by filtration and washed with methanol. After extraction with *o*-dichlorobenzene at 180 °C, the polymeric fraction, free from inorganic compounds, was subjected to GPC to determine the molecular weight. Under appropriate conditions, a polyethylene with a very high molecular weight such as 1,500,000 was obtained. This is in sharp contrast with the case under homogeneous conditions using the $Cp_2TiCl_2$/MAO system, where the molecular weight of the polymer was only as low as 100,000. Using the Ti-MCM-41/MAO system, a polyethylene with a much higher molecular weight was obtained by reducing the mole ratio Al/Ti. In these cases, $^{13}C$ NMR spectroscopy showed that the produced polymers are linear without any branch structures. It should be also noted that $AlMe_3$ and $AlEt_3$ serve as effective co-catalysts for the polymerization of ethylene with Ti-MCM-41. Thus, Ti-MCM-41 has a potential utility for the synthesis of linear, high molecular-weight polyethylene.

## Conclusion

A recent progress in the chemistry of mesoporous zeolites has made it possible to modify chemical and physical properties of the channels. In the present paper, we have shown that mesoporous zeolites are interesting materials as nano-flasks for controlled polymerization of a variety of monomers. Fine-tuning of the surface properties by incorporation of transition metal atoms onto/into the silicate framework is one of the subjects worthy of further investigation.

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