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Direct conversion of polyamides to ω -hydroxyalkanoic acid derivatives by using supercritical MeOH

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We examined the decomposition of polyamides such as nylon-6 and nylon-12 by using supercritical MeOH as the reaction media. The treatment of waste nylon-6 with supercritical MeOH resulted in smooth depolymerization, forming caprolactam as the first product which was then converted to a mixture of methyl 6-hydroxycapronate and methyl 5-hexenoate in a ratio of approximately 1:1. The reaction progress was traced using gas chromatography (GC) analyses, and precise product distribution was estimated. During the decomposition of nylon-6, N-methylcaprolactam and methyl 6-(N,N-dimethylamino)capronate were detected as intermediates. The sum of the all detectable products and intermediates exceeded 80%. In addition, we examined the decomposition reaction initiating from caprolactam, N-methylcaprolactam, and methyl N,N-dimethylcapronate under similar reaction conditions, and observed that the final two products were formed in similar yields and ratios. Kinetic analyses by using a simulation study based on the experimental data were performed, and kinetic parameters for each step were estimated. Nylon-12 underwent similar conversion to produce methyl 12-hydroxydodecanoate in good yield. Because methyl ω -hydroxyalkanoate is known to be an important intermediate in the chemical industry, the present method has the potential for producing valuable compounds from waste material. Thus, the first upgrade in the chemical recycling of plastics was accomplished.

Introduction

Polyamides such as nylon are used in our daily lives. Huge amounts of them are continually manufactured and discarded every year. In order to conserve carbon resources, waste polyamides should not be simply discarded but recycled through an appropriate chemical process. Among the many recycling methods so far developed, monomer recycling, which enables rebuilt plastics to be prepared from waste plastics, is an ideal method for reaching this goal.¹ The monomer recycling requires the depolymerization process in which polyamides are converted to the corresponding monomer. The conversion of polyamides to monomeric compounds has been previously investigated.^{2,3} Hydrolysis by using supercritical or subcritical water was examined for this purpose, although monomeric amines and amino acids were also decomposed under these reaction conditions.⁴ Thermolysis of polyamides5 and acid hydrolysis6 also offer good methods for the conversion. However, although these methods are useful for the conversion of the polymers to their corresponding monomers, there are no known methods that directly convert polymers to compounds other than their monomers. In addition to these, current methods of monomer recycling are not always economically viable because this process is usually more expensive than other methods for treating waste plastics. If the process of the chemical treatment of waste plastics could produce compounds or polymers more valuable than simple reborn plastics, such process would offer increased value and may solve the economic problems. However, to the best of our knowledge, there have been no such examples reported thus far.

During the course of our investigation on the development of a new chemical recycling system for polyamide plastics,⁷ we observed that the treatment of nylon-6 with supercritical MeOH resulted in the formation of methyl 6-hydroxycapronate and methyl 5-hexenoate in a selective manner, and not the anticipated monomeric caprolactam. 6-Hydroxycapronic acid derivatives are regarded as valuable chemical materials because the current average price of caprolactam, for example, is about 2.2 USD/kg, while the average price of hydroxycarboxylic acid derivatives (including 6-hydroxycapronic acid) is about 14.6 USD/kg (2008 figures).⁸ This large price difference suggested that this process has the potential to become a new method for the formation

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of valuable compounds from valueless waste materials. To our best of knowledge, this is the first economical upgrading of polymers through the depolymerization process. We believe that the present method will open new avenues in the development of the chemical recycling of plastics. In this paper we report the full details of the depolymerization of nylon-6 in supercritical MeOH.

Results and discussion

Depolymerization of nylon-6 in supercritical MeOH

Nylon-6 and MeOH were added to a sealed stainless steel tube and heated to 330 °C (Scheme 1). The pressure inside the vessel increased to 27.0 MPa, around which MeOH achieved its supercritical phase. We consider supercritical coordinates of pure MeOH because the solute is present in small quantity (7.5%w/w). The reaction vessel was maintained at the same temperature for 6 h and then rapidly cooled using a dryice/MeOH bath. The reaction mixture was then analyzed using gas chromatography (GC). The reaction products were identified by comparing the retention times and fragment patterns in mass spectra with authentic compounds that are usually commercially available. The GC analyses indicated that the following six compounds were formed as main products in the reaction: caprolactam 1, N-methylcaprolactam 2, methyl 6-(N,N-dimethylamino)capronate 3, methyl 6-hydroxycapronate 4, methyl 5-hexenoate 5 and methyl 6-methoxycapronate 6 (Scheme 1). Although other small peaks in the GC were observed, they could not be identified or quantified because of their size. The main product yields were quantified by curvefitting methods, using 1-hexanol as an internal standard that was added after the reaction. The yields were determined in chemical yields per caprolactam unit, where, Yield (mol%) = products (mmol)/amounts of caprolactam units (mmol) in nylon 6×100 Amounts of caprolactam units (mmol) in nylon-6 = nylon-6(mg)/113 (molecular weight of caprolactam 1)

Fig. 1 shows a typical course of the reaction of nylon-6 at 330 °C. The reaction mixture remained heterogeneous for the first hour of the reaction, suggesting that the depolymerization of nylon-6 was not yet completed and that insoluble oligomeric polyamides still remained in the reaction mixture. A colourless homogeneous solution was obtained after 1.5 h, indicating that most of the polyamide was converted to monomeric compounds. Caprolactam 1 was the main product in the early stage of the reaction, with a yield reaching 30% after 1 h. Thereafter, compounds 2 and 3 were formed as intermediate products, and their yields increased gradually to reach peak values approximately 2 h after the reaction started. The yield



Fig. 1 Treatment of nylon-6 in supercritical MeOH at 330 °C.

of compound 1 then decreased to approximately 0% after 3 h. In the very early stage of the reaction, the final products, compounds 4 and 5, were undetectable, but after 40 min their vields increased in proportion to the reaction time, reaching 42% and 28%, respectively, after 4 h. The yields of compounds 4 and 5 thereafter remained at this maximum level, clearly indicating that they remained stable and unchanged under the reaction conditions. The product ratio of compound 4 to compound 5 was approximately 1.5:1. We also attempted the isolation of compound 4. The removal of MeOH under reduced pressure resulted in oily products from which compound 5 was readily removed because of its volatility. The chromatographic purification of the residue resulted in pure compound 4 in 44% yield. Compound 6 was detected after 3 h, although the yield was still 3% after 6 h. The sum of the yields of all main products and intermediates reached more than 80%, indicating that the present product analyses have traced all of the main compounds of the reaction.

We next examined this process for the decomposition reaction of waste nylon-6 (Scheme 2). The waste nylon-6 was obtained in a factory of nylon-6 as a residue of the distillation process. It contained 78 wt% of oligomer of polyamide and 22 wt% of caprolactam. Treatment of the waste (abt 0.3 g) with MeOH (4 g) at 350 °C for 3 h resulted in the formation of a mixture of decomposed products 1 to 6. The mixture was analyzed by GC which showed that the yields of the products were 0.5% for 1, 2% for 2, 0.8% for 3, 34% for 4, 33% for 5 and 0% for



Scheme 1 Depolymerization of nylon-6 with supercritical methanol.

 Table 1
 Maximum yields of the products 1–6 during depolymerization of nylon-6 with supercritical MeOH

T∕°C	1; Yield (%) ^{<i>a</i>}	2; Yield (%) ^{<i>a</i>}	3; Yield (%) ^a	4 ; Yield (%) ^{<i>a</i>}	5 ; Yield (%) ^{<i>a</i>}	6 ; Yield (%) ^{<i>a</i>}	total yield (%) ^a
300 330 350 370	29(240) 27(80) 24(60) 20(40)	15(240) 14(120) 14(80) 12(40)	16(240) 12(100) 12(80) 13(40)	20(360) 42(300) 39(160) 40(100)	$\frac{-^{b}(-)}{28(300)}$ 31(160) 33(100)	n.d.¢(—) 3(300) 6(360) 7(300)	77(240) 81(300) 80(160) 81(100)

^{*a*} The yield was determined by GC analyses. The reaction time when reaching the maximum yield is shown in parentheses. ^{*b*} Not determined. ^{*c*} Not detected.



Scheme 2 Depolymerization of waste nylon-6 in supercritical methanol.

6. The reaction profile was very similar to the decomposition reaction of pure nylon-6. Thus, the procedure was useful for the depolymerization and chemical conversion process of waste nylon-6.

Mechanistic studies

We next examined the conversion of nylon-6 at various temperatures. The peak yields of compounds 1 to 6 are summarized in Table 1. The reaction conducted at other temperatures showed a similar trend in product formation, as shown in Fig. 1. Thus, compound 1 was formed as the first intermediate, and then the yields of compounds 2 and 3 increased with decrease in the yield of 1. Compounds 4 and 5 were then formed as final products. The reaction at 300 °C progressed very slowly and an insoluble polyamide oligomer was observed in the reaction mixture after 3 h. The reaction seemed to be incomplete even after 6 h because the yields of compounds 4 and 5 remained at lower levels than those achieved in subsequent reactions. When the reaction was conducted at 350 °C, the reaction rate increased and the entire reaction was completed within 3 h. The yields of compounds 4 and 5 reached 39% and 31%, respectively, after 160 min. These values were similar to the yields achieved when the reaction was performed at 330 °C. However, the yields at 350 °C gradually decreased after 3 h, clearly indicating that the decomposition of compounds 4 and 5 occurred under these reaction conditions. The same trend was observed when the reaction was performed at 370 °C. Although the reaction completed within 2 h, the yields of compounds 4 and 5 decreased relatively rapidly than those in the reaction at 350 °C. Thus, compounds 4 and 5 decomposed when exposed to temperature of 350 °C or higher.

These results suggest a reaction pathway as shown in Scheme 3. Initially, the polymer linkage of nylon-6 was broken to yield monomeric caprolactam 1. *N*-Methylation by supercritical MeOH⁹ and ring opening subsequently occurred to yield the intermediate compounds 2 and 3. The terminal amino group in compounds 2 and 3 then performed a substitution

Table 2 Yields of compounds 4, 5 and 6 through decomposition of nylon-6, and compounds 1, 2 and 3 in supercritical MeOH at $330 \degree$ C for 6 h

Starting material	4 ; Yield (%) ^{<i>a</i>}	5 ; Yield (%) ^{<i>a</i>}	6; Yield (%) ^a	Total yield (%) ^a
Nylon-6	42	28	2	82
1	39	31	3	82
2	37	30	2	75
3	26	23	5	55
" GC yield	ds.			

reaction to yield compound 4 and an elimination reaction to yield compound 5. It should be noted that the yield of compound 6 approached 0%, indicating that virtually no substitution by MeOH occurred under these reaction conditions.

The reactions initiating from compounds 1, 2 and 3 under similar conditions at 330 °C were next conducted, and product analyses were performed in a similar manner. The reaction profiles are depicted in Fig. 2 to 4, and the results are summarized in Table 2.



Scheme 3 Possible reaction pathway of depolymerization of nylon-6 with supercritical MeOH.



Fig. 2 Treatment of caprolactam (compound 1) with supercritical MeOH at 330 $^{\circ}\mathrm{C}.$



Fig. 3 Treatment of *N*-methylcaprolactam (compound 2) with supercritical MeOH at 330 $^{\circ}$ C.

The treatment of compound 1 with supercritical MeOH at 330 °C resulted in the formation of compounds 2 to 6 (Fig. 2). Compound 1 was consumed entirely after 4 h. Compounds 2 and 3 were formed in the early stage of the reaction and their yields reached approximately 20% after 2 h. The yields of compounds 2 and 3 then gradually decreased and compounds 4 and 5 were formed instead. The entire reaction was completed after 5 or 6 h, when the yields of compounds 4 and 5 were estimated to be 39% and 31%, respectively. These yields were almost same as the yields of all products exceeded 80%, indicating that most reaction products were traced. Again, it should be noted that no appreciable formation of compound 6 was observed.

The treatment of compound **2** under the same reaction conditions yielded results similar to the reaction from compound **1** (Fig. 3). Thus, compound **2** disappeared after 4 h. Compound **3** was formed first and reached its peak yield in 100 min. The yields of compounds **4** and **5** gradually increased, and those



Fig. 4 Treatment of 6-N,N-dimethylcapronate (compound 3) with supercritical MeOH at 330 °C.

compounds became the final products. The yields of compounds **4** and **5** reached 37% and 30%, respectively, which were almost the equal to those in the reaction initiating from nylon-6.

The reaction initiating from compound **3** yielded compounds **4** and **5** directly, and no other intermediates were observed in the reaction mixture (Fig. 4). The concentration of compound **3** rapidly decreased, and it was entirely consumed within 90 min. The yields of compounds **4** and **5** finally reached 35% and 28%, respectively.

Kinetic simulation

To analyze the kinetic behaviour of the reaction, we examined a simulation of product distribution. For the analysis, we postulated that the reaction progressed through the pathway shown in Scheme 4, in which nylon-6 firstly gave caprolactam 1. Caprolactam 1 underwent N-methylation and ring opening to give compound 3 via compound 2. To simplify the simulation, we treated the sum of the yields of compounds 2 and 3 as the intermediate. Intermediate 3 was then converted to 6hydroxycapronate 4 via nucleophilic substitution or 5-hexenoate 5 via elimination reaction. Compound 6 was converted from compound 4 but this reaction rate should be low because very small amounts of 6 were formed in the actual reaction. The degradation of nylon-6 into caprolactam 1 was regarded as a first-order because the concentration of MeOH does not change appreciably under the present reaction condition. Other conversion steps were also considered to occur as a firstorder irreversible reaction. The calculations of the reaction time courses were performed considering that the reaction occurred in an isothermal batch reactor free of mass transfer effect. The composition in the reactor changed with reaction time (unsteady-state operation). The results are illustrated in Fig. 5.

The optimizations were performed by a downhill simplex method using the software 'ModelMaker' obtained from Cherwell Scientific Publishing Ltd, Oxford (the U.K.). Initially, we attempted to use actual values for the simulation. However, we encountered difficulties when fitting actual data, particularly at



Scheme 4 Postulated reaction pathway for the depolymerization of nylon-6 in supercritical MeOH.



Fig. 5 Simulated profile of the reaction of nylon-6 in supercritical MeOH at 330 °C. Circles and squares are based on the experimental values and the lines are based on simulation.

the very early stage of the reaction. An induction period at the beginning of the reaction seemed to exist, possibly due to the delay time during heating the reaction vessels to the desired temperature. Indeed, we observed that 20-30 min was necessary to increase the temperature of the reaction vessels above 300 °C. We examined this delay in the simulations and finally determined that introducing an induction period of 22 min provided a good fit for the simulation. We performed this simulation for the first 118 min of the reaction. The coefficient showing the goodnessof-fit was 0.983. Thus, the time course of each product fitted well with the actual product distribution. The kinetic values for the each reaction were estimated to be $k_1 = 1.47 \times 10^{-2} \text{ min}^{-1}$, $k_2 = 2.91 \times 10^{-2} \text{ min}^{-1}$, $k_3 = 1.19 \times 10^{-2} \text{ min}^{-1}$, and $k_4 = 8.16 \times 10^{-2} \text{ min}^{-1}$ 10^{-3} min⁻¹, respectively. The substitution/elimination ratio (4/5) that was predicted from the kinetic values (k_3/k_4) was calculated to be 1.46, which is close to the actual value of 1.5. The product distribution of the reaction at different temperatures was also simulated. The observed kinetic values, fitting coefficient and induction periods are summarized in Table 3.

Considering these values, we next attempted to estimate the activation energy parameter. The Arrhenius plots for these values are illustrated in Fig. 6. The plots exhibit a good



Fig. 6 Temperature dependency of reaction rates (Arrhenius plots).

linear relationship between 1/T and $\ln k_{obs}$. Based on the slopes calculated from Fig. 6, the activation energies for each step were estimated to be 94.2 kJ mol⁻¹ for the first step, nylon-6 to compound 1, 100.1 kJ mol⁻¹ for the second step, *N*-alkylation from compound 1, 84.8 kJ mol⁻¹ for the formation of compound 4, and 94.4 kJ mol⁻¹ for the formation of compound 5. Although the *N*-alkylation step was slightly slower than the other steps, the reaction rates and activation energies for all steps were in similar value. Thus, the reaction progressed in a stepwise manner, such that intermediates 1, 2, and 3 were observed in the reaction mixture. The chemoselectivity between compounds 4 and 5 was determined by the difference in the reaction rates between k₃ and k₄.

Depolymerization of nylon-12 in supercritical MeOH

Similar selective formation of methyl ω -hydroxyalkanoate was observed in the reaction of nylon-12 (Scheme 5). The treatment of nylon-12 with supercritical MeOH at 330 °C resulted in a smooth depolymerization of the polymer, as depicted in Scheme 5 and Fig. 7.

The reaction progressed in a manner similar to that for nylon-6. Methyl 12-(N,N-dimethylamino)laurate 7 was formed as the intermediate, and then the conversion to methyl

 Table 3
 Estimated kinetic parameters of the reaction

T∕°C	$k_1 (10^{-2} \min^{-1})$	$k_2 (10^{-2} \min^{-1})$	$k_3 (10^{-2} \min^{-1})$	$k_4 (10^{-2} \min^{-1})$	Induction time (min)	Coefficient
300	0.403	0.990	0.469	0.281	39	0.935
330	1.47	2.91	1.19	0.816	22	0.983
350	2.04	4.90	1.91	1.40	17	0.966
370	3.63	10.16	3.31	2.45	16	0.984



Scheme 5 Depolymerization of nylon-12 with supercritical MeOH.



Fig. 7 Treatment of nylon-12 with supercritical MeOH at 330 °C.

12-hydroxylaurate **8** and methyl 11-dodecenoate **9** occurred. Cyclic intermediates such as laurolactam were not observed, possibly because the formation of the cyclic amide that requires a large cyclic-ring formation from the open-chain monomer is not easy. The total yield again exceeded 80%, such that almost all reaction products were traced through the GC analysis. The yield of compound **8** reached 59% after 5 h. It should be noted that the methoxy derivative **10** was formed in approximately 4%.

The reaction temperature was also important. To obtain 12-hydroxycapronate **8** in good yield, 330 °C was the best temperature. When the reaction was performed at 370 °C, the yield of **8** decreased as the reaction time was prolonged. On the other hand, the reaction performed at 310 °C took place very slow and compound **8** was formed in 38% even after 6 h.

Conclusion

We successfully developed a process for the direct conversion of hydroxycapronic acid derivatives from nylon-6. The treatment of nylon-6 with supercritical MeOH produced methyl 6-hydroxycaplonate 4 and methyl 5-hexenoate 5 in a 1.5:1ratio. In this process, nylon was converted to methyl 6hydroxycaplonate 4, which is more valuable than caprolactam 1, the nylon-6 monomer. The reaction propagates through the formation of caprolactam (compound 1), *N*-methylcaprolactam (compound 2), and methyl *N*,*N*-dimethylcapronate (compound 3) as intermediates. Compounds 4 and 5 were stable and did not decompose under the reaction conditions at 330 °C. A kinetic simulation achieved an acceptable curve fitting when an induction period was introduced, and the kinetic parameters for each reaction were estimated. This procedure was useful for the conversion of nylon-12 to corresponding hydroxyalkanoic acid derivatives. Because the market value of hydroxyalkanoic acid derivatives is higher than that of simple monomeric lactams, the present procedure provides the first upgrading depolymerization procedure for the chemical recycling of nylon-6. New developments in the recycling of plastics by using this concept are anticipated. Further studies on this depolymerization procedure are in progress in our laboratory.

Experimental

Materials

Nylon-6 (Mw = 22000) and nylon-12 (Mw = 30000) were supplied from Ube Industries as a gift. MeOH, reagent grade, was purchased from Katayama chemical Inc. Osaka Japan, All other chemicals were purchased from Aldrich or Tokyo Chemical Industry (TCI).

General procedures for depolymerization of nylon-6 in MeOH

New nylon chips (0.3 g, Mw = 22000) and MeOH (4 g) were added to a 10 mL reaction vessel (7.35 mm id × 23 cm stainless tube, capped both ends by swagelok nuts) under argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (300 to 370 °C) for the appropriate time. The pressure reached 27.0 MPa. The reaction vessel was cooled with dry-ice/MeOH bath, and 1-hexanol was added as an internal standard. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 (0.25 mm id × 30 m) column) and quantified by curve fitting methods.

General procedures for depolymerization of nylon-12 in MeOH

New nylon chips (0.3 g, $Mw = 30\,000$) and MeOH (4 g) were added to a 10 mL reaction vessel under argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (330 °C) for the appropriate time. The reaction vessel was cooled with dry-ice/MeOH bath, and dimethyl phthalate was added as an internal standard. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 (0.25 mm id × 30 m) column) and quantified by curve fitting methods.

Isolation of methyl 6-hydroxycapronate (compound 4)

New nylon chips (0.3018 g, $Mw = 22\,000$) and MeOH (4 g) were added to a 10 mL reaction vessel under argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (330 °C) for 6 h. The reaction vessel was cooled with dry-ice/MeOH bath. MeOH was removed under reduced pressure and the residue was purified through flash chromatography (silica gel/hexane-ethyl acetate 10:1, then 1:1). Methyl 6-hydroxycapronate (compound 4) was isolated in 44% yield (0.1771 g, 1.212 mmol). Colourless oil. ¹H NMR $\delta_{\rm H}$ (270 MHz, d₃-CDCl₃): 1.33–1.40 (2H, m, -CH₂-), 1.52-1.71 (4H, m, -CH₂CH₂-), 2.33 (2H, t, J = 7.6 Hz, $-CH_{2-CO_{2}Me}$, 3.18 (1 H, s, OH), 3.58 (2H, t, J = 6.3 Hz, $-CH_{2-}$ OH), 3.67 (3H, s, $-CO_2CH_3$); ¹³C δ_C (67.5 MHz, d₃-CDCl₃): 24.4 (C5), 25.1 (C4), 32.0 (C3), 33.7 (C2), 51.2 (-CO₂CH₃), 62.0 (C6), 174.1 (C1). HRMS (CI) [M + 1]: calculated for $C_7 H_{15} O_3$, 147.1021; observed 147.1021. Methyl 5-hexenoate (compound **5**). ¹H NMR $\delta_{\rm H}$ (400 MHz, d₃-CDCl₃): 1.73 (2H, m, J = 7.3 Hz, $-CH_2CH_2CH_2-$), 2.09 (2H, q, J = 7.0 Hz, $= CHCH_2CH_2CH_2-$), 2.32 (2H, t, J = 7.3 Hz, $-CH_2CO_2Me$), 3.67 (3H, s, CO_2CH_3), 4.96-5.05 (2H, m, CH2=CH-), 5.72-5.82 (1H, m, CH2=CH-); ¹³C $\delta_{\rm C}$ (100 MHz, d₃-CDCl₃): 24.2 (C3), 33.2 (C4), 33.4 (C2), 51.6 (-CO₂CH₃), 115.5 (C6), 137.8 (C5), 174.1 (C1). MS (EI) m/z 128 (M+, 30), 110 (19), 97 (35), 74 (100).

Parameter estimation and simulation

Numerical integrations and optimizations by using the Runge– Kutta method and Simplex algorithm, respectively, were performed to estimate the kinetic parameters and to simulate the reactions. The optimizations were performed by a downhill simplex method using the software 'ModelMaker' obtained from Cherwell Scientific Publishing Ltd, Oxford (U.K.). The objective function is a residual sum of squares for minimization of the difference between the calculated values and the experimental data.

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References

- 1 *Technology for Feedstock Recycling of Plastic Wastes*, Research Association of Feedstock Recycling of Plastics, Japan, ed. CMC books, Tokyo, Japan, 2005.
- 2 For review: (a) M. B. Polk, Synthetic Methods in Step-Growth Polymers, 527–574, ed. by M. E. Rogers and T. E. Long, John Wiley & Sons, 2003; (b) M. Kopietz and U. Seeliger, Recycling and Recovery of Plastics, 502–511, ed. by J. Brandrup, Hanser Munich, Germany, 1996; (c) Y. Honjo, Purasuchikkusu, 1996, 47, 41–45; (d) N. Kusakawa, Kagaku Kogyo, 1994, 45, 571–576; (e) A. Miyake and K. Kimura, Porima Daijesuto, 1993, 45, 6–26.
- 3 (a) Zs. Czegeny and M. Blazso, J. Anal. Appl. Pyrolysis, 2001, 58–59, 95–104; (b) I. M. Smolensky, Fiz. Khim. Tverd. Tela, 2001, 2, 747–753; (c) M. B. Polk, L. L. Leboeuf, M. Shah, C.-Y. Won, X. Hu and

W. Ding, Polym.-Plast. Technol. Eng., 1999, 38, 459-470; (d) G. A. Kalfas, Polym. React. Eng., 1998, 6, 41-67; P. Ruiz-Donaire, J. J. Bou, S. Munoz-Guerra and A. Rodriguez-Galan, J. Appl. Polym. Sci., 1995, 58, 41-54; (e) M. Langhammer, I. Luederwald and M. Weingaertner, Makromol. Chem., 1986, 187, 829-835; (f) A. Ballisteri, D. Garozzo, M. Giuffrida, G. Impallomenri and G. Montaudo, Polym. Degrad. Stab., 1989, 23, 25; (g) H. Ohtani, T. Nagaya, Y. Sugimura and S. Tsuge, J. Anal. Appl. Pyrolysis, 1982, 4, 117; (h) P. N. Lavrenko, O. V. Okatova and A. B. Mel'nikov, Vysokomol. Soedin. Ser. A, 1981, 23, 532-539; (i) V. A. Pakharenko and E. M. Kirienko, Khim. Tekhnol., 1980, 25–27; (j) K. Furukawa and C. Tsukamoto, Kobunshi Ronbunshu, 1980, 37, 617-625; (k) Y. Nagase, T. Komatsu, Y. Sumiya, K. Ikeda and Y. Sekine, Nippon Kagaku Kaishi, 1979, 1560-1568; (1) K. Furukawa, K. Take and C. Tsukamoto, Kobunshi Ronbunshu, 1979, 36, 507-515; (m) I. Lunerwald, F. Merz and M. Rothe, Angew. Makromol. Chem., 1978, 67, 193; (n) I. Luederwald and F. Merz, Angew. Makromol. Chem., 1978, 74, 165-185; (o) V. A. Bershtein, L. M. Egorova and V. V. Solov'ev, Mekh. Polim., 1977, 854-860; (p) N. V. Lukasheva, A. V. Volokhina and G. I. Kudryavtsev, Vysokomol Soedin, Ser. B, 1975, 173, 207-209; (q) T. Ohtsubo, Nippon Kagaku Kaishi, 1974, 337-341; (r) H. R. Kricheldorf and E. Leppert, Makromol. Chem., 1974, 175, 1731-1749; (s) T. Konomi and H. Tani, J. Polym. Sci., Part A: Polym. Chem., 1970, 8, 1261-1268; (t) E. P. Krasnov and L. B. Sokolov, Vysokomol. Soedin. Khim. Svoistva i Modifikatsiva Polimerov, Sb. Statei, 1964, 275-281; (u) N. Ogata, Bull. Chem. Soc. Jpn., 1961, 34, 1201; (v) T. I. Shein and V. N. Topchibasheva, Khim. Volokna., 1959, 21-24.

- 4 (a) M. Goto, J. Supercrit. Fluids, 2009, 47, 500; (b) M. Goto, M. Sasaki and T. Hirose, J. Mater. Sci., 2006, 41, 1509; (c) T. Iwaya, M. Sasaki and M. Goto, Polym. Degrad. Stab., 2006, 91, 1989; (d) L. Meng, Y. Zhang, Y. Huang, M. Shibata and R. Yosomiya, Polym. Degrad. Stab., 2004, 83, 389; (e) O. Sato, N. Saito and Y. Ikushima, Nettowaku Porima, 2003, 24, 46–54; (f) O. Sato and Y. Ikushima, Kobunshi Ronbunshu, 2001, 58, 533; (g) M. Goto, M. Umeda, A. Kodama, T. Hirose and S. Nagaoka, Kobunshi Ronbunshu, 2001, 58, 548.
- 5 (a) H. Bockhorn, S. Donner, M. Gernsbeck, A. Hornung and U. Hornunga, J. Anal. Appl. Pyrolysis, 2001, 58–59, 79–94; (b) M. Herrera, G. Matuschek and A. Kettrup, Chemosphere, 2001, 42, 601–607; (c) H. Bockhorn, A. Hornung, U. Hornung and J. Weichmann, Thermochim. Acta, 1999, 337, 97; (d) S. Czernik, C. C. Elam, R. J. Evans, R. R. Meglen, L. Moens and K. Tatsumoto, J. Anal. Appl. Pyrolysis, 1998, 46, 51; (e) I. Vulic and R. E. W. E. Jacobs, Polym. Bull, 1993, 31, 55–60; (f) A. Ballistreri, D. Garozzo, M. Giurida and G. Montaudo, Macromolecules, 1987, 20, 2991–2997; (g) A. Ballistreri, D. Garozzo, M. Giurida, G. Impallomeni and G. Montaudo, Polym. Degrad. Stab., 1988, 23, 25–41.
- 6 (a) S. Shukla, A. M. Harad and D. Mahato, J. Appl. Polym. Sci., 2006, 100, 186; (b) U. Klun and A. Krazan, Polym. Adv. Technol., 2002, 13, 817–822.
- 7 (a) A. Kamimura, Y. Oishi, K. Kaiso, T. Sugimoto and K. Kashiwagi, *ChemSusChem*, 2008, 1, 82–84; (b) A. Kamimura and S. Yamamoto, *Org. Lett.*, 2007, 9, 2533–2535; (c) A. Kamimura and S. Yamamoto, *Polym. Adv. Technol.*, 2008, 19, 1391–1395; (d) S. Yamamoto and A. Kamimura, *Chem. Lett.*, 2009, 39, 1066–1067; (e) K. Kaiso, T. Sugimoto, K. Kasiwagi and A. Kamimura, *Chem. Lett.*, 2011, 40, 370–371.
- 8 See homepage of JETRO; http://www.jetro.go.jp.
- 9 (a) T. Oku and T. Ikariya, Angew. Chem., Int. Ed., 2002, 41, 3476; (b) P. Licence, W. K. Gray, M. Sokolova and M. Poliakoff, J. Am. Chem. Soc., 2005, 127, 293; (c) Y. Takebayashi, Y. Morita, H. Sakai, M. Abe, S. Yoda, T. Furuya, T. Sugeta and K. Otake, Chem. Commun., 2005, 3965.