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Dehydrochlorination behavior of polychloroprene during thermal degradation

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ABSTRACT

The thermal degradation behavior of polychloroprene (PCP) is analyzed by thermogravimetric (TG) analysis and simultaneous thermogravimetry–mass spectrometry (TG–MS). The weight loss in PCP during the thermal degradation is found to occur in four stages. The apparent activation energies are 70–90, 120–180, 250–340, and 290–300 kJ mol^{-1} in the first, second, third, and fourth stages, respectively. Furthermore, the degradation products are analyzed *in situ* by mass spectrometry. HCl is mainly produced in the first and second stages. Chlorinated organic compounds such as 2-chloro-1,3-butadiene and chlorobenzene are produced in the second stage. Aromatics, particularly the polycyclic compounds such as naphthalene, are produced in the third and fourth stages. In addition, the effect of temperature on the dehydrochlorination of PCP during isothermal degradation is also examined. Among select temperatures, the degree of dehydrochlorination of PCP is the highest at 500 °C. It is more difficult to recycle the Cl in PCP as HCl as compared to the Cl in poly(vinyl chloride) (PVC) due to the production of chlorinated organic compounds.

1. Introduction

Synthetic rubbers have been widely used in tyres, hoses, industrial rubbers, cables, wires, adhesives, belts, etc. In Japan, approximately 1,536,000 t of synthetic rubbers were produced in 2004 [1]. On the other hand, the amount of waste rubber generated in 2004 was 47,000 t, and 44% of it was recycled [2]. As compared to the percentages of recycled slag and waste metal in 2004, i.e., 90% and 88%, respectively, the percentage of recycled waste rubber was very less. Therefore, it is socially desirable to recycle maximum quantity of waste rubber and waste plastic. One of the recycling methods is the production of fuels and basic chemicals such as BTX aromatics (benzene, toluene, and xylenes) by the pyrolysis of waste rubber [3]. Various rubber pyrolysis technologies have been developed, which employ fluid beds, rotary kilns, molten salts, or cross-flow shaft systems [3]. However, few types of synthetic rubbers, e.g., chloroprene rubber and epichlorohydrin rubber, contain chlorine. This results in the corrosion of apparatus caused by the production of hydrochloric acid during the rubber pyrolysis and also results in the generation of residual chlorine in the produced fuels and basic chemicals [4–6]. Therefore, the chlorine-containing rubbers should be preferably dechlorinated initially.

The degradation behavior of poly(vinyl chloride) (PVC) has already been examined using simultaneous thermogravimetry–mass spectrometry (TG–MS) by our research group for improving the dehydrochlorination process in the feedstock recycling of waste plastics [7]. The dehydrochlorination of PVC up to 650 °C in He is found to be divided into three degradation stages, namely, two dehydrochlorinations and a polyene-aromatic network breakdown. In addition, the effect of temperature on the dehydrochlorination of PVC in N_2 atomosphere during isothermal degradation has also been examined [8]. The degree of dehydrochlorination of PVC is nearly 100% over 260 °C. PVC is almost completely dehydrochlorinated at moderate temperature. This is attributed to the cleavage of the C–Cl bonds in PVC because the Cl atom is bonded to a C atom from the C–C bonds present in its structure (Fig. 1). On the other hand, polychloroprene (PCP) is a raw material for chloroprene rubber, which is a representative of chlorine-containing rubbers. Although the molecular structure of PCP is similar to that of PVC, the Cl atom in PCP is bonded to a C atom from the C=C double bonds present in its structure (Fig. 1). Therefore, the cleavage of the C–Cl bonds in PCP may be harder than that in PVC, which could pose a problem in the dehydrochlorination of PCP.

Some researchers have examined the pyrolysis of PCP. Kaminsky et al. have reported the pyrolysis of PCP rubber in a fluidized-bed reactor on a laboratory scale at 593 °C [4]. The degradation products comprise gas components (e.g. HCl and hydrocarbons), oil components (e.g. aromatic hydrocarbons), carbon black, char, tar, and water [4]. Gardner and McNeill have reported that the degradation of PCP occurs predominantly in two stages–HCl is lost in the first step, while in the second step, volatile hydrocarbons are produced through chain scission [9–11]. This degradation mechanism is supported by the solid-state ^{13}C NMR study of the char-forming

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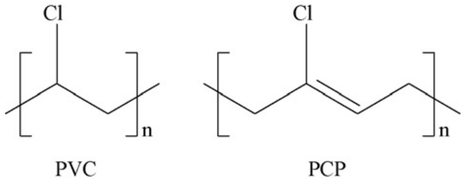

Fig. 1. Structures of PVC and PCP.

processes in PCP by Dick et al. [12]. Mehl et al. have proposed a lumped kinetic model of PCP thermal degradation [5]. However, these experiments have not examined the thermal degradation products of PCP *in situ*. Recently, Aracil et al. have reported the TG–MS analysis of the thermo-oxidative decomposition of PCP [13]. However, H_2O, CO, HCl, and CO_2 are analyzed only by MS, and other volatile compounds are not detected.

The objective of this study is to examine the dehydrochlorination of PCP, which is employed to recycle chlorine-containing rubbers such as chloroprene rubber. The thermal degradation behavior of PCP is carefully examined by TG and differential thermal analysis (DTG). The apparent activation energy is estimated on the basis of the weight loss in PCP at each stage of the thermal degradation. Furthermore, the degradation products of PCP, particularly the volatile compounds, are analyzed *in situ* by MS. In addition, the effect of temperature on the dehydrochlorination of PCP during the isothermal degradation is also examined.

2. Experimental

PCP was purchased from Aldrich (Missouri, USA). It consisted of 85% and 10% of trans and cis forms, respectively. The PCP powder was sieved to obtain particles with a diameter less than 1 mm, which were then used in the experiment. The elemental analysis of PCP showed that it contained 54.0, 5.8, and 39.8 wt.% of C, H, and Cl, respectively.

2.1. Analysis of thermal degradation behavior of PCP

The thermal degradation behavior of PCP was examined using a TG–DTA analyzer (TG/DTA 6200; Seiko Instruments, Chiba, Japan) in flowing He (40 ml min^{-1}). After He gas replacement for 30 min, a 7-mg sample was heated from 50 to 900 °C at rates of 5 to 100 °C min^{-1}. In addition, the degradation products of PCP heated at the rate of 5 °C min^{-1} were analyzed *in situ* by simultaneous TG–MS (5973; Hewlett–Packard, Palo Alto, CA). A schematic representation of TG–MS has been published previously [7]. The degradation products were introduced into the MS ion source through an inactivated stainless capillary tube heated at 270 °C in order to prevent the condensation of the evolved products.

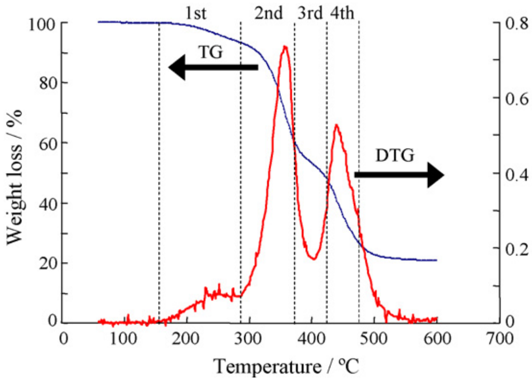

Fig. 3. TG and DTG curves of PCP at heating rate of 5 °C min^{-1}.

2.2. Dehydrochlorination of PCP during isothermal degradation

The experimental apparatus used for the isothermal degradation of PCP is shown in Fig. 2. A quartz reaction tube was heated at the required temperature using the electric furnace, and He gas was flowed through it at 40 ml min^{-1} for 30 min. Then, an Al boat containing 30 mg of PCP was inserted into the quartz reaction tube. PCP was degraded at 350–600 °C for 70 min under the He flow. The evolved HCl was collected in a trap (0 °C) containing 25 ml of 0.1 mol l^{-1} NaOH solution. The oil that was produced was removed by taking up in two air traps (0 °C) cooled with ice. The NaOH solution trap was replaced with a new one after 5, 10, 15, 20, 30, 50, and 70 min, and the amounts of Cl^- in the traps were determined using an ion chromatograph (DX-100; Dionex Corp.) and a column (eluent: 35 mmol l^{-1} NaOH; flow rate: 1.5 ml min^{-1}; AS16A; Dionex Corp., Sunnyvale, CA). In addition, the weights of the residues after the degradations for 70 min were measured, and the compositions of the residues were identified by elemental analysis.

3. Results and discussion

3.1. Analysis of thermal degradation behavior of PCP

Fig. 3 shows the TG and DTG curves of PCP at a heating rate of 5 °C min^{-1}. The thermal degradation of PCP was divided into four stages: the first stage (weight loss of 0–8%) at 150–290 °C, second stage (weight loss of 8–44%) at 290–380 °C, third stage (weight loss of 44–52%) at 380–420 °C, and fourth stage (weight loss of 52–64%) at 420–480 °C. The apparent activation energies at the four degradation stages based on the weight losses in PCP were estimated from the TG curves at the heating rates of 5 to 100 °C min^{-1} using the Ozawa method [14]. In this method, initially, the equation of

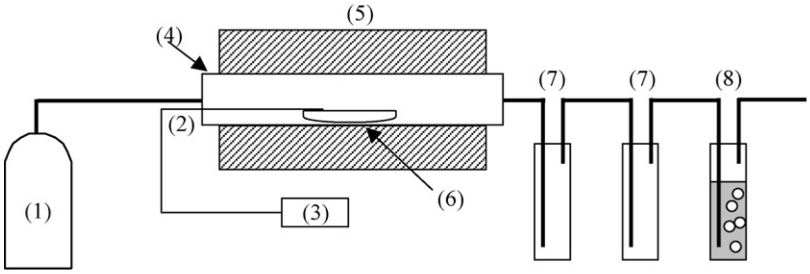

Fig. 2. Experimental setup for isothermal degradation of PCP. (1) He cylinder, (2) thermocouple, (3) electric source, (4) quartz reaction tube, (5) electric furnace, (6) Al boat, (7) air trap (0 °C), and (8) NaOH solution trap (0 °C).

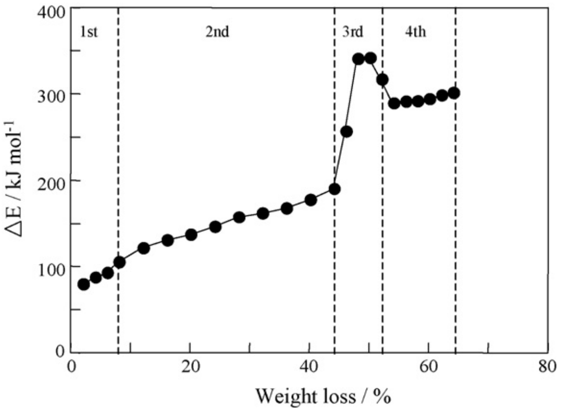

Fig. 4. Variation in activation energy with weight loss in PCP.

the degradation reaction is defined as follows:

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = Aexp\left(\frac{-\Delta E}{RT}\right)f(x) \tag{1}$$

where x is the degree of weight loss; t, the time; A, the frequency factor; ΔE, the activation energy; R, the gas constant; T, the absolute temperature; and $f(x)$, a function of x. For the thermal analysis, T is a function of t and $\mathrm{d}T/\mathrm{d}t = B$ is usually employed. B denotes the heating rate, and it is constant. Finally, Eq. (1) is transformed into Eq. (2) as follows:

$$\log B = -0.4567\frac{\Delta E}{RT} + \text{const.} \tag{2}$$

Even if x remains the same, T differs depending on the heating rates. By plotting $\log B$ vs. $1/T$ for each x, a straight line with a slope of $-0.4567\Delta E/R$ is obtained. Therefore, the activation energy (ΔE) corresponding to each degree of weight loss, i.e., x, is obtained. The variation in the activation energy with the weight loss in PCP is shown in Fig. 4. The activation energy is calculated to be 70–90, 120–180, 250–340, and 290–300 kJ mol^{-1} for the first, second, third and fourth stages, respectively. The third stage is found to have the largest activation energy among the four stages.

Fig. 5 shows the TG curve of PCP and the selected ion chromatogram of the major products in the thermal degradation of PCP at a heating rate of 5 °C min^{-1}. Signals at m/z 36, 77, 88, 91, 92, 106, 112, 128, and 176 are observed corresponding to the molecular ion peaks of hydrogen chloride, phenyl ion, the monomer of 2-chloro-1,3-butadiene, tropylium ion, toluene, xylene, chlorobenzene, naphthalene, and the dimer of 2-chloro-1,3-butadiene, respectively. In the first stage (150–290 °C), mainly hydrogen chloride is detected. In the second stage (290–380 °C), the intensity of molecular ion peak of hydrogen chloride increases. In addition, the chromatogram shows the presence of the monomer and dimer of 2-chloro-1,3-butadiene, phenyl ion, tropylium ion, and naphthalene. The phenyl and tropylium ions are characteristic fragment ions of benzene derivative and benzene substituted with an alkyl. The benzene derivative is probably derived from aromatic compounds such as chlorobenzene, toluene, and xylene. The parent molecules of the tropylium ion are considered to be aromatic compounds such as toluene and xylene because the chromatogram of the tropylium ion is similar to that of toluene and xylene, as shown in Fig. 5(b). In the third stage (380–420 °C), the intensity of the molecular ion peaks of hydrogen chloride and the monomer and dimer of 2-chloro-1,3-butadiene decreases. In the fourth stage (420–480 °C), phenyl ion, tropylium ion, and naphthalene are remarkably detected in the chromatogram.

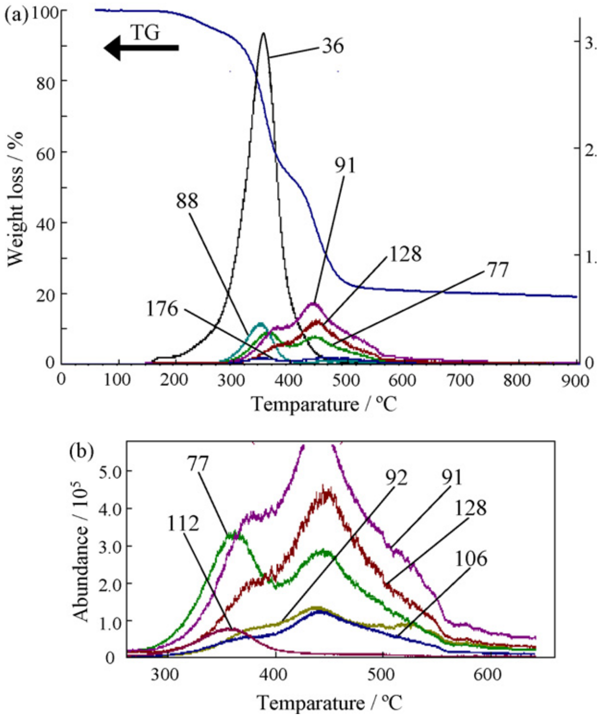

Fig. 5. TG curve of PCP and chromatogram of selected ion of major products in thermal degradation of PCP at heating rate of 5 °C min^{-1} (36: hydrogen chloride, 77: phenyl ion, 88: monomer of 2-chloro-1,3-butadiene, 91: tropylium ion, 92: toluene, 106: xylene, 112: chlorobenzene, 128: naphthalene, and 176: dimer of 2-chloro-1,3-butadiene).

Hydrogen chloride is detected in all the stages, indicating that the thermal degradation of PCP results in the dehydrochlorination reactions in all the stages. The dehydrochlorination of PCP is particularly remarkable in the second stage. This dehydrochlorination is caused by the cleavage of the C–Cl bonds between the Cl and C atoms from C=C double bonds. Furthermore, the cleavage of the C–C single bonds probably results in the production of monomer of 2-chloro-1,3-butadiene. In addition, the cycloaddition reaction of the monomer probably results in the production of dimer of 2-chloro-1,3-butadiene and aromatic compounds such as chlorobenzene, toluene, xylene, and naphthalene. In the third stage, the residues generated by the dehydrochlorination of PCP are probably formed by unsaturated linkages including the aromatic structure, suggesting that the residues have been stabilized. This probably results in the largest activation energy in the third stage with the thermal degradation of PCP, as shown in Fig. 4. The residues continue to be degraded in the fourth stage, resulting in a remarkable production of aromatic compounds including polycyclic compounds such as naphthalene.

To summarize, the thermal degradation of PCP causes the dehydrochlorination. With the increasing temperature, chlorinated organic compounds such as 2-chloro-1,3-butadiene and chlorobenzene are produced, followed by the production of aromatic compounds such as naphthalene.

3.2. Dehydrochlorination of PCP during isothermal degradation

Fig. 6 shows the variation in the degree of dehydrochlorination with time during the isothermal degradation of PCP at 350–600 °C. This experiment was performed using the apparatus shown in Fig. 2. The degree of dehydrochlorination is defined as the percentage of amount of Cl dehydrochlorinated from PCP to the net amount of Cl contained in the PCP. For all tempera-

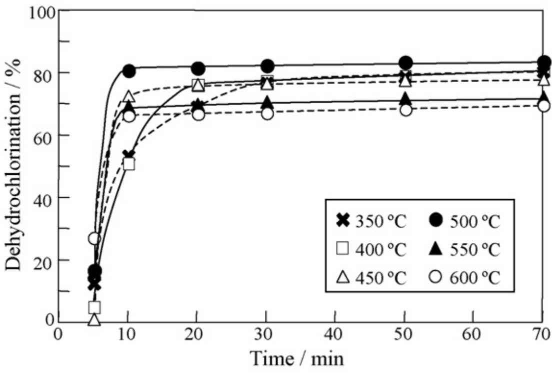

Fig. 6. Variation in degree of dehydrochlorination with time during isothermal degradation of PCP at 350–600 °C.

Table 1
Yields of HCl, degradation products, and residues obtained by isothermal degradation of PCP for 70 min (wt.%)

	Temperature (°C)					
	350	400	450	500	550	600
HCl	32.7	32.9	31.8	34.1	29.4	28.4
Degradation products (except HCl)*	11.0	31.2	40.0	48.1	51.2	56.9
Residues	56.3	35.9	28.2	17.8	19.5	14.7

* The amount of the degradation products was calculated by subtracting the amounts of HCl and the residues from the amount of PCP.

tures, the degree of dehydrochlorination increases with time. The degree of dehydrochlorination is almost constant over 10 min for 500–600 °C, over 20 min for 400–450 °C, and over 30 min for 350 °C. For 70 min, the degree of dehydrochlorination was approximately 80% at 350–450 °C, and its largest value is 83% at 500 °C. However, the degree of dehydrochlorination for 70 min decreases with increasing temperature from 500 to 600 °C, and its lowest value is 71% at 600 °C.

Table 1 shows the yields of HCl, degradation products, and residues obtained by the isothermal degradation of PCP for 70 min. In this case, the amount of degradation products is calculated by subtracting the amounts of HCl and residues from the amount of PCP. With the increasing temperature, the yield of the residues decreases, while the yield of the degradation products increases. The yields of HCl are approximately 30% at all temperatures. The results in Table 1 suggest that the increase in temperature has a significant effect on the increase in the yield of the degradation products generated from the residues. Table 2 lists the chemical compositions of the residues obtained by the isothermal degradation of PCP for 70 min. The contents of Cl in the residues at all temperatures are less than 3 wt.%. Since the content of Cl in PCP is 39.8 wt.%, the contents of Cl in the residues are extremely low. This supports the fact that the isothermal degradation of PCP results in dehydrochlorination. From the results in Tables 1 and 2, the percentages of the Cl in the components to the net Cl amount in PCP are calculated, which are listed in Table 3. In this case, the components are HCl, degradation products, and residues obtained by the isothermal degradation of PCP for 70 min. On increasing the temperature from 350 to 500 °C, the percentage of Cl increases slightly for HCl, while it decreases slightly for the residues. The percentage of Cl in the degradation products is almost constant. This suggests that the increase in the temperature results in the dehydrochlorination of the residues. Compared to the results at 500 and 600 °C, in this case, the percentages of Cl in the residues are the same—approximately 1%. The percentage of Cl decreases significantly for HCl and increases significantly for the degradation products. This indicates that the decrease in the degree of dehydrochlorination corresponds to the increase in the Cl amount contained in the degradation products. This is certainly caused by the simultaneous reactions of dehydrochlorination of PCP and the production of chlorinated organic compounds. The decrease in the degree of dehydrochlorination with increasing the temperature from 500 to 600 °C (Fig. 6) is certainly attributed to the production of chlorinated organic compounds, which is confirmed by the detection of monomer and dimer of 2-chloro-1,3-butadiene in the MS spectra shown in Fig. 5. It is considered that the thermal degradation of PCP results in the production of char on the surface of the PCP powder. In particular, the rate of production of char increases at a temperature of more than 500 °C. This probably results in the presence of the degradation products inside the char layer produced on the surface of the PCP powder. This facilitates a secondary reaction, which is the reaction of HCl generated from PCP with the degradation products inside the char layer, resulting in the production of chlorinated organic compounds [15].

Table 2
Chemical compositions of residues obtained by isothermal degradation of PCP for 70 min (wt.%)

	Temperature (°C)		
	350	500	600
C	84.1	85.5	84.3
H	7.0	3.7	2.7
Cl	2.8	2.9	2.9

Table 3
Percentages of Cl amount contained in the components to the net Cl amount in PCP (%)

Components*	Temperature (°C)		
	350	500	600
HCl	80.0	83.2	70.5
Degradration products (except HCl)	16.1	15.5	28.4
Residues	3.9	1.3	1.1

* The components were obtained by the isothermal degradation of PCP for 70 min.

For the isothermal degradation of PVC, the degree of dehydrochlorination was close to 100% at a temperature of more than 260 °C [8]. In contrast, the highest degree of dehydrochlorination for PCP is 83% at 500 °C, and it was lower than that for PVC. As compared to the case of PVC, it was found to be more difficult for the Cl contained in PCP to be recycled as HCl. Approximately 99% of the Cl contained in PCP is found to be dechlorinated as HCl and chlorinated organic compounds at a temperature of more than 500 °C.

4. Conclusions

The thermal degradation of PCP is found to occur in four stages. The apparent activation energies are 70–90, 120–180, 250–340, and 290–300 kJ mol^{-1} in the first, second, third, and fourth stages, respectively. HCl is mainly produced in the first and second stages. Chlorinated organic compounds such as 2-chloro-1,3-butadiene and chlorobenzene are produced in the second stage. Aromatics, particularly polycyclic compounds such as naphthalene, are produced in the third and fourth stages. It is found that it is more difficult to recycle the Cl in PCP as HCl than the Cl in PVC during the isothermal degradation of PCP. The dehydrochlorination of PCP requires thermal degradation at a high temperature for the cleavage of the C–Cl bonds between the Cl and C atoms from C=C double bonds. However, the thermal degradation of PCP at high temperature not only causes dehydrochlorination but also produces chlorinated organic compounds. This results in the production of less HCl from PCP.

References

[1] The Japan Rubber Manufacturers Association, http://www.jrma.gr.jp/.
[2] Ministry of the Environment, Government of Japan, http://www.env.go.jp/index.html.
[3] A. Buekens, in: J. Scheirs, W. Kaminsky (Eds.), Feedstock Recycling and Pyrolysis of Waste Plastics, John Wiley & Sons, Ltd., UK, 2006, p. 35.
[4] W. Kaminsky, C. Mennerich, J.T. Andersson, S. Gotting, Polym. Degrad. Stab. 71 (2001) 39.
[5] M. Mehl, A. Marongiu, T. Faravelli, G. Bozzano, M. Dente, E. Ranzi, J. Anal. Appl. Pyrol. 72 (2004) 253.
[6] T. Bhaskar, Y. Sakata, in: J. Scheirs, W. Kaminsky (Eds.), Feedstock Recycling and Pyrolysis of Waste Plastics, John Wiley & Sons, Ltd., UK, 2006, pp. 498–502.
[7] T. Yoshioka, T. Akama, M. Uchida, A. Okuwaki, Chem. Lett. 29 (2000) 322.
[8] T. Yoshioka, N. Saitoh, A. Okuwaki, Chem. Lett. 34 (2005) 70.
[9] D.L. Gardner, I.C. McNeill, Eur. Polym. J. 7 (1971) 569.
[10] D.L. Gardner, I.C. McNeill, Eur. Polym. J. 7 (1971) 593.
[11] D.L. Gardner, I.C. McNeill, Eur. Polym. J. 7 (1971) 603.
[12] C.M. Dick, J.J. Liggat, C.E. Snape, Polym. Degrad. Stab. 74 (2001) 397.
[13] I. Aracil, R. Font, J.A. Conesa, A. Fullana, J. Anal. Appl. Pyrol. 79 (2007) 327.
[14] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[15] G. Eklund, J.R. Pedersen, B. Stromberg, Chemosphere 16 (1987) 161.