

Synthesis and Properties of Poly[4,4-bis(acetoxymethyl)-1,6-heptadiyne]

Yun-Hi Kim

Gyeongsang National University, Research Institute of Industrial Technology, Chinju 660-701, Korea

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The polymerization of 4,4-bis(acetoxymethyl)-1,6-heptadiyne (BAH) was carried out by MoCl_5 and WCl_6 with various organometallic cocatalysts. MoCl_5 -based catalysts were more effective than WCl_6 -based ones for the cyclopolymerization of BAH. Poly(BAH) was characterized to have polymer backbone with conjugated double bond and cyclic structure by IR, UV-visible, and ^1H - and ^{13}C NMR spectroscopies. The polymer was stable up to 310 °C and 5% weight loss show up at 350 °C. The resulting dark violet polymer exhibited good solubility in common organic solvents and could be cast on a glass plate to give film with good mechanical properties. It was found that oxygen permeability (PO_2) and permselectivity (PO_2/PN_2) of the resulting polymer were 15.2 barrer and 2.84, respectively.

Introduction

During the past decades, extensive studies on the polymerization of simple mono- and disubstituted acetylenes have been made to improve such problems of polyacetylene as its lack of processibility and its thermal and environmental instability.^{1,2} However, substituted polyacetylenes usually had low effective conjugation length due to their hindered coplanarity. But, cyclopolymers prepared from 1,6-heptadiyne derivatives have more coplanar polyene structure because of their particular steric effect although they are derivatives of substituted polyacetylenes.^{3,4}

We have reported on the polymerization of 1,6-heptadiyne derivatives with various functional groups by using MoCl_5 and WCl_6 based catalyst systems.⁵⁻¹⁵ The corresponding polymers have good solubility in organic solvents and long term stability toward oxidation. They have also various functionalities such as electrical conductivity,⁵⁻¹⁰ photoconductivity,¹² and side chain liquid crystallinity^{13,15} by the introduction of proper functional groups.

Recently, we also have been studied on poly(1,6-heptadiyne derivative)s as gas permeable membrane by introducing proper functional groups such as perfluoroalkylester and t-butyltrimethylsiloxy group at 4-position of 1,6-heptadiyne.^{7,14,15} Most of these polymers exhibited relatively worse mechanical properties due to weak interchain attraction. However, there is no report on the poly(1,6-heptadiyne derivative)s containing acetate group which is expected to have good mechanical properties resulted from strong interchain interaction.

This article deals with the synthesis, structure characterization, and properties of poly[4,4-bis(acetoxymethyl)-1,6-heptadiyne]. The mechanical properties and gas separation characteristics of the resulting polymer are also studied.

Experimental

Material. Propargyl bromide (Aldrich Chem. Co., 80% solution of toluene) and diethylmalonate (Aldrich Chem. Co., 99%) were dried over calcium hydride and fractionally distilled prior to use. MoCl_5 and WCl_6 (Aldrich Chem. Co., resublimed 99.9%) were used without further purification.

Tetra-n-butyltin and ethylaluminum chloride (Aldrich Chem. Co.) were used as received. LiAlH_4 and acetyl chloride were also used without further purification. All solvents were used after purification according to conventional methods.⁵

Preparation 4,4-bis(hydroxymethyl)-1,6-heptadiyne (BHOMH). Diethyl dipropargyl-malonate (33 g, 140 mmol) which was prepared by literature method⁷ was dissolved in 80 mL of diethyl ether. The solution was added dropwise over a period of 1 h to a suspension of LiAlH_4 (8.83 g, 220 mmol) in 300 mL of diethyl ether at room temperature. The reaction mixture was refluxed for additional 6 h. Water was added dropwise to the gray suspension until the evolution of H_2 was ceased. The reaction mixture was extracted with diethyl ether and the solution was dried over anhydrous MgSO_4 . The ether was removed *in vacuo* to give a white solid product that could be recrystallized from ether (17.6 g, 82%); ^1H NMR δ 3.69 (s, 4H, OCH_2), 2.55 (br s, 2H, OH), 2.34 (d, 4H, CH_2), 2.01 (t, 2H, $\equiv\text{CH}$); ^{13}C NMR δ 80.1 ($-\text{C}\equiv$), 71.0 ($\equiv\text{CH}$), 66.3 (OCH_2), 42.0 (quarternary C), 21.6 ($\text{CH}_2\text{C}\equiv$). Anal. Calcd for $\text{C}_6\text{H}_{12}\text{O}_2$: C, 71.03; H, 7.95. Found: C, 71.01; H, 7.90.

Preparation 4,4-bis(acetoxymethyl)-1,6-heptadiyne (BAMH). Acetyl chloride (7.8 g, 10 mol) was added to the mixture of BHOMH (7 g, 4.6 mmol) and 200 mL of triethyl amine in an ice bath. The mixture was refluxed during 12 h. Then the reaction solution was cooled and poured into cold water, and was extracted with diethyl ether. The organic layer was dried over anhydrous MgSO_4 and the volatile compounds were removed *in vacuo*. The resulting oily product was distilled to afford a colorless liquid (Yield: 92%, Bp: 101 °C/0.1 mmHg); ^1H NMR δ 4.1 (s, 4H, OCH_2), 2.5 (d, 4H, $\equiv\text{C}-\text{CH}_2$), 2.3 (s, 6H, CH_3), 2.1 (t, 2H, $\equiv\text{CH}$); IR cm^{-1} 3300 ($\equiv\text{C}-\text{H}$), 2120 ($\text{C}\equiv\text{C}$), 1750 ($\text{C}=\text{O}$); Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_4$: C, 66.10; H, 6.78. Found: C, 66.02; H, 6.73.

Instruments for characterization. ^1H - and ^{13}C NMR spectra were recorded with a Bruker AM-200 spectrometer and chemical shifts were reported in ppm with TMS as internal standard. Infrared spectra were measured on a Bomem MB-100 FT spectrophotometer. Thermogravimetric analysis was conducted with a DuPont TGA

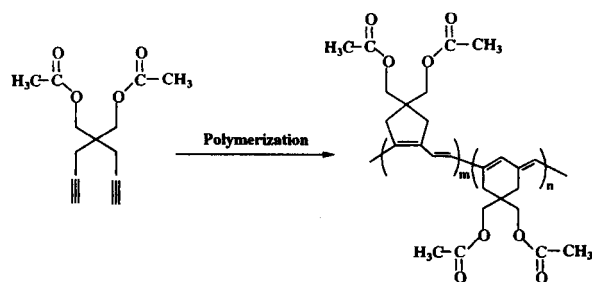
9900 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C/min. Number average molecular weights (M_n) were determined in THF solution by a Waters GPC-150C calibrated with polystyrene standards. Electrical conductivities were measured by the 2-point probe dc method employing a Hewlett-Packard 6216A power supply and Keithley 485 picoammeter. Tensile tests were conducted at 25 °C with the rate of strain fixed at 86%/min on an Instron 1122. The size of the specimen was $35 \times 10 \times 0.2$ mm. Gas permeabilities for the polymer membrane with about 40 μm of thickness were measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane. The upstream was maintained to a constant pressure of 5 kgf/cm² of either pure O₂ or N₂ gas during the experimental period, and the downstream was opened to the atmosphere. A bubble gas flowmeter was employed to measure the permeation flux, steady-state from which the gas permeability was calculated. Elemental analysis was performed with a Perkin Elmer 240DS elemental analyzer.

Polymerization. All procedure for the preparation of catalyst systems and polymerization were carried out under dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent as 0.1 M solutions before use. A typical polymerization procedure was as follows: Solvent, catalyst solution and when needed, cocatalyst solution were injected into a 20 mL ampule equipped with a rubber septum. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, monomer dissolved in each solvent was injected into the polymerization ampule. After the mixture was allowed to react at 60 °C for 24 h, the polymerization was terminated by adding a small amount of methanol and chloroform was added to dissolve polymer. The resulting solution was poured into a large amount of methanol, and the polymer was filtered and dried under vacuum at 40 °C for 24 h. Anal. Calcd for poly(BAMH) (C₁₃H₁₆O₄)_n: C, 66.10; H, 6.78; Found: C, 65.96; H, 6.67.

Doping. The iodine doping was performed by exposing the polymer film or pellet to iodine vapor in a vacuum desiccator (initially at 0.5 mmHg) at 20 °C for 12 h. The dopant concentration was calculated from weight uptake method.

Results and Discussions

The polymerization of BAMH was carried out by MoCl₅- and WCl₆-based transition metal catalysts under various reaction conditions. Table 1 shows the results of the poly-



Scheme 1.

merization of BAMH. It was found that MoCl₅-based catalysts was more effective than WCl₆-based ones for the cyclopolymerization of BAMH. (*n*-Bu)₄Sn and Et₂AlCl have been known to be excellent co-catalysts for the polymerization of mono- and disubstituted acetylenes.^{19,20} However, (*n*-Bu)₄Sn used as co-catalyst with MoCl₅ hardly affected the polymer yield and number average molecular weight (M_n) of poly(BAMH). In the case of Et₂AlCl used as co-catalyst with MoCl₅, the polymer yield as well as number average molecular weight were rather decreased. WCl₆ exhibits remarkably lower catalytic activity than MoCl₅. This results are similar to that of 1,6-heptadiyne derivatives which have polar functional groups such as hydroxy and ester.^{7,8,9}

The structure of the polymer was analyzed by ¹H- and ¹³C NMR, IR, and UV-visible spectroscopies and elemental analysis. Figure 1 represents the ¹H NMR spectrum of poly(BAMH). While the acetylenic proton peak at 2.1 ppm disappeared, the new broad peak which is assignable to the proton of conjugated double bond appeared in the range of 6.0-6.8 ppm in the ¹H NMR spectrum. As shown in Figure 2, the IR spectrum of poly(BAMH) shows the carbon-carbon stretching band of conjugated double bond at 1600-1650 cm⁻¹. On the other hand, the acetylenic carbon-hydrogen stretching band (3300 cm⁻¹) and carbon-carbon stretching band (2120 cm⁻¹) of triple bond which are characteristic absorption bands of the monomer did not show up at all. Figure 3 shows the ¹³C NMR spectra of BAMH and poly(BAMH). In the spectrum of poly(BAMH), while acetylenic carbon peaks at 80 and 71 ppm disappeared, carbon peaks of the conjugated double bond appeared at 123 and 138 ppm. The peak of methylene carbon adjacent to quaternary carbon is shifted from 20 ppm to 43 ppm by cyclopolymerization. The UV-Visible spectrum (Figure 4) of the polymer obtained from chloroform solution exhibit two characteristic broad peaks (λ_{max} =550, 590 nm) in the range of 400-600 nm, which is due to the $\pi \rightarrow \pi^*$ transition of conjugated polyenes. The fact that the λ_{max} of poly(BAMH) is remarkably red-shifted as compared with other poly-

Table 1. Polymerization of 4,4-Bis(acetoxymethyl)-1,6-heptadiyne by Transition Metal Catalysts^a

Experimental Number	Catalyst System ^b (mole ratio)	Polymer yield (%)	Number Average Molecular Weight(M_n) ^c
1	MoCl ₅	99	110000
2	MoCl ₅ ^d	92	150000
3	MoCl ₅ :(<i>n</i> -Bu) ₄ Sn(1:2)	94	125000
4	MoCl ₅ :Et ₂ AlCl(1:2)	78	80000
5	WCl ₆	10	-
6	WCl ₆ :(<i>n</i> -Bu) ₄ Sn(1:2)	10	-
7	WCl ₆ :Et ₂ AlCl(1:2)	12	-
8	WCl ₆ :EtAlCl ₂ (1:2)	15	-

^aPolymerization was carried out at 60 °C for 24 h. Initial monomer concentration ($[M]_0$) was 0.125 M and mole ratio of monomer to catalyst was 50. ^bMixture of catalyst and cocatalyst in 1,4-dioxane was aged at 30 °C for 15 min. before use as cocatalyst. ^cDetermined by GPC with polystyrene standards. ^dInitial monomer concentration ($[M]_0$) was 0.125 M and mole ratio of monomer to catalyst was 100.

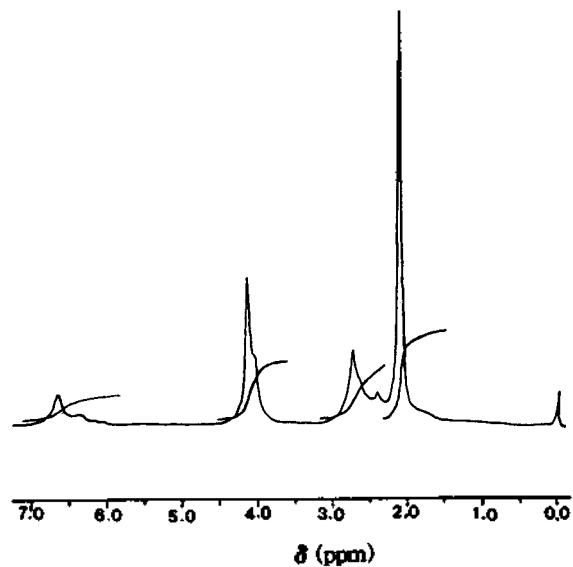


Figure 1. A ^1H NMR spectrum of poly(BAMH) (CDCl_3).

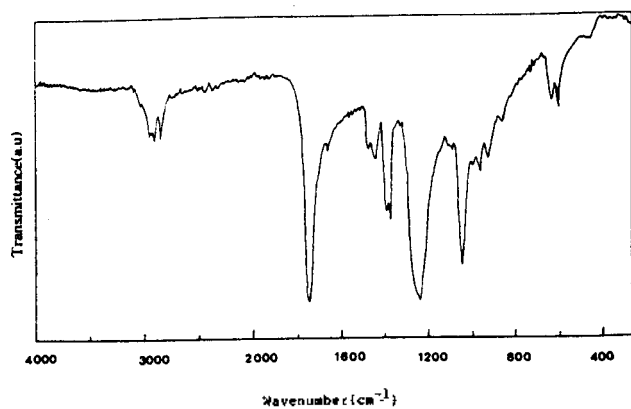


Figure 2. A IR spectrum of poly(BAMH) (KBr pellet).

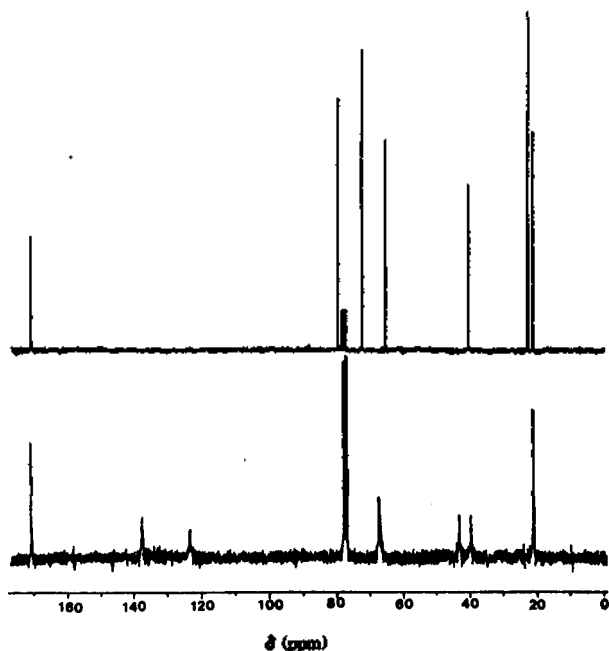


Figure 3. ^{13}C NMR spectra of BAMH and poly(BAMH) (CDCl_3).

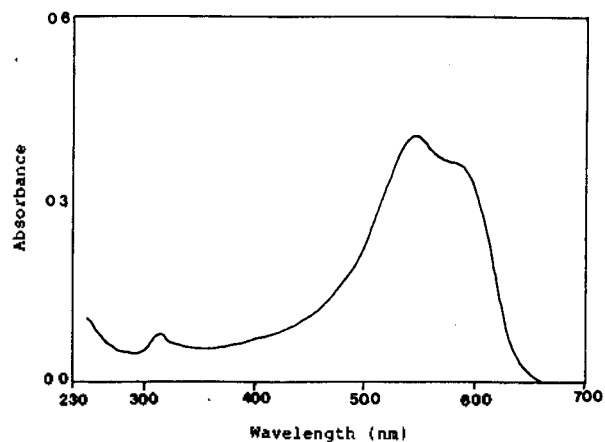


Figure 4. A UV-Visible spectra of poly(BAMH) in chloroform ($[\text{M}]=1 \times 10^{-5}$ M).

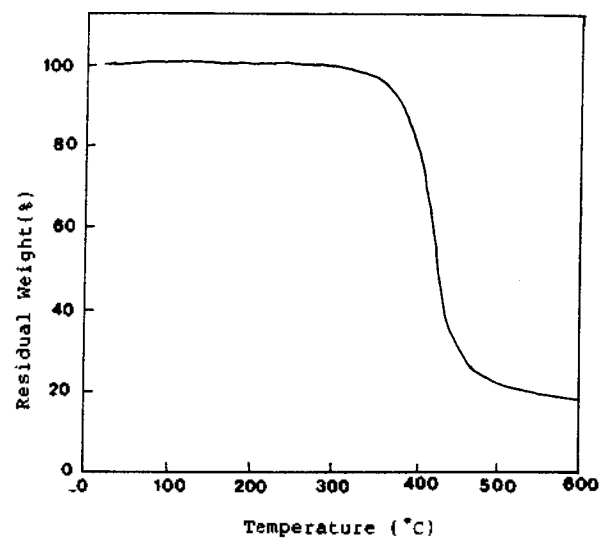


Figure 5. A TGA thermogram of poly(BAMH).

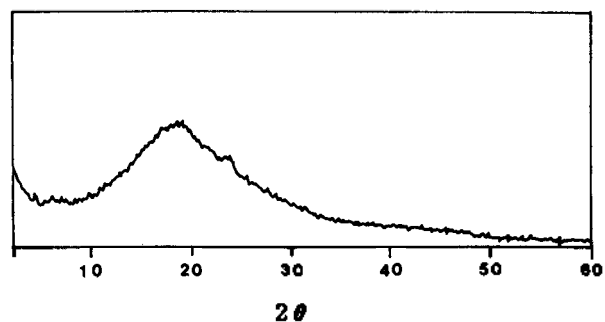


Figure 6. A X-ray diffractogram of poly(BAMH).

(acetylene derivative)s means that the polymer backbone is a highly conjugated double bond.^{2,18} From the obtained spectroscopic data, we can conclude that the polymer has planar conjugated backbone and recurring five and/or six membered cyclic ring structure as shown in Scheme 1.^{18,21} It is difficult to know the exact composition ratio of five membered ring to six membered one. However, we can suppose that

Table 2. Mechanical Properties, Oxygen Permeabilities and Permselectivities of Several Poly(1,6-heptadiyne derivative)s

Parameter	Poly (BAMH)	Poly ^a (DFHDPM)	Poly ^b (TFEDPM)	Poly ^c (HFPDPM)	Poly ^d (BTSH)	Poly ^e (DEDPM)
E, MPa	1400	700	1160	750	340	4800
σ_B , MPa	75	20	28	18	9	104
γ_B , %	10.5	9	11.1	20	2.8	3.4
PO_2 , barrer	15.2	80	12.8	7.14	320	3.3
PO_2/PN_2	2.84	2.8	1.6	1.7	2.3	1.8

^aData from ref. 16; Poly(DFHDPM)=poly[bis(dodecafluoroheptyl)dipropargylmalonate]. ^bData from ref. 9; Poly(TFEDPM)=poly[bis(2,2,2-trifluoroethyl)dipropargylmalonate]. ^cData from ref. 9; Poly(HFPDPM)=poly[bis(1,1,1,3,3,3-hexafluoro-2-propyl)dipropargylmalonate]. ^dData from ref. 17; Poly(BTSH)=poly[4,4-bis(*t*-butyldimethylsiloxy)methyl-1,6-heptadiyne]. ^eData from ref. 7; Poly(DEDPM)=poly(diethylidipropargylmalonate). ^fYoung's modulus. ^gTensile strength. ^hElongation at break. ⁱIn units of cm³(STP)cm/(cm²scmHg).

poly(BAMH) may have five-membered rings predominantly rather than six-membered one, because as shown in the ¹³C NMR spectrum of poly(BAMH), the quarternary carbon of resulting polymer showed up at 40 ppm as one sharp peak to be able to conclude that poly(BAMH) has almost one kind of ring.²¹ The data for the elemental analysis of poly(BAMH) found are well consistent with the theoretical values.

The TGA thermogram of poly(BAMH) under nitrogen atmosphere (Figure 5) shows that the polymer is thermally stable up to 310 °C. A 5% weight loss of poly(BAMH) was observed at 350 °C and residual weight at 600 °C was 20%. Poly(BAMH) has a relatively high thermal stability as compared with other polyacetylene derivatives.^{7,10}

The obtained polymer was completely soluble in common organic solvents such as chlorobenzene, toluene, chloroform, tetrahydrofuran, dimethylformamide, and ethylacetate but it was insoluble in polar protic solvents and low- and non-polar solvents such as methanol, ethyl ether, *n*-hexane, and carbon tetrachloride etc. The morphology of poly(BAMH) was investigated by X-ray diffraction analysis (Figure 6). As shown in Figure 6, because the peaks in the diffraction pattern are all broad and the ratio of the half height width to diffraction angle ($\Delta 2\theta/\theta$) is greater than about 0.4, poly(BAMH) is believed to be amorphous. The electrical conductivity of film type poly(BAMH) is 4.5×10^{-13} S/cm. Doping of poly(BAMH) by I₂ rouse up a remarkable increase of the electrical conductivity. The electrical conductivity of iodine-doped film [(C₁₃H₁₆O₄)₁(I₂)_{0.3}] is 1.5×10^{-3} S/cm. The morphology and electrical conductivity of poly(BAMH) are similar with other poly(1,6-heptadiyne derivative)s. A dark-violet homogeneous film was easily obtained by casting the polymer solution in chloroform on a glass plate. In order to evaluate the possibility of poly(BAMH) for the practical application as membrane, the mechanical properties, oxygen permeability (PO_2) and permselectivities of oxygen to nitrogen (PO_2/PN_2) of poly(BAMH) film were examined. Table 2 lists the mechanical properties, PO_2 and PO_2/PN_2 for several poly(1,6-heptadiyne derivative)s containing various functional groups.^{7,9,16,17} The mechanical properties of poly(BAMH) considerably increase as compared with those of the poly(1,6-heptadiyne derivative)s with bulky *t*-butyldimethylsilyloxymethyl or perfluoroalkyl esters. It is believed that high mechanical properties of poly(BAMH) is due that interpolymer attraction resulted from acetate group is stronger than those from oth-

er functional groups. As shown in Table 2, poly(BAMH) has 15.2 barrer of relatively high oxygen permeabilities (PO_2) and 2.84 of moderately high permselectivities (PO_2/PN_2) as compared with other poly(1,6-heptadiyne derivative)s. This result may be explained by the fact that acetoxy functional group of poly(BAMH) afford larger free volume and/or oxygen solubility needed for gas permeation than substituents of poly(DEDPM), poly(TFEDPM) and poly(HFPDPM).

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MAS NMR and XRD Study on the Vanadium Site of Vanadium Silicate Mesoporous Molecular Sieve MCM-41

Dong Ho Park, Chi-Feng Cheng*, and Jacek Klinowski*

Department of Chemistry, Inje University, Kimhai 621-749, Korea

**Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U. K.*

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A wide range ($10 < \text{Si/V}$) of mesoporous vanadium silicate molecular sieves with the MCM-41 structure have been synthesized using vanadyl sulfate as the source of vanadium and characterized by XRD, ^{51}V MAS NMR and ^{29}Si MAS NMR. The increase of the unit cell parameter and the decrease of Q_3/Q_4 ratio of ^{29}Si spectra with the vanadium content suggest the incorporation of vanadium in the framework of MCM-41 structure. ^{51}V MAS NMR demonstrates that vanadiums in as-synthesized V-MCM-41 are present in the chemical environment of octahedra and octahedral vanadium is decreased and tetrahedral vanadium is increased inversely with raising the calcination temperature. Though the thermal treatment in rotor of hydrated sample resulted in the change from tetrahedral environment to octahedral one and the steaming and the acid treatment affect to the chemical environment of vanadium, the spectrum similar to originally calcined sample is regenerated after recalcination. This indicates that the vanadium is belong to the framework in a relatively exposed site. The best quality XRD pattern of the product of $\text{Si/V}=27$ may be attributable to heterogeneous nucleation mechanism. V-MCM-41s having the Si/V ratio lower than 20 are completely collapsed after calcination.

Introduction

Microporous (pore diameter ≤ 20 Å) and mesoporous (20–100 Å) inorganic materials admit molecules below a certain critical size into their extensive internal space, which makes them of considerable interest as heterogeneous catalysts and sorbents.

In recent years increasing attention has been directed toward the study of new mesoporous material MCM-41,¹ since Kresge *et al.* discovered a new family of molecular sieves designated as M41S. Especially metal-substituted MCM-41 such as Ti ,² V ,³ Ga ,⁴ Mn ,⁵ B ,⁶ and Fe ⁷ are interesting due to their catalytic properties in addition to the potential of catalytic reaction of large molecule within the mesopore varying from 15 Å to 100 Å. The established importance of vanadium compounds as catalysts for oxidation reactions has made vanadium containing MCM-41 attractive.

V-MCM-41 as well as other vanadium containing molecular sieves which are reported to have superior catalytic activity in the ammoxidation of propane and xylenes,^{8,9} oxidation of butadiene to furan,¹⁰ and oxidative dehydrogenation of propane to propylene¹¹ seem to have different and/or in some case improved catalytic performances compared to supported vanadium oxide catalysts for the

selective oxidation of large organic molecules using hydrogen peroxide.³ Some recent data showed that vanadium in V-MCM-41 belongs to the molecular sieve framework and resides on the surface of the channels in a relatively exposed position. Vanadium in MCM-41 may be either in the framework of molecular sieve or present as some foreign species, possibly bound chemically at the surface.³

We have prepared a series of vanadium silicate MCM-41 having a wide range of Si/V ratio more than 10 and especially vanadium highly containing MCM-41 of good quality. The chemical environment of vanadium using ^{51}V MAS NMR was characterized. We want to acquire better understanding of properties of vanadium in order to modify and improve the catalytic activity of V-MCM-41.

Experimental Section

The synthesis of V-MCM-41 was carried out by the following procedure. 6 g of fused silica (Cab-O-Sil, M5, BDH) was added to the NaOH solution made of 1.36 g NaOH (Fision) and 58 g H_2O and stirred for 2 h. To this solution, vanadyl sulfate ($\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ 99%: Aldrich) solution at various concentration depending on the Si/V ratio with 25 g H_2O was added and stirred for 3 h. Surfactant CTABr