Macromol. Symp. **2003**, *197*, 157—169

Synthesis and Thermal Properties of Epoxy Resins from Ester- Carboxylic Acid Derivative of Alcoholysis Lignin

Shigeo Hirose,[1] Tatsuko Hatakeyama,[2] Hyoe Hatakeyama[3]*

[1] National Institute of Advanced Industrial Science and Technology, Central 5, Tsukuba, Ibaraki 305-8565, Japan
[2] Otsuma Women's University, 12 Sanbancho, Chiyoda-ku, Tokyo 102-8357, Japan
[3] Fukui University of Technology, 3-6-1, Gakuen, Fukui-city, Fukui 910-8501, Japan

Summary: Alcoholysis lignin (AL) was dissolved in ethylene glycol and the obtained mixture was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (AL-polyacid, ALPA). Ethylene glycol-polyacid (EGPA) was also prepared from ethylene glycol. The obtained mixture of ester carboxylic acid derivatives was treated with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form ester-epoxy resins. The curing reaction was analyzed by Ozawa's method using differential scanning calorimetry. The activation energy of curing reaction in the initial step was found to be ca. 84 kJ mol^{-1}. The molar ratios of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratios) were varied from 0.8 to 1.3. The contents of ALPA in the mixture of ALPA and EGPA were also varied from 0 to 100 %. Thermal properties of epoxy resins were studied by DSC and thermogravimetry. Glass transition temperatures of epoxy resins showed a maximum value of -11.5 °C when [EPOXY]/[AA] ratio was 1.1. T_g increased with increasing ALPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal degradation temperatures of epoxy resins slightly decreased with increasing ALPA contents.

Keywords: alcoholysis lignin; epoxy resins; ester-carboxylic acid; phase transition; thermal degradation

Introduction

The main plant components such as cellulose, hemicellulose and lignin are recognized as the most important renewable resources, since the amount of their production is very large [1]. Therefore, their utilization has been extensively studied in the past. Lignin has a highly branched chemical structure consisting of phenyl propane units which are connected mainly by ether linkages. It is known that lignin is too brittle as a polymeric material [2]. Therefore, many chemical and

DOI: 10.1002/masy.200350715

physical modifications have been attempted in order to improve the mechanical properties of lignin . In the last ten years, synthetic polymers, which were derived from lignin on the basis of molecular design concerning the functional groups of lignin such as phenylene, hydroxyl and methoxyl groups, were extensively studied in our laboratory [3, 4]. Recently, it was found that polyurethanes derived from lignin and from lignin-based caprolactones show excellent thermal and mechanical properties and also biodegradability [5 - 9].

Epoxy resins are known to be one of the important thermoset polymers, since they are used in adhesives, composites and elastomers. In the past, many researchers studied ether-type of lignin-based epoxy resins [10-12]. Recently, aliphatic polyesters, such as polycaprolactones, poly(ethylene succinate), poly(lactic acid), have drawn much attention due to their biodegradability. In a previous study, we have investigated the synthesis and the thermal properties of ester-type epoxy resins, which can be derived from lignin, poly(ethylene glycol) diglycidyl ether and azelaic anhydride [13]. It was reported that ester-type epoxy resins with hydroxyl groups attached to the β-carbons of ester groups can be prepared by reaction of epoxy compounds with carboxylic acids in the presence of amine catalysts [14]. It is expected that epoxy resins with the above chemical structures have appropriate hydrophilic properties that will increase the compatibility with fillers with hydrophilic surface such as plant materials. Prior to the preparation of composite materials, in the present study, an ester-carboxylic acid derivative of lignin was synthesized from alcoholysis lignin (AL) and succinic acid anhydride. The obtained ester-carboxylic acid derivative of AL was reacted with ethylene glycol diglycidyl ether (EGDGE) to form epoxy resins under the various conditions. The behaviour of the curing reactions was studied by differential scanning calorimetry (DSC). Furthermore, the thermal properties of the obtained epoxy resins were studied by DSC and thermogravimetry (TG).

Experimental

Materials

Alcoholysis lignin (AL) was kindly supplied by Repap Co., U. S. A., and it was dried in vacuum at 70 °C. Other reagents such as ethylene glycol (EG), succinic anhydride (SA), ethylene glycol diglycidyl ether (EGDGE), dimethylbenzylamine (DMBA) were commercially obtained from Wako Pure Chemical Industries Ltd., Japan. The above reagents were used without further purification.

Synthesis of ester-carboxylic acid derivatives of AL and EG

AL polyacid (ALPA) was obtained as follows. 50g AL was dissolved in 50g EG at 80 °C. Succinic anhydride 196 g and DMBA 2.69 g were added to the above solution, and the mixture was stirred at 80 °C for 6 hr. EG polyacid (EGPA) was prepared from EG in the same manner as ALPA.

Synthesis of epoxy resins

LPA was mixed well with EGDGE at 80 °C, and the mixture was allowed to stand at 130 °C for 5 hr in an oven. The molar ratios of carboxylic acid groups to epoxy groups [EPOXY]/[ACID] ratio (mol $\mathrm{mol^{-1}}$) were varied at 0.8, 0.9, 1.0, 1.1, 1.2 and 1.3. ALPA contents were also varied at 0, 20, 40, 60, 80 and 100 %. The [EPOXY]/[ACID] ratios and the ALPA contents were calculated by the following equations.

$$\text{[EPOXY]/[ACID] ratio (mol/mol)} = (M_{EGDGE}\, W_{EGDGE}) / (M_{ALPA}\, W_{ALPA} + M_{EGPA}\, W_{EGPA})$$
$$\text{ALPA content (\%)} = 100\, W_{ALPA} / (W_{ALPA} + W_{EGPA})$$

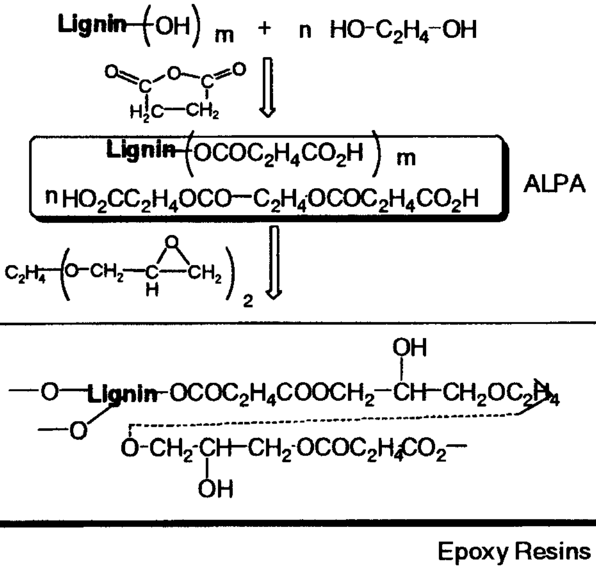
where M_{EGDGE} is the mole number of epoxy groups per gram of EGDGE (7.7 mmol $\mathrm{g^{-1}}$), W_{EGDGE} the weight of EGDGE, M_{ALPA} the mole number of carboxylic acid groups per gram of ALPA (6.62 mmol $\mathrm{g^{-1}}$), W_{ALPA} the weight of ALPA, M_{EGPA} the mole number of carboxylic acid groups per gram of EGPA (7.63 mmol $\mathrm{g^{-1}}$), W_{EGPA} the weight of EGPA.

Measurements

A Perkin-Elmer 2000 Fourier transform infrared spectrometer was used for infrared spectrometry. The measurements were carried out on KBr pellets. A Seiko DSC 220 was used for differential scanning calorimetry (DSC). For the measurement of curing reaction of epoxy resins, samples were heated from 30 °C to 260 °C at heating rates of 2, 2.5, 3, 4 and 5 °C min^{-1}. The activation energy (E) of the curing reaction of the epoxy resin was obtained by the method reported by Ozawa [15]. Ca. 5 mg of each sample was placed in a sealed stainless vessel. The curing reaction was also observed under isothermal conditions at 130 °C. The phase transition of epoxy resins were investigated from – 60 °C to 80 °C at 10 °C min^{-1} heating rate using ca. 5 mg of samples. The samples were heated at 130 °C in aluminum pans and maintained at this temperature for 10 min, then they were quenched to – 60 °C . The glass transition temperatures (T_g's) were determined according to the method reported by Nakamura et al. [16]. The heat capacity variation at T_g (ΔC_p) was also determined from the DSC curves. A Seiko TG/DTA 220 was used for thermogravimetry (TG). The measurements were carried out on 5 mg samples at 10 °C min^{-1} heating rate under 300 mL min^{-1}nitrogen flow. Thermal degradation temperatures (T_d's) were determined according to the method reported by Hatakeyama [17].

Results and Discussion

In the present study, epoxy resins were synthesized as follows. AL was dissolved in the same amount by weight of EG, and the obtained mixture was reacted with succinic anhydride to form the mixture of ester-carboxylic acid derivatives of AL and EG (AL polyacid, ALPA). Epoxy resins were obtained by the reaction of ALPA with EGDGE. The reaction scheme is shown in Scheme 1. The chemical structure of the obtained ALPA was confirmed by FTIR.



Scheme 1. Reaction scheme for the synthesis of ALPA and epoxy resins.

The characteristic absorption peaks of carboxylic acid groups at about 1780, 2700 and 3200 cm^{-1}, and those of ester groups at 1720, 1200 cm^{-1} are observed in the spectrum of ALPA (Fig. 1). The FTIR spectrum of an epoxy resin after curing at 130 °C for 5 hr (Fig. 1) shows the characteristic absorption peaks of ester groups at 1720 and 1200 cm^{-1} and hydroxyl groups at 3300 cm^{-1}.

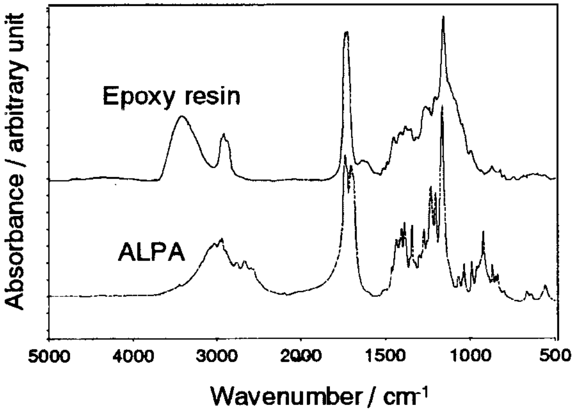


Figure 1. FTIR spectra of ALPA and epoxy resin prepared with [EPOXY]/[ACID] ratio = 1.

The curing reaction behavior was studied by DSC. Fig. 2 shows DSC curves of curing reaction of epoxy resin of various heating rates. An exothermic peak due to the curing reaction is observed for each curve between ca. 90 and 230 °C, suggesting that the curing reaction occurs in this temperature region. The DSC curve at 2 °C min^{-1}, which is the slowest heating rate, shows a maximum at ca. 130 - 140 °C. It was also observed that the exothermal process when curing at 130 °C ceased after about 150 min (DSC curve not shown). Therefore, the curing of epoxy resins in this study was carried out at 130 °C for 5 hr in order to complete the curing. The activation energy of the curing reaction was calculated by the integral method reported by Ozawa [15], assuming that the curing reaction proceeds according to Arhenius equation. The conversion rates were calculated from the reaction heat determined by DSC. Fig. 3 shows the relationship between the logarithm of the heating rate and the reciprocal of the temperature where a constant conversion is reached at each heating rate. As shown in Fig. 3, straight lines with the same slope are obtained for lines with conversion lower than 60 %. The calculated E is 83.5 kJ mol^{-1} and this activation energy is slightly higher than 68.6 kJ mol^{-1} that is the value reported for the addition reaction of acetic acid and epichlorohydrin catalyzed by chromium acetate [18]. These results indicate that the curing reaction proceeds apparently in a single step until the conversion is 60 %. At conversions higher than 80 %, the activation energy increased gradually, suggesting that the reaction proceeds by a different mechanism.

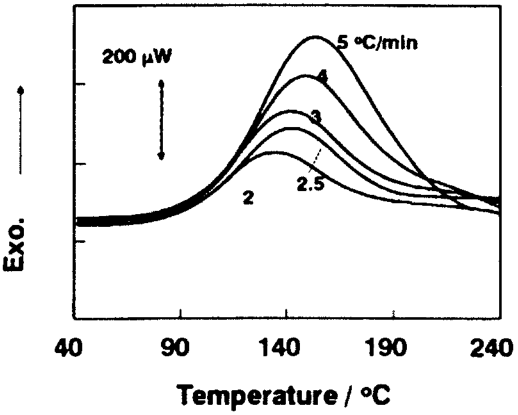


Figure 2. DSC curves of the curing reaction of various heating rates. Numbers indicate the heating rate. The [EPOXY]/[ACID] ratio is 1.

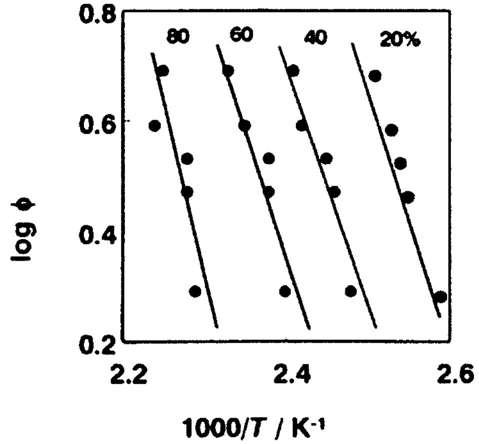


Figure 3. Relationship between the logarithm of the heating rate and the reciprocal of the temperature where a constant conversion is reached. Numbers indicate the conversion extent.

Phase transition of epoxy resins was studied by DSC. Fig. 4 shows DSC curves of epoxy resins with various [EPOXY]/[ACID] ratios. In each DSC curve, the baseline shift due to the glass transition is observed. The glass transition temperatures (T_g's) were determined from the DSC curves. Fig. 5 shows the relationship between T_g and the [EPOXY]/[ACID] ratio of epoxy resins. Tg initially increases with increasing [EPOXY]/[ACID] ratios and reaches a maximum at [EPOXY]/[ACID] ratio = 1.1. These results indicate that the highest cross-linking density occurs at [EPOXY]/[ACID] ratio 1.1.

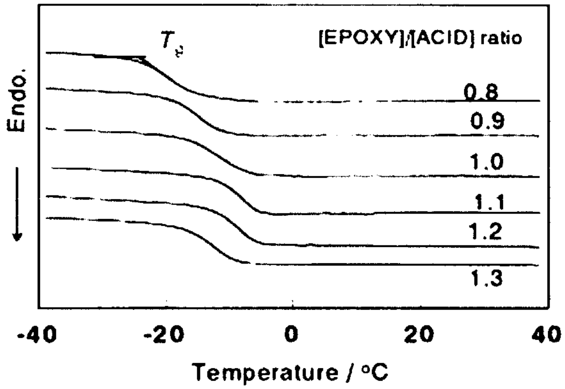


Figure 4. DSC curves of epoxy resins with various [EPOXY]/[ACID] ratios. Numbers indicate [EPOXY]/[ACID] ratios.

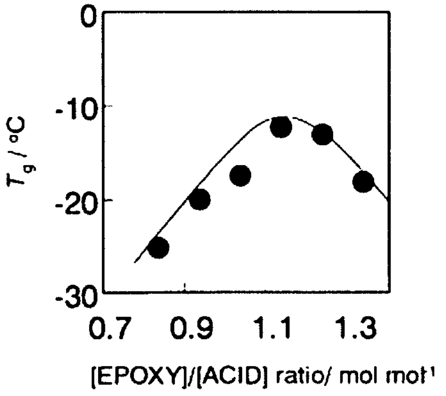


Figure 5. Relationship between T_g and [EPOXY]/[ACID] ratio of epoxy resins.

Fig. 6 shows the DSC curves of epoxy resins with various ALPA contents. Fig. 7 shows that T_g increases and ΔC_p decreases with increasing the ALPA content of epoxy resin. The above results indicate that lignin act as a hard segment in epoxy resin molecules. It is known that lignin is a highly branched polymer consisting of phenyl propane units, which are mainly connected by ether linkages. At the same time, each lignin molecule contains a number of hydroxyl groups [1]. Accordingly, it is considered that lignin acts as cross-linking agent and that the chain length of epoxy resins between cross-links decrease with the increase in ALPA content in epoxy resins. The increase in the chain lengths between cross-linking points enhances the main chain molecular motion.

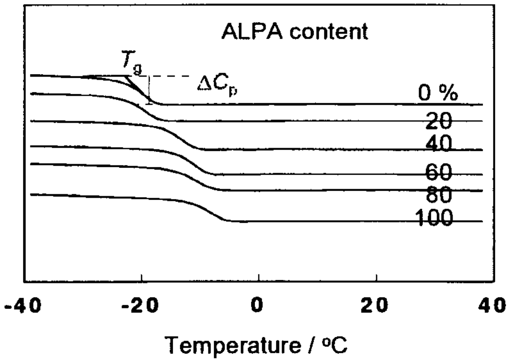


Figure 6. DSC curves of epoxy resins with various ALPA contents. Numbers indicate the ALPA contents.

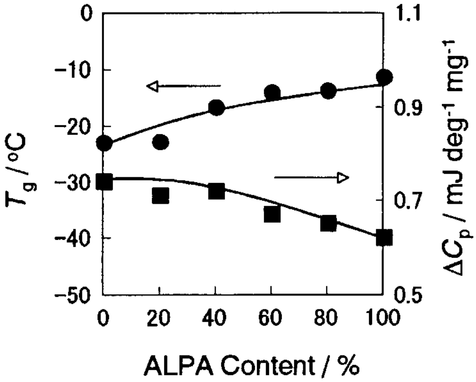


Figure 7. Changes of T_g and ΔC_p with the ALPA content of epoxy resins.

The thermal decomposition behavior of the starting materials and of the epoxy resins was studied by TG. Fig. 8 shows TG and differential TG (DTG) curves of the starting materials such as ALPA, EGPA and EGDGE. It is observed that the thermal degradation process occurs in two steps. The decomposition temperatues in the lower temperature region (T_{d1}) and in the higher temperature region (T_{d2}) were determined. T_{d1}'s of the starting materials are 190, 210 and 133 °C while T_{d2}'s are 335, 367 and 203 °C, respectively. It is known that carboxylic acid and epoxy groups are thermally unstable. Accordingly, it is considered that those groups decompose in the T_{d1} region. Fig. 9 shows TG and differential TG (DTG) curves of epoxy resins with various ALPA contents. The decomposition process apparently occurs in a smooth single step and no degradation is observed in the T_{d1} region. This indicates that thermally unstable carboxylic acid and epoxy groups were converted into thermally more stable ester groups. Thermal decomposition temperatures (T_d's) and mass residue at 500 °C (MR) were determined from the TG curves. Fig. 10 shows that T_d slightly decreases with increasing ALPA content. It is known that lignin is relatively thermally unstable [6]. However, the degree of the decrease in T_d values is very small. Therefore, it can be said that lignin becomes thermally more stable after the introduction into the epoxy resin molecules. Fig. 10 also shows that the mass residue at 500 °C

(MR) with the increasing content of ALPA in epoxy resins. It is know that lignin molecules react each other to form a condensed char-like material, when it is heated in nitrogen. Therefore, it is considered that the materials in the residue at 500 °C are mainly formed by the reaction of lignin in epoxy resins during the decomposition process. The above consideration is supported by the fact that the MR of APLA is higher than that of EGPA, as shown in Fig. 8.

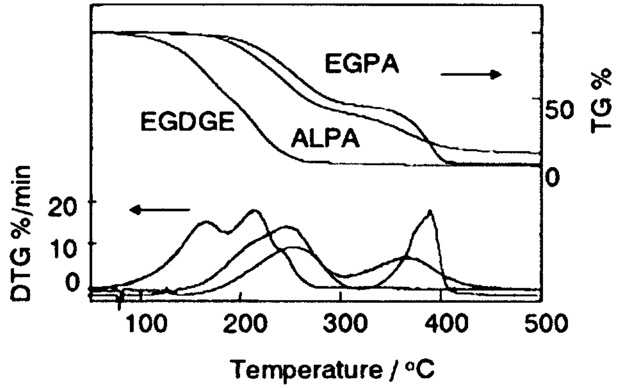


Figure 8. TG and differential TG (DTG) curves of ALPA, EGPA and EGDGE.

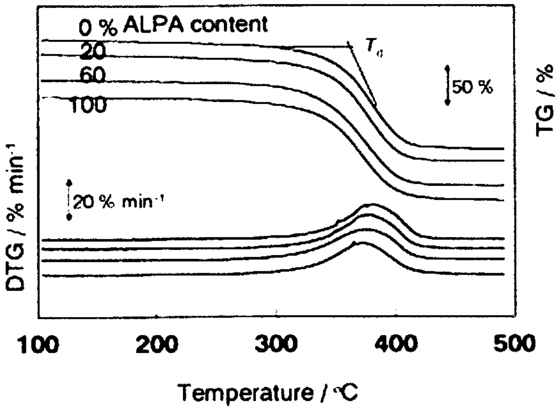


Figure 9. TG and differential TG (DTG) curves of epoxy resins.

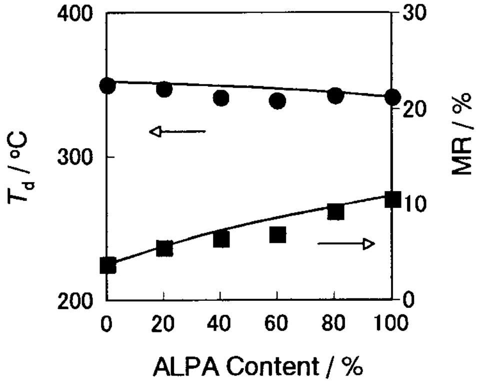


Figure 10. Dependence of T_d and mass residue at 500 °C (MR) on the ALPA content of epoxy resins.

Conclusion

Ester-carboxylic acid derivative (ALPA) of alcoholysis lignin (AL) was synthesized in a solution of AL in ethylene glycol (EG). Epoxy resins were obtained by the reaction of the ester-carboxylic acid derivatives with ethylene glycol diglycidyl ether (EGDGE) in the presence of a catalytic amount of dimethylbenzyl amine (DMBA). The activation energy of the curing reaction between carboxylic acid and epoxide groups was 83.5 kJ mol^{-1}. T_g increased with increasing ALPA contents in the epoxy resin, suggesting that lignin acts as a hard segment. T_d slightly decreased with increasing ALPA content in epoxy resin. However, the decrease in T_d was small, suggesting that the thermal stability of the obtained epoxy resins is not affected by the introduction of lignin molecules into the epoxy resin molecular chains.

[1] K. Kringstad, in *Future Sources of Organic Raw Mterials – CHEMRAWN* I., L. E. St. Pierre *et. al.* Eds., Pergamon Press, 1980, p. 627.
[2] G. Dai in *Lignins*, K. V. Sarkanene, C. H. Ludwig Eds., Wiley-Interscience, New York 1971, p. 697.
[3] H. Hatakeyama, S. Hirose, T. Hatakeyama, K. Nakamura, K. Kobashigawa, N. Morohoshi, *J. Macromol. Sci.*, **1995**, A32, 743.
[4] H. Hatakeyama, *J. Therm. Anal. Calorimetry*, in press
[5] K. Nakamura, T. Hatakeyama, H. Hatakeyama, *Poly. Adv. Technol.*, **1992**, 2, 41.
[6] S. Hirose, K. Kobashigawa, Y. Izuta, H. Hatakeyama, *Polym. Intl.*, **1998**, 47, 247.
[7] S. Hirose, T. Hatakeyama, Y. Izuta, H. Hatakeyama, *J. Therm. Anal. Calorimetry*, in press

[8] H. Hatakeyama, Y. Izuta, S. Hirose, T. Yoshida, T. Hatakeyama, in "*Recent Advances in Environmentally Compatible Polymers*", J. F. Kennedy, P. A. Williams, G. O. Phillips, H. Hatakeyama Eds., Woodhead Publisher Ltd., Chichester 2001, P. 33.
[9] T. Hatakeyama, Y. Izuta, S. Hirose, H. Hatakeyama, Polymer **2002**, 43, 1177.
[10] H. Ito, N. Shiraishi, Mokuza Gakkaishi **1987**, 33, 393.
[11] D. Feldman, D. Banu, *J. Polym. Sci., Polym. Chem.* **1989**, 26, 973.
[12] K. Hofmann, W. G. Glasser, *Macromol. Chem. Phys.* **1994**, 195, 65.
[13] S. Hirose, M. Kobayashi, H. Kimura, H. Hatakeyama, in "*Recent Advances in Environmentally Compatible Polymers*", J. F. Kennedy, P. A. Williams, G. O. Phillips, H. Hatakeyama Eds., Woodhead Publisher Ltd., Chichester 2001, P. 73.
[14] M. Shinbo, T. Nakaya, T. Takahama, *J. Polym. Sci., Polym. Phys.* **1986**, 24, 1931.
[15] T. Ozawa, *Bull. Chem. Soc., Japan* **1965**, 38, 1881.
[16] S. Nakamura, M. Todoki, , K. Nakamura and H. Kanetsuna, *Thermochimica Acta* **1988**, 163, 136.
[17] T. Hatakeyama and F. X. Quin, "*Thermal Analysis*", John-Wiley & Sons Ltd., Chichester, 1994, P. 38/64.
[18] W. Bukowski, Org. Process Res. Dev. **2002**, 6, 10.