

Dehydrochlorination Behavior of Flexible PVC Pellets in NaOH Solutions at Elevated Temperature

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ABSTRACT: Flexible PVC pellets were treated at 150–250°C in 0–7M NaOH solutions for 0–12 h. The degree of dehydrochlorination of flexible PVC pellets increased with increasing reaction temperature and was about 100% at 250°C over 5 h. A porous char, 2–16 μm in pore size, was produced. The dehydrochlorination of PVC in the flexible PVC was proceeded by a first-order reaction in alkaline solution. The maximum rate of the dehydrochlorination for flexible PVC was reached at 5M NaOH. The apparent activation energies were 22–35 kcal/mol in 1–7M NaOH for flexible PVC. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2171–2177, 1998

Key words: flexible PVC; dehydrochlorination; porous char; first-order reaction; alkaline solution

INTRODUCTION

Development of new fuel and feedstock recycle processes for PVC materials is expected to increase the recycle degree of waste plastics as the amount of waste plastics increases year-by-year. There are several problems for the incineration of waste PVC materials and waste plastics containing it. PVC materials, about 10% of the total waste plastic, produce HCl, damage an incinerator, and yield toxic substances such as dioxins.

The recycle degree of agricultural PVC film is as high as 34% and one-sixth of the amount of cable jacketing waste is used as material recycle. However, the material recycle of waste PVC materials has reached almost the limit in Japan.

Many studies have been done as follows: In the dry process, activated carbon and ion-exchange resin have been studied for the effective use of the char produced from PVC.^{1–4} As fuel recycle, by utilizing pyrolysis equipment with two screws rotating in opposite directions, PVC was decomposed at 320°C to gases and organic melt, and

then HCl was recovered.⁵ It utilizes the method in which the chloride in PVC film is eliminated first and olefinic plastics are pyrolyzed and liquefied. Advanced liquefaction processes for waste plastics separated from refuse are under development.⁶

On the other hand, various wet processes have been studied at elevated temperature. PVC powder has been oxidized by oxygen in a concentrated alkaline solution, yielding benzene carboxylic acids and 34 C % of oxalic acid.^{7,8} Water-soluble acids were obtained by oxygen oxidation of PVC in alkaline solutions.⁹ Dehydrochlorination treatments of PVC wastes were investigated up to 400°C in an alkaline solution.¹⁰ Small amounts of PVC monomer were recovered from PVC powder under 22–27 MPa oxygen at 380–450°C,¹¹ while chlorinated organic compounds were byproducts. Under hydrothermal degradation in an alkaline solution, the carbon number of the resulting oil was large and a small amount of chlorinated organic compounds was found.¹² Large amounts of chlorinated organic compounds are formed in the dehydrochlorination of waste plastics. Therefore, it is important to develop any reaction processes without producing chlorinated organic compounds in the feed stock recycles such as liquefac-

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Table I Composition of Flexible PVC Pellet (wt %)

PVC	36.8
CaCO ₃	28.3
DINP	23.9
Chlorinated paraffin	6.99
Alkylbenzene	1.84
Pb stabilizer	1.10
Calcium stearate	0.74
Wax	0.37

DINP: C₆H₄(COOC₉H₂₀)₂.

tion and conversion to raw chemicals. Dehydrochlorination of PVC in aqueous solution at elevated temperature gives no chlorinated organic compounds and yields porous char. Thus, it is favorable for the pretreatment of waste plastics.

PVC materials containing a stabilizer and plasticizer are utilized in various areas as rigid and flexible PVC. For example, flexible PVC is used for agricultural film, wire and cable jacketing, and packing film, etc. The behavior of the dehydrochlorination of PVC materials has not been studied, nor have any kinetic studies been done. In this article, the effect of NaOH concentration and temperature on the dehydrochlorination of flexible PVC pellets were studied in an aqueous solution at elevated temperatures to develop a new feed stock recycle of PVC. In addition, the produced char was examined by SEM and the pore size was measured.

EXPERIMENTAL

Sample and Reagents

The composition of the flexible PVC used is shown in Table I. All chemicals were reagent grade.

Reaction System

An outline of an electric furnace with a rotating Al block is depicted in Figure 1. PTFE-lined SUS sealed tubes are set up in the Al block and rotated up to 100 rpm by an extended geared motor. The temperature in the electric furnace is controlled $\pm 2^\circ\text{C}$ at the prescribed temperature.

Experimental Procedure

Two-tenths of a gram of $5\phi \times 2$ mm of flexible PVC pellet and 20 mL of 0–7M NaOH solutions were each put into 25-mL SUS-316 tubes. Several

tubes were put in the Al block heated to the prescribed temperature and held during the reaction. The time required to increase the temperature inside the tubes was measured to be 1.8 h for 180°C, 2.0 h for 200°C, 2.2 h for 210°C, 2.5 h for 225°C, and 3.0 h for 250°C. The rotation was started at 33 rpm as soon as the tubes were set in. After the reaction, the tubes were removed and cooled at room temperature. The reaction product was filtered with a 1G4 glass filter weighed previously. The reaction solution was prepared to dilute the filtrate to 100 mL. Residues were washed with water and dried in a silicagel desiccator.

Analyses

One portion of the reaction solution was passed through a H⁺ cation-exchange resin (Amberlight IR-120B(H)) to remove Na⁺, and the chloride ion in the eluent was determined by ion chromatography. No chlorinated product was detected in the *n*-hexane extract from the product solution by gas chromatography (GC). The surface of residues was observed by a scanning electron microscope (SEM).

Definition

The degree of dehydrochlorination and weight loss are calculated as follows:

Dehydrochlorination (%)

$$\{(m_{\text{Cl},0} - m_{\text{Cl},t})/m_{\text{Cl},0}\} \times 100 \quad (1)$$

Weight loss (%) $\{(W_0 - W_t)/W_0\} \times 100 \quad (2)$

where $m_{\text{Cl},0}$ is number of moles of Cl in the reaction solution; $m_{\text{Cl},t}$, the number of moles of Cl contained in PVC; and W_0 and W_t , the quantities of the sample before and after the reaction, respectively.

The degree of dehydrochlorination obtained by eq. (1) was equal to the degree from elementary analysis of Cl in residues within an error of 1%. The degree of dehydrochlorination was calculated from the total Cl contained in both PVC and chlorinated paraffin.

RESULTS AND DISCUSSION

Degradation of Flexible PVC Pellet

Shape of Residues

SEM photographs shown in Figure 2 are as follows: (A) is flexible PVC and (B) is a sectional

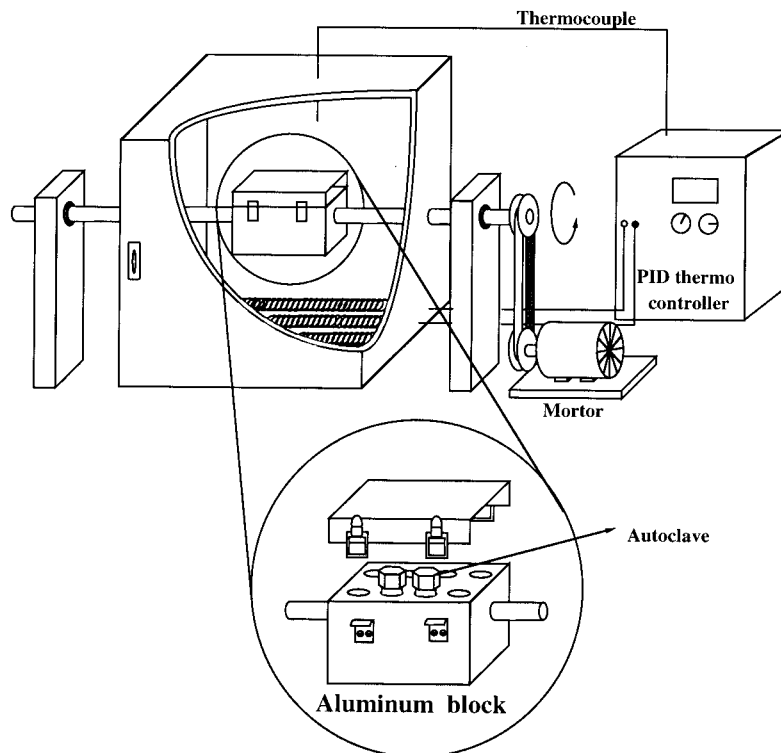


Figure 1 Electric furnace with a rotating Al block.

view of the residue of the granular flexible PVC with a 73.7% degree of dehydrochlorination charred at 225°C, in 3M NaOH for 12 h. Many pores of about 16 μm in size were observed inside the char from the flexible PVC. These pores, similar to ones produced by the hydrolysis of DOP and dehydrochlorination of agricultural PVC film,^{13,14} were produced by the decomposition of additives and dehydrochlorination of PVC as well.

Reaction Process

Observed and calculated weight loss curves of the flexible PVC examined at 225 and 250°C in 3M NaOH are shown in Figure 3. The weight loss was calculated from the degree of dehydrochlorination.

The difference between the observed and calculated values was large even in the beginning and increased gradually with time. This is because the flexible PVC contains large amounts of CaCO_3 (filling material) and DINP (plasticizer), besides 36.8% of PVC. They were decomposed in the early stage of the reaction, and their degradation rates were faster than those of dehydrochlorination. The weight loss was constant at 250°C after 5 h, because the dehydrochlorination had almost reached 100%.

Effect of Reaction Conditions on the Dehydrochlorination of Flexible PVC

Temperature

The dehydrochlorination curves of flexible PVC in 5M NaOH at 200–250°C are shown in Figure 4. The dehydrochlorination was already underway at 0 h, as the reaction time was determined after the temperature inside the tubes reached that prescribed. The rate of dehydrochlorination increased rapidly with temperature and the flexible PVC was entirely dehydrochlorinated at 250°C for 5 h.

NaOH Concentration

The effect of NaOH concentration on the degree of dehydrochlorination of flexible PVC at 225°C for 0–12 h is shown in Figure 5. The rate of dehydrochlorination increased with the concentration to 5M NaOH but dropped at 7M. Dehydrochlorination of PVC has been reported not to be affected by the alkali concentration until 10M at 250–400°C.¹⁵ This result does not agree with the present results, perhaps because the previous work was performed with pure PVC powder in a higher temperature range without stirring. The present results prove that the NaOH concentration af-

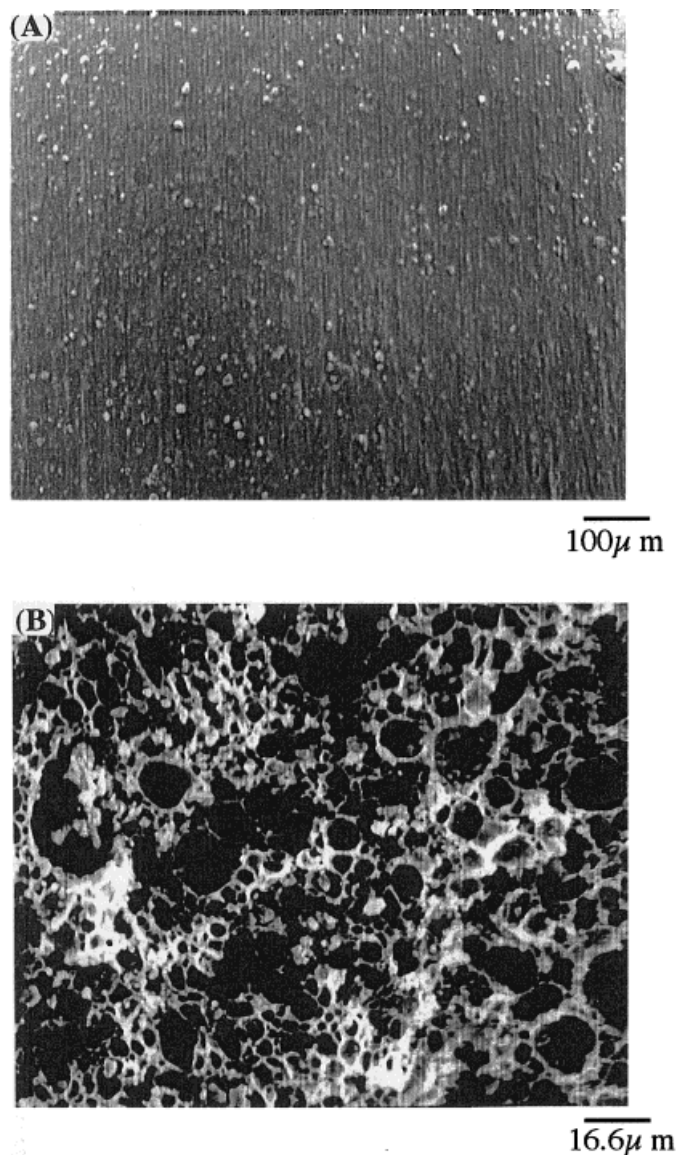


Figure 2 SEM photographs of (A) flexible PVC pellet and (B) residue of flexible PVC pellet in 3M NaOH at 225°C for 12 h.

affected the dehydrochlorination of flexible PVC material below 250°C.

Kinetics and Mechanism of the Dehydrochlorination

Dehydrochlorination of pure PVC powder proceeds in first order in the following cases: pyrolysis under nitrogen¹⁶ and in alkaline solutions.^{13,14} Consequently, it may be considered that the dehydrochlorination of PVC in flexible PVC also proceeds in first order. Equation (3) represents the first-order kinetics for the dehydrochlorination of flexible PVC in a NaOH solution:

$$-\ln(1 - X) = kt \quad (3)$$

where t is the reaction time; X , the degree of dehydrochlorination; and k , the apparent rate constant.

The first-order plot of the dehydrochlorination for flexible PVC at 200–250°C in 5M NaOH is shown in Figure 6. These plots show a good linearity, although these lines do not pass through the origin at 0 h due to the preheat time. Thus, this dehydrochlorination process can be expressed by a first-order reaction similar to previous work.

An Arrhenius plot of the apparent rate constant k calculated from these slopes is represented

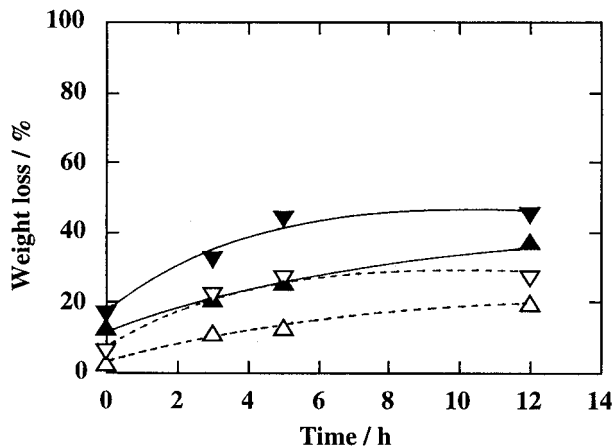


Figure 3 Observed and calculated weight loss curves of flexible PVC pellet in 3M NaOH. Weight loss observed: (—▲—) 225°C; (—▼—) 250°C. Weight loss calculated: (---△---) 225°C; (---▽---) 250°C. (----) Calculated value of decomposition due to the dehydrochlorination.

in Figure 7. The Arrhenius plot is linear and the apparent activation energy is 23 kcal/mol, indicating that the dehydrochlorination process is rate-controlling.

Figure 8 shows the effect of NaOH concentration and temperature on the apparent rate constant, k , for flexible PVC. The apparent rate constant showed a maximum at 5M NaOH concentration over the range of temperatures studied. The acceleration in rate can be explained as follows: At some point during the experiments, the

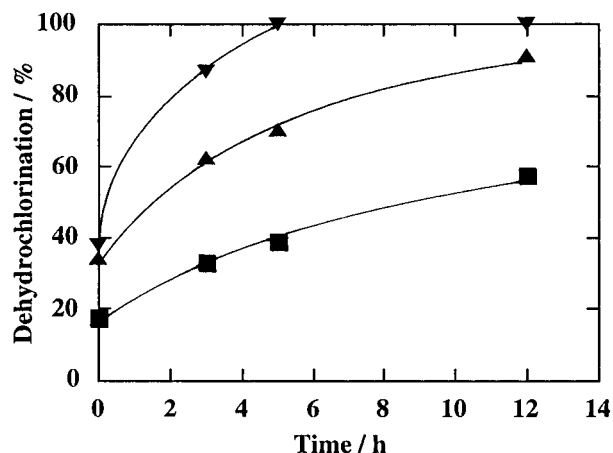


Figure 4 Effect of temperature on the degree of dehydrochlorination of flexible PVC pellets in 5M NaOH. Temp (°C): (—■—) 200°C; (—▲—) 225°C; (—▼—) 250°C.

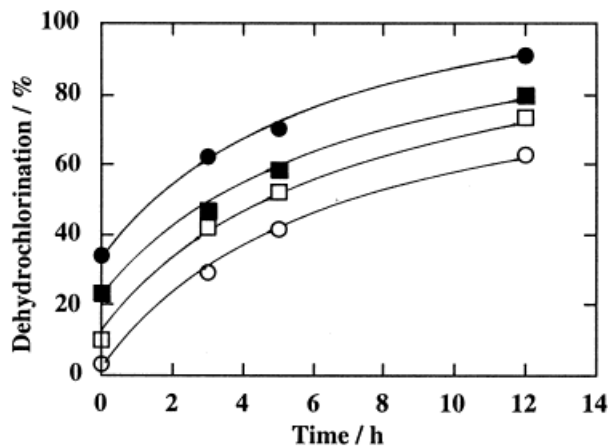


Figure 5 Effect of NaOH concentration on the degree of dehydrochlorination of flexible PVC pellet at 225°C. NaOH (M): (—○—) 1; (—□—) 3; (—●—) 5; (—■—) 7.

flexible PVC pellet is converted to a porous char that has an expanded volume over the mother flexible PVC pellet. Therefore, in this state, there is improved mass transfer caused by the higher porosity. The decrease in the apparent rate constant in Figure 8 can be explained as follows: As the concentration of NaOH increases, transport properties such as density also increase. Since the solid has become porous, a mass- and heat-transfer effect is present due to the solid-liquid contact. In addition, there is the possibility of lowering the NaOH concentration by acids released during decomposition. Under the experimental conditions, however, the total amount of NaOH

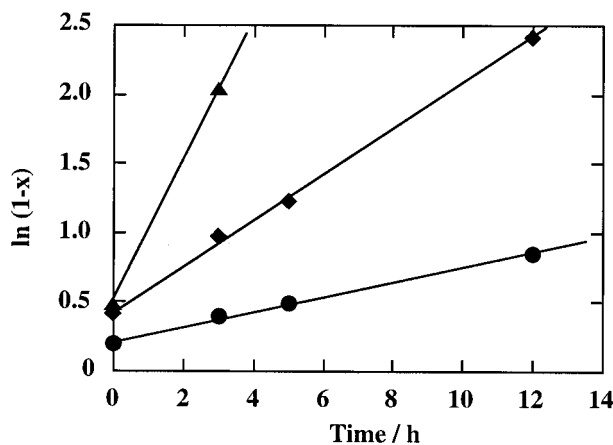


Figure 6 First-order plot of the dehydrochlorination of flexible PVC pellet in 5M NaOH. Temp (°C): (—●—) 200; (—◆—) 225; (—▲—) 250.

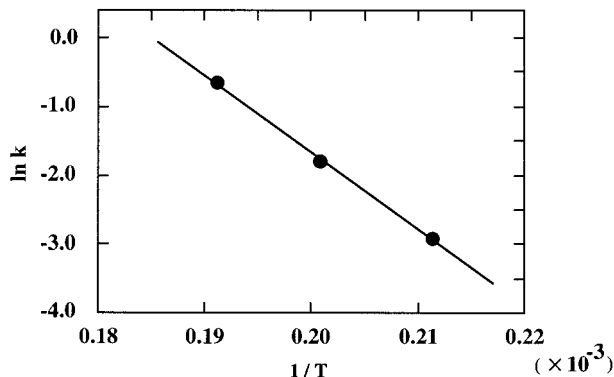


Figure 7 Arrhenius plot of the apparent rate constant of dehydrochlorination for flexible PVC pellet in 5M NaOH.

consumed by HCl produced from PVC and chlorinated paraffin, phthalic acid from the hydrolysis of DINP, and CaCO_3 correspond to only 0.16M. Thus, it is thought that the variation in the shape of char greatly affects the apparent rate constant (Fig. 2).

The effect of NaOH concentration on the apparent activation energy of the dehydrochlorination of flexible PVC is shown in Figure 9. Clearly, the NaOH concentration affected the apparent activation energy. The rate of dehydrochlorination seems to be controlled by any chemical reaction step from the values of activation energy, and the true rate constant should be dependent only on the temperature. Consequently, this relationship may result not from the effect of NaOH on the reaction mechanism at the molecular level, but from the change in the shape of char. Now, re-

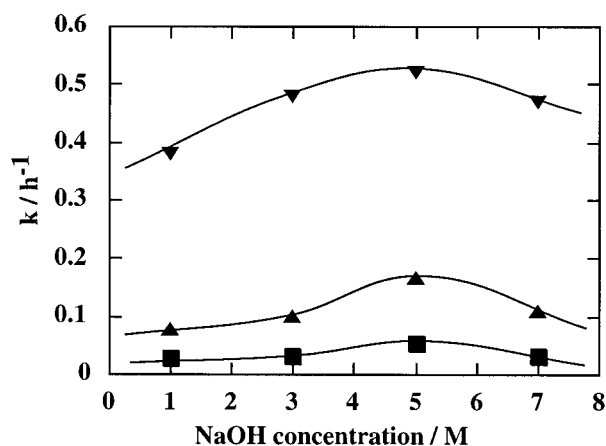


Figure 8 Effect of NaOH concentration and temperature on the apparent rate constant of flexible PVC pellet. Temp (°C): (—■—) 200; (—▲—) 225; (—▼—) 250.

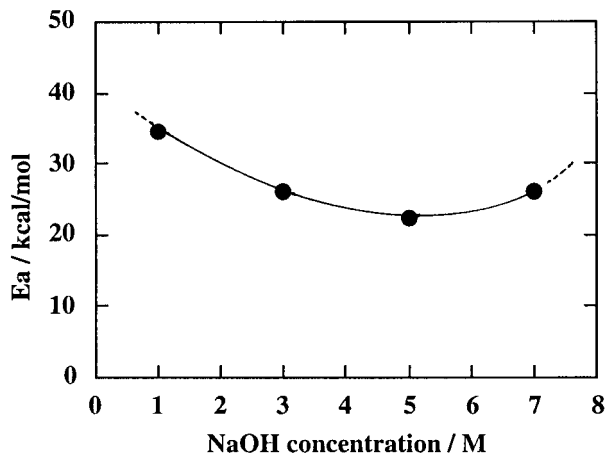


Figure 9 Effect of NaOH concentration on the activation energy of flexible PVC pellet.

search on the shape of char is in progress and further studies are planned using pure PVC powder.

CONCLUSIONS

1. The degree of dehydrochlorination of flexible PVC pellets increased with increasing reaction temperature and was about 100% at 250°C over 3 h.
2. Many pores about 16 μm in size were observed in the char from flexible PVC at 225°C in 3M NaOH for 12 h.
3. The dehydrochlorination of PVC in flexible PVC proceeded by a first-order reaction in the alkaline solution.
4. The apparent activation energies were 22–35 kcal/mol in the range 1–7M NaOH.
5. The maximum rate of the dehydrochlorination for flexible PVC was reached at 5M NaOH.

REFERENCES

1. R. E. Franklin, *Proc. R. Soc. A*, **209**, 196 (1951).
2. J. J. Kipling, J. N. Sherwood, P. V. Shooter, and N. R. Thompson, *Carbon*, **1**, 315 (1964).
3. E. W. J. Mitchell and D. G. Pearson, *J. Appl. Chem.*, **17**, 171 (1967).
4. M. Suzuki, S. Tsuge, and T. Takeuchi, *J. Polym. Sci. A-1*, **10**, 1051 (1972).
5. K. Saito, *Nihon Sangyou Gijyutsu Shinkou Siryou*, **215**, 37 (1992).
6. Rekiseikoyu Co. Ltd., *Advanced Waste Plastics Liq-uefaction Plant*, 1996.

7. T. Yoshioka, K. Furukawa, S. Yasuda, T. Sato, and A. Okuwaki, in *The 2nd International Symposium on East Asian Resources Recycling Technology*, 1993, p. 100.
8. T. Yoshioka, S. Yasuda, K. Kawamura, T. Sato, and A. Okuwaki, *Nippon Kagaku Kaishi*, 534 (1992).
9. E. Sorensen and A. B. Bjerre, *Waste Mgmt.*, **12**, 349 (1992).
10. H. Enomoto, A. Hatakeyama, and Y. Kato, *Jpn. Soc. Waste Mgmt. Res.*, **6**, 16 (1995).
11. S. Lee, M. A. Gencer, K. L. Fullerton, and F. O. Azam, U.S. Pat. 5,386,055 (1995).
12. Y. Maesawa, *Nihon Kikai Kannkyou Symp.*, **2**, 186 (1992).
13. S.-M. Shin, S. Watanabe, T. Yoshioka, and A. Okuwaki, in *The 3rd International Symposium on East Asian Resources Recycling Technology*, 1995, p. 11.
14. S.-M. Shin, S. Watanabe, T. Yoshioka, and A. Okuwaki, *Nippon Kagaku Kaishi*, 64 (1997).
15. T. Funazukuri, T. Mochizuki, T. Arai, and N. Wakao, *Nippon Kagaku Kougaku Ronbunshu*, 579 (1994).
16. G. Talamini and G. Pezzin, *Macromol. Chem.*, **39**, 26 (1960).