Characterization of Thermal Degradation of PTT

Bull. Korean Chem. Soc. **2012**, Vol. 33, No. 3   833

Characterization of Thermal Degradation of Polytrimethylene Terephthalate by MALDI-TOF Mass Spectrometry[†]

Sungwoo Jang, Eun Kyung Yang, Sung Il Jin, Young Dal Cho,[‡] Eun Kyung Choe,[‡] and Chan Ryang Park[*]

Department of Chemistry, Kookmin University, Seoul 136-702, Korea. [*]E-mail: crpark@kookmin.ac.kr
[‡]Textile Ecology Laboratory, Korea Institute of Industrial Technology, Ansan, Korea

The thermal degradation products of polytrimethylene terephthalate (PTT) obtained by heating the sample in the temperature range of 250-360 ºC under non-oxidative conditions was characterized using MALDI-TOF (matrix assisted laser desorption/ionization) mass spectrometry. The structures of the degradation products were determined and the relative compositions were estimated. The MALDI-TOF mass spectra of the thermally degraded PTT sample showed three main series of oligomer products with different end groups, which were carboxyl/carboxyl, carboxyl/allyl, and allyl/allyl. In contrast to the thermal degradation of polyethylene terephthalate (PET), the oligomers containing terephthalic anhydrides were not detected, whereas the formation of oligomers containing the unsaturated allyl ester group was confirmed by mass assignment. From these results, it was concluded that the thermal degradation of PTT proceeds exclusively through the β-CH hydrogen transfer mechanism, which is in accordance with the proposed reaction mechanism for the thermal degradation of polybutylene terephthalate (PBT).

Key Words : MALDI-TOF MS, PTT, Thermal degradation, β-CH hydrogen transfer, End group

Introduction

Polytrimethylene terephthalate (PTT) is produced through a condensation or transesterification process from the two monomer units, 1,3-propanediol (PDO) and terephthalic acid or dimethyl terephthalate.[1] However, PTT's value as a commercial polymer improved in the late 1990s with the development of more efficient methods to produce PDO *via* hydroformylation of ethylene oxide by using corn as the base material for PDO production. Through these developments, PTT is expected to compete with polybutylene terephthalate (PBT) or polyethylene terephthalate (PET), which have been more successful than PTT to date.

For this reason, the thermal degradation processes concerning PET[2-9] and PBT[8-12] have received continuing attention. Thermal degradation mechanisms of PET and PBT have been mainly investigated using the mass spectra obtained from direct pyrolysis mass spectrometry (DPMS) and MS/MS techniques to determine the structure of thermal degradation products. On the other hand, relatively few studies on the thermal stability of PTT have been reported through weight loss measurement using thermogravimetry.[13,14]

Recently, a parallel study on the isothermal degradation of PET[16] and PBT[17] in the temperature range of 270-370 °C and 270-350 °C, respectively, was reported by Montaudo and coworkers. Using MALDI-TOF mass spectrometry and NMR analysis, different thermal degradation behavior between PET and PBT was observed. For thermal degradation of PET, the vinyl-ester terminated oligomers were not detected, whereas the formation of oligomers containing terephthalic anhydride units was apparent in the MALDI spectra. In contrast to PET, the formation of the butenyl ester terminated oligomers was observed in the thermal degradation of PBT, whereas the anhydride-containing oligomers were not detected at all. The different thermal degradation behavior of PET and PBT was interpreted in terms of the different reactivity of the vinyl and butenyl end groups on the one hand, and also on the basis of structural differences such as methylene chain lengths of the two polymers.

In this paper, we report the characterization of the isothermal degradation products of PTT in the temperature range of 250-360 °C by means of MALDI-TOF mass spectrometry. MALDI analyses of the thermal degradation products of PTT have not been reported yet to the best of our knowledge. The structural analysis and characterization of the hydrolytic degradation products of PTT have been reported previously using MALDI-TOF MS in our laboratory.[19] From a viewpoint of molecular structure, PTT has three methylene moieties in the chain, which is in between PET and PBT in terms of methylene chain lengths. Therefore, it is interesting to investigate how a small change in chain flexibility and functionality of the end group affects the mechanism of the thermal degradation of PTT by analyzing the degradation products using MALDI TOF mass spectrometry.

Experimental Section

A detailed description of the apparatus and experimental procedures used in this study has been reported previously.[19] In brief, the linear time-of-flight mass spectrometer was set

---

up in positive ion mode with the capability for high-voltage acceleration up to ± 30 kV. The TOF chamber was equipped with a microchannel plate at one end of the 1.2 m-long flight tube to detect ions generated from the matrix-assisted laser desorption/ionization process. The third harmonic of Nd:YAG laser (355 nm, 6-7 ns pulse width) was used for desorption of analytes and the laser beam was loosely focused onto the 1/4 inch diameter probe tip at a 45° angle.

The materials used in MALDI sample preparation such as matrixes, solvents and metal adducts were purchased from Aldrich Chemical Co. Dithranol, trifluoroacetic acid (TFA), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), sodium trifluoro-acetate (NaTFA) were used as supplied. For mass calibration and optimization of spectral resolution, angiotensin II, $P_{14}R$ (synthetic peptide), ACTH fragment 18-39, insulin oxidized B chain, and polystyrenes (M_w = 4,000) were also purchased from Aldrich.

PTT supplied by DuPont was ground to powder and dried under vacuum at 60 °C for 3 days before use. The thermal degradation of PTT was carried out by placing 0.5 g of solid PTT samples in a 3-necked round-bottom flask surrounded by heating mantles equipped with a digital heat controller. PTT samples were isothermally heated for 1 hour at various temperatures of 250 °C - 360 °C under the continuous flow of N_2 to prevent unwanted oxidation reactions. The degraded samples were cooled quickly and refluxed with methanol for 12 hours and dried under vacuum at 80 °C for 3 days before MALDI analysis.

Results and Discussion

The MALDI-TOF mass spectrum of the original PTT sample is presented in Figure 1(a), and its structural and compositional determination has been reported previously.[19] The unheated PTT sample contains a dominant fraction of cyclic oligomers and a small amount of several linear oligomers with a different combination of end groups. Besides the cyclic forms (series D), the minor components include oligomers containing carboxyl/OH (series A), carboxyl/carboxyl (series B), and OH/OH end groups (series C). Another cyclic form is also present as a minor component and classified as series E, for which the corresponding structure for PET has been reported in a previous study.[16] The sodiated structures of oligomers present in unheated PTT samples are listed in Table 1. By adding up the apparent peak intensities, it has been estimated that about 85% of oligomers are present in cyclic form in the mass range of 1,000-5,000 Da (repeat unit n = 4-22).

The MALDI-TOF mass spectra of PTT samples heated for 1 hour at 250-360 °C are presented in Figure 1(b)-(e). The mass of the monomer unit, 206.2 Da, is seen as the spacing between the signals of the similarly terminated oligomer chains. Assigned oligomer structures corresponding to each series of peaks with different end groups are summarized in Table 1. Absolute ion masses and the number of repeat units are also tabulated. As shown by the spectra in Figure 1(b) and 1(c), heating the sample up to 280 °C for 1 hour did not
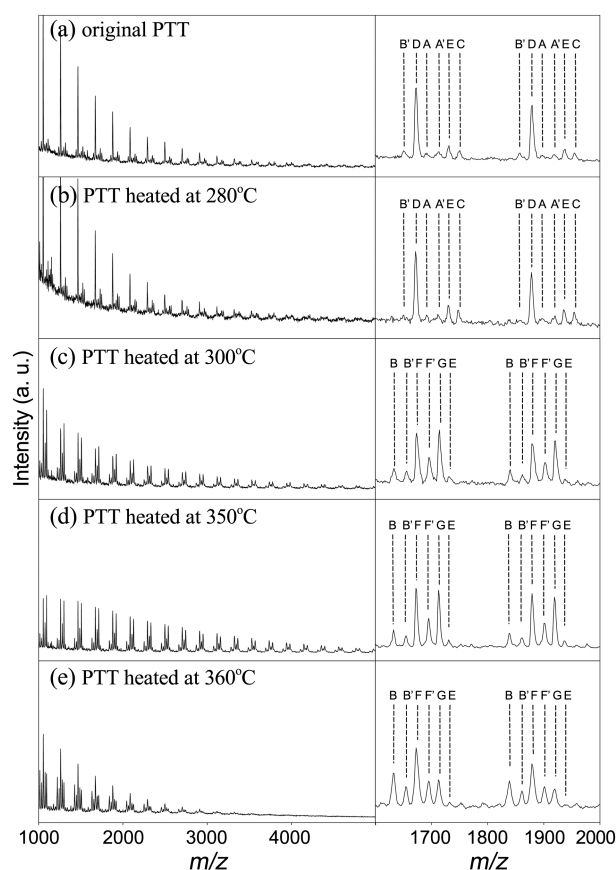

Figure 1. MALDI-TOF mass spectra of (a) unheated PTT and the samples heated for 1 hour at (b) 280 °C, (c) 300 °C, (d) 350 °C, and (e) 360 °C. Structural assignments are described in the text and Table 1. Enlarged section of each spectrum in the mass range of 1,600-2,000 Da is also presented.

induce significant decomposition of PTT, whereas considerable decompositions were evident above 300 °C.

Appearance of new mass peaks in Figure 1(c) indicates that thermal degradation begins at approximately 280-300 °C. Above 300 °C, the amount of cyclic oligomers drastically decreases and the thermal degradation products with different end groups prominently appear in the MALDI spectra. The overlap of mass peaks at m/z = 206.2n (series D and F) will be discussed later. The main mass spectral feature of the MALDI spectra obtained from the heated sample is based on three series of intense peaks, which are PTT oligomers containing carboxyl/carboxyl (series B), carboxyl/allyl (series F), and allyl/allyl end groups (series G). The oligomers containing metal ions as salt forms are designated by single or double primes depending on the number of metal ions included. Series B and F are capable of holding metal ions in salt form due to the presence of acidic carboxyl end groups, whereas series D, E and G can be present only in molecular form.

Structural assignment of the MALDI spectra clearly shows that the formation of terephthalic anhydride containing oligomers does not occur at all, at least as the final product, whereas the allyl-ester terminated oligomers (series F and G) constitute a majority of the PTT degradation products. The

Table 1. Structural assignment of the peaks displayed in the MALDI-TOF mass spectra of the PTT samples reported in Figure 1

Species	Structure	n	M+Na⁺
A		8	1,691
A'		8	1,713
B		7	1,633
B'		7	1,654
C		8	1,749
D		8	1,673
E		8	1,731
F		7	1,673
F'		7	1,695
G		7	1,713

mechanism is essentially identical to that proposed for the thermal degradation of PBT, rather than that of PET, where the latter includes formation of oligomers containing anhydride. Thermal degradation of polyalkylene terephthalate is now generally known to proceed *via* a retrograde Diels-Alder type reaction, which involves a six-membered cyclic transition state, and generates open chain oligomers with alkylene and carboxyl end groups as shown in Scheme 1. The reaction is often called a β-CH hydrogen transfer reaction.[8]

Caution should be exercised in assigning the mass peaks corresponding to $m/z = 206.2n$. The open-chain oligomers containing carboxyl/allyl end groups (series F) are isobaric with the cyclic oligomers (series D) since series F itself is generated from series D *via* β-CH hydrogen transfer.

Fortunately, however, the sodium salt form of carboxyl/allyl ended oligomers (series F') has been detected in the mass spectra. In the previous work on the hydrolytic degradation of PTT,[19] the relative intensity ratio of ~2:1 was observed for the analogous series of molecular form (series A) and salt form (series A'), where series A and A' denote the oligomers containing carboxyl/OH end groups. Therefore, it is reasonable to assume the same ratio for series F and F' in the present study based on the similar combination of end groups. From this assumption, it can be deduced that the mass peaks at $m/z = 206.2n$ in Figure 1(b) (280 °C) are mostly due to cyclic forms (series D), whereas those in Figure 1(c)-(e) (over 300 °C) can be attributed almost exclusively to the oligomers containing carboxyl/allyl end groups (series F). The validity of this assumption will be discussed in terms of

(a)

(b)
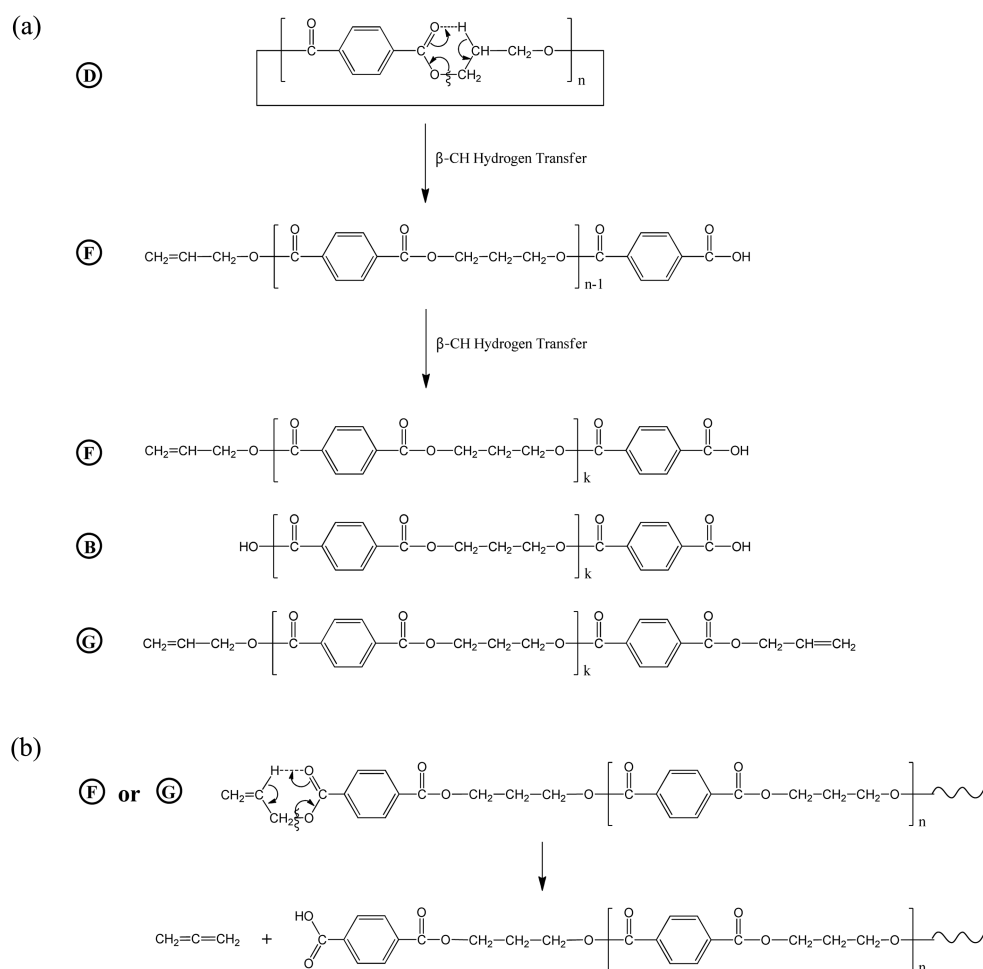
Scheme 1. (a) β-CH hydrogen transfer reaction to generate alkenyl ended and carboxyl ended oligomers, (b) β-CH hydrogen transfer reaction at alkenyl terminal.

quantitative analysis of the degradation products.

According to Scheme 1, the cyclic oligomers decompose to the oligomers bearing carboxyl/allyl end groups (series F) *via* β-CH hydrogen transfer. Subsequent decomposition of series F by the same mechanism generates the oligomers containing carboxyl/carboxyl (series B) and allyl/allyl end groups (series G), or two F series, due to the presence of two symmetric ester bonds in the chain. Further fragmentation of series B *via* β-CH hydrogen transfer produces series B and F, whereas series G produces series G and F, and so forth. Assuming that the β-CH hydrogen transfer occurs exclusively and randomly throughout the degradation process, the relative abundance of series F, G and B is expected to be 2:1:1 at equilibrium. When the ratio is compared with the relative intensity distributions of product series F, G, and B in Figure 1(c)-(e), the agreement is favorable in a qualitative sense under the assumption that the ionization yields of differently terminated oligomers are not very different.

The distributions of relative abundances of the main series of linear oligomer products (series F, G, and B) at a few selected temperatures are plotted as a function of number of unit masses n in Figure 2 as well as that of the cyclics before thermal degradation (series D). Based on this distribution,

the normalized abundance of PTT oligomers corresponding to different series produced from 1 hour heating is displayed against the processing temperature in Figure 3. The approximate equilibrium ratio of 2:1:1 for the relative abundance of series F, G and B is apparent from Figure 3, where it is assumed that the mass peak at $m/z = 206.2n$ is mostly contributed by series F above 300 °C.

Invariance of the relative abundance of the differently terminated oligomers with regards to heating temperature strongly implies that the thermal degradation of PTT proceeds exclusively through β-CH hydrogen transfer, as presented in Scheme 1. This conclusion is in agreement with the previous report by Kiibler and coworkers on the thermal degradation of PTT using different experimental methods.[15] In their investigation, the rate constants for the thermal degradation of PTT determined by monitoring the increase of allyl end groups using NMR and by monitoring molecular weight degradation using a viscometer showed excellent agreement. If other significant degradation mechanisms in addition to β-CH hydrogen transfer were involved simultaneously, the rate determined from molecular weight degradation would be greater than that determined from the increase in allyl end groups.
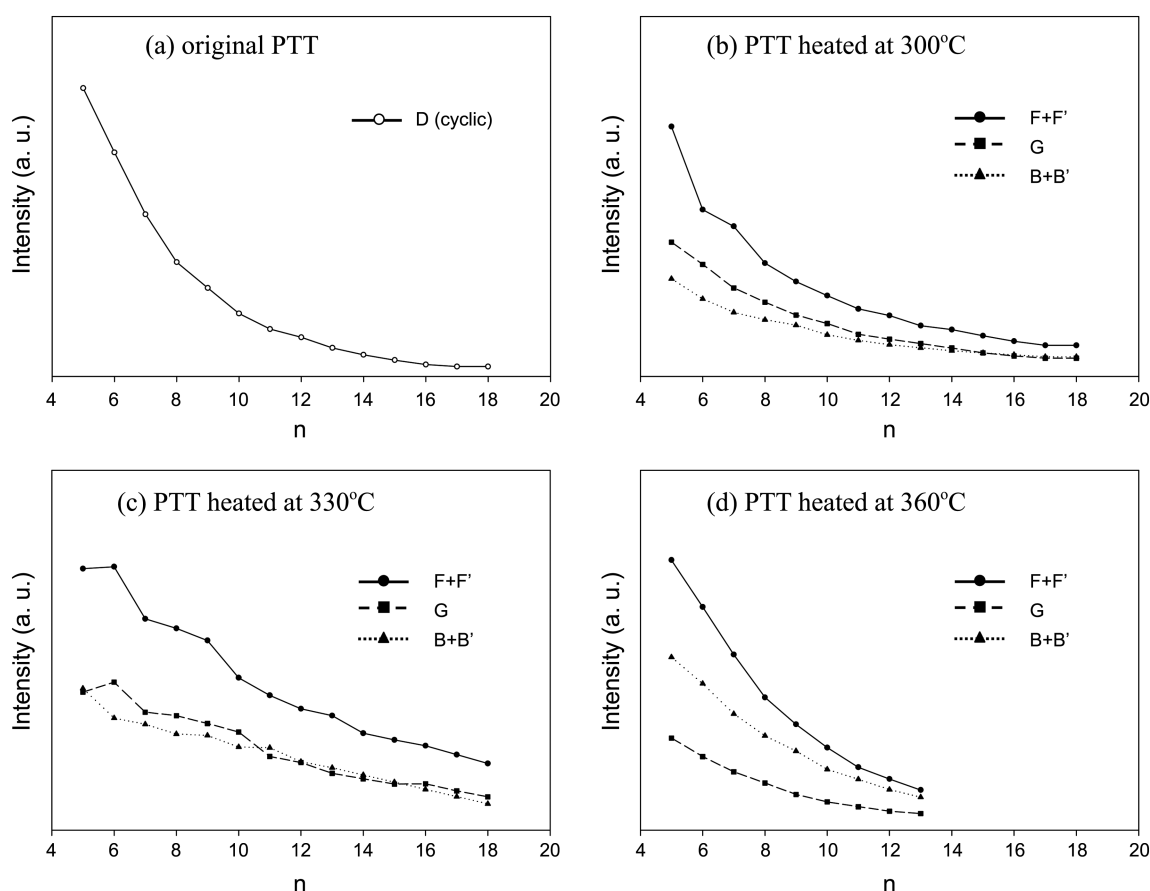
Figure 2. Distribution of relative abundance of the oligomers as a function of number of unit masses n; (a) before thermal degradation, and after heating the sample for 1 hour (b) at 300 °C, (c) at 330 °C, and (d) at 360 °C.
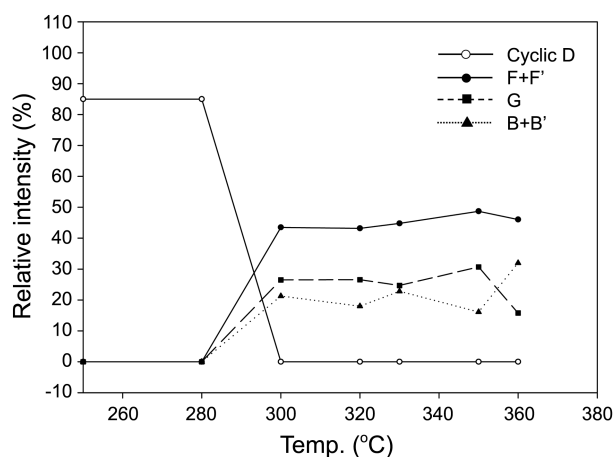

Figure 3. Plot of the normalized abundance of oligomers corresponding to different series of PTT produced from 1 hour heating against the processing temperature: (a) series D, (b) series F, (c) series G, and (d) series B.

A β-CH hydrogen transfer reaction at the allyl terminal of PTT produces allene and carboxyl ended oligomers, which means it provides an extra route to the production of series B. As a matter of fact, the previous study on PBT[17] shows that the amount of carboxyl/carboxyl ended oligomers (series B and B) relative to carboxyl/butenyl (corresponding to series F and F in PTT) or butenyl/butenyl end groups

(corresponding to series G in PTT) is much greater than that obtained for PTT in this study. Moreover, it has been observed that those ratios (corresponding to B/G or B/F in PTT) continuously increase as the heating temperature rises from 280 °C to 320 °C. For the present study, however, the relative intensity of series B is maintained relatively constant up to 330 °C, which implies that the loss of allene (Scheme 1(b)) is not significantly involved in the thermal degradation of PTT in this temperature range (< 330 °C). In other words, the formation of relatively stable butadiene from PBT is more favorable compared to the formation of allene from PTT at this temperature range. At the higher temperature of 360 °C, a distinct increase of the carboxyl/carboxyl ended oligomers (series B) has been observed in this study, whereas the oligomers of series F and G decreased (Figure 1(e) and Figure 3). The standard heat of formations (ΔH_f) of acetylene, allene, and butadiene are 227, 192, and 110 kJ/mol,[20] respectively, which means that formation of acetylene *via* β-CH hydrogen transfer in PET is not very favorable even from a thermodynamic viewpoint.

Taking together the previously reported observations and the discussion so far, the fates of alkenyl end groups seem to depend on both the relative reactivity of the end groups and the reaction temperature. The relative importance of each reaction route depends on the temperature due to the difference of activation energies for the corresponding reaction

path. Therefore, the final product distribution comes out differently according to the degradation temperature. Thermal degradation studies of these polyesters at a wider range of temperatures using MALDI-TOF is currently in progress in our laboratory to obtain more information on the relative importance of each reaction route.

Conclusions

The characterization of thermal degradation products of PTT supplied by DuPont in the temperature range of 250-360 °C were conducted using a linear MALDI-TOF mass spectrometer. Time-to-mass conversion using standard masses enabled us to determine accurate mass values and distinguish all the oligomers bearing different end groups produced from thermal degradation. Above 300 °C, it was found that the thermal degradation of PTT occurs drastically and reaches equilibrium rapidly.

The MALDI-TOF mass spectra of thermally degraded PTT samples showed three main series of oligomers with different end groups, which are carboxyl/carboxyl, carboxyl/allyl, and allyl/allyl. Formation of anhydride containing oligomers, which is known as a characteristic pathway for thermal degradation of PET, was not detected. The thermal degradation products of PTT are well understood exclusively by the β-CH hydrogen transfer reaction, which has been successfully applied to the thermal degradation of PBT. In spite of structural similarities in the three polyesters, the thermal degradation of PTT followed a mechanism very close to that of PBT rather than PET. .

References

1. Traub, H. L.; Hirt, P.; Herlinger, H.; Oppermann, W. *Angew. Makromol. Chem.* **1995**, *230*, 179.
2. Montaudo, G.; Puglisi, C.; Samperi, F. *Polymer Degradation and Stability* **1991**, *31*, 291.
3. Khemani, K. C. *Polymer Degradation and Stability* **2000**, *67*, 91.
4. Dzieciol, M.; Trzeszczynski, J. *J. Appl. Polym. Sci.* **2000**, *77*, 1894.
5. Holland, B. J.; Hay, J. N. *Polymer* **2002**, *43*, 1835.
6. Al-AbdulRazzak, S.; Jabarin, S. A. *Polym. Int.* **2002**, *51*, 164.
7. MacDonald, W. A. *Polym. Int.* **2002**, *51*, 923.
8. Montaudo, G.; Puglisi, C.; Samperi, F. *Polymer Degradation and Stability* **1993**, *42*, 13.
9. Botelho, G.; Queiro's, A.; Liberal, S.; Gijsman, P. *Polymer Degradation and Stability* **2001**, *74*, 39.
10. Bennekom, A. C. M.; Willemsen, P. A. A. T.; Gaymans, R. J. *Polymer* **1996**, *37*, 5447.
11. Manabe, N.; Yokota, Y. *Polymer Degradation and Stability* **2000**, *69*, 183.
12. Koshiduka, T.; Ohkawa, T.; Takeda, K. *Polymer Degradation and Stability* **2003**, *79*, 1.
13. Wang, X. S.; Li, X. G.; Yan, D. *Polymer Degradation and Stability* **2000**, *69*, 361.
14. Wang, X. S.; Li, X. G.; Yan, D. *J. Appl. Polym. Sci.* **2002**, *84*, 1600.
15. Kelsey, D. R.; Kiibler, K. S.; Tutunjian, P. N. *Polymer* **2005**, *46*, 8937.
16. Samperi, F.; Puglisi, C.; Alicatk, R.; Montaudo, G. *Polymer Degradation and Stability* **2004**, *83*, 3.
17. Samperi, F.; Puglisi, C.; Alicatk, R.; Montaudo, G. *Polymer Degradation and Stability* **2004**, *83*, 11.
18. Zimmerman, H.; Kim, N. T. *Polym. Eng. Sci.* **1980**, *20*, 680.
19. Yang, E. K.; Jang, S.; Cho, Y. D.; Choe, E. K.; Park, C. R. *Bull. Korean Chem. Soc.* **2011**, *32*, 477.
20. Benson, S. W. *Thermochemical Kinetics*; John Wiley & Sons: New York, 1976.