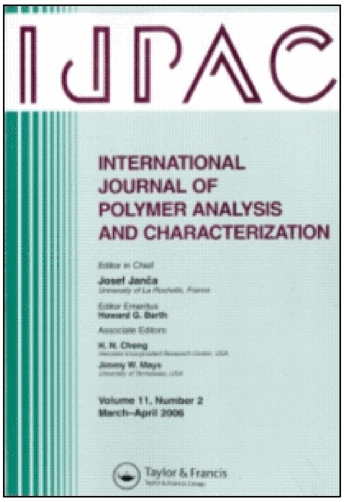

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Evaluation of High Molecular Weight Species Produced during Thermal Degradation of Poly(Vinyl Alcohol)

R. T. Pogue[a][b]; K. L. Ackley[a]; V. Majidi[a]
[a] Department of Chemistry, University of Kentucky, Lexington, KY [b] University of Dayton Research Institute, Dayton, OH

To cite this Article Pogue, R. T. , Ackley, K. L. and Majidi, V.(1997) 'Evaluation of High Molecular Weight Species Produced during Thermal Degradation of Poly(Vinyl Alcohol)', International Journal of Polymer Analysis and Characterization, 3: 3, 193 — 202

To link to this Article: DOI: 10.1080/10236669708032764

URL: http://dx.doi.org/10.1080/10236669708032764

Int. J Polym Anal. Charact.,
1997 Vol 3, pp. 193–202
Reprints available directly from the publisher
Photocopying permitted by license only

Evaluation of High Molecular Weight Species Produced during Thermal Degradation of Poly(Vinyl Alcohol)

R. T. POGUE*,†, K. L. ACKLEY and V. MAJIDI

Department of Chemistry, University of Kentucky, Lexington, KY 40506

(Received 20 November 1995; In final form 26 August 1996)

Thermal decomposition during pyrolysis of poly(vinyl alcohol) (PVA) was investigated using off-line pyrolysis gas chromatography mass spectrometry (Py-GCMS). Observation of a yellow-brown smoke produced when PVA was heated at elevated temperatures indicated that the liquid products may contain highly conjugated chromophores not previously reported. Collection of the resulting pyrolysis mixtures and subsequent analysis by GC-MS confirmed the presence of conjugated, high-molecular-weight compounds in the product mixture. Identification of individual components indicates that the mechanism of degradation involves dehydration followed by random chain scission and cyclization to produce conjugated molecules of moderate to high molecular weight.

Keywords: Thermal degradation, GC-MS, vinyl polymers, poly(vinyl alcohol)

INTRODUCTION

The behavior of polymers during pyrolysis has been a source of significant interest.[1,2] Knowledge of the reactions which occur during thermal degradation may allow for the development of heat resistant materials, as well as identification of possible toxins produced when polymers are heated to elevated temperatures.

---

*Corresponding author.

†Present address: University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0131.

Polymers may pyrolyze by one of three general mechanisms or by some combination of the three. One process, random scission, involves cleavage of the polymer backbone resulting in the formation of large macroradicals. Polymers undergoing random scission exhibit low monomer yields and a rapid decrease in molecular weight during the initial stages of pyrolysis. Degradation may also take place by elimination of low molecular weight fragments other than monomer. This pathway results in significant mass loss as volatile fragments are eliminated from the polymer. The third mechanism, depolymerization, proceeds by the sequential cleavage of the monomer. With this mechanism, molecular weight changes little during the initial stages of pyrolysis, and the reaction proceeds until the polymer is completely depolymerized. Polymers which decompose by depolymerization produce volatile products with high yields of monomer. Considering the above degradation routes, knowledge of the volatile materials produced during pyrolysis may help reveal the mechanism of degradation within the polymeric structure.

Evolved gas analysis (EGA) has proven to be a powerful tool for studying thermal degradation in polymeric systems.[3] Thermal degradation in polyimide films,[4] syterene-isoprene block copolymer,[5] poly(vinylchloride) (PVC),[6] and polybutadiene sulfone[7] have been investigated using EGA.

Previous studies have sought to identify the composition of the pyrolytic products of PVA.[8–10] Water, acetaldehyde, crotonaldehyde, benzaldehyde and phenyl acetate were identified by Futama and Tanaka[10] as pyrolytic products resulting from the degradation of PVA films. Quantitative results, however, were not given. Ettre and Varadi[8] determined that acetaldehyde was the major product from 500–700°C. At 800°C carbon monoxide was the most abundant. They also determined that several low molecular weight compounds (C_n, $n < 4$) were produced during PVA degradation. Ettre and Varadi[8] did not identify any large molecular weight compounds in the evolved gases. Furthermore pyrolysis products evolved at 500°C could not be identified.

The mechanism of thermal degradation of PVC has been studied extensively.[11,12] Using differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetric analysis (TGA), Chatterjee *et al.*[12] determined that thermal degradation of PVC occurs in four steps. The first step toward thermal degradation is an initiation step. The second step is characterized almost exclusively by dehydrochlorination. Next, the polymer undergoes structural reorganization, and the final transition involves structural degradation resulting in the evolution of hydrocarbons. HCl molecules eliminated during dehydrochlorination (stage 2) must evolve from successive monomer units. The sequential elimination of HCl is believed to be a result of the activation of the pendant alpha to an alkene bond. The initiation of the degradation has been suggested to begin at chain ends or at chain defects where head-to-head addition or allylic chlorines are present.[13]

Gilbert and Kipling[9] suggested a degradation mechanism for PVA which is similar to that of PVC. A water molecule is eliminated from the PVA structure resulting in the formation of a carbon-carbon double bond in the polymeric chain. After the initial dehydration, the hydrogen alpha to the double bond and the nearest hydroxyl group become active, allowing for subsequent elimination of water molecules. The degradation could possibly be initiated at the site of chain defects since 1–2% of the chain linkages have been shown to be head-to-head linkages.[14] Such a mechanism would result in a pyrolytic residue with a highly conjugated structure. The formation of conjugated volatiles, however, was not addressed by the Gilbert and Kipling model. In their work, a material balance was determined for the solid, liquid and gaseous products from PVA. Only the evolved gases, however, were given further examination.[9]

Boon[15] determined that off-line pyrolysis gives improved sensitivity by allowing optimization of pyrolysis conditions. During on-line pyrolysis, high molecular weight volatiles may condense before reaching the GC column, therefore high molecular weight components are discriminated. Off-line pyrolysis, however, allows high-molecular-weight volatiles to be recovered before GC-MS analysis.

In this study, evolved gas analysis was performed using off-line pyrolysis gas chromatography mass spectrometry (Py-GCMS) on poly(vinyl alcohol). Results indicate that cyclic, highly conjugated compounds are present in the volatile mixture. The presence of these compounds suggests that revisions are needed in the current model describing thermal degradation in PVA.

METHODS

Instruments

A Hewlett Packard (Palo Alto, CA) 5890 Series II+ GC equipped with a 5972 mass selective detector was employed for GC-MS analysis. To achieve separation, a 30-m Hewlett Packard (Palo Alto, CA) HP-5MS capillary column with 0.25-mm ID, and 0.25-μm film thickness was used. Thermogravimetric analysis was performed on a TA Instruments (New Castle, DE) 2950 high resolution thermogravimetric analyzer. Mass selective detection for TGA-MS was carried out using a quadrupole mass analyzer controlled through software written, in house, using ASYST 4.0 (Asyst Software Technologies, Inc., Rochester, NY).

Materials

Poly(vinyl alcohol) was purchased from Scientific Polymer Products Inc. (Ontario, NY) (2 and 3 × 10^3 g/mol samples (M_w)) and ICN Biochemicals (Aurora, OH) (22, 31, 77, and 100 × 10^3 g/mol samples (M_w)). All samples were used without further purification. TGA samples were placed onto a platinum sample pan and analyzed using the instrumentation described above. Char samples were prepared by placing a known amount of PVA into a ceramic crucible. The crucible was then placed into a preheated ceramic furnace and allowed to char under a bath of N_2 gas. For GC-MS analysis, samples were collected by placing a glass tube bent into a "cold-finger" configuration packed with glass wool into a hole in the furnace door. The glass tube was cooled to 0°C by placing the cold finger into an ice bath. Pyrolysis products were drawn into the tube by applying vacuum and extracted from the glass wool using HPLC grade methanol.

RESULTS AND DISCUSSION

Determination of Appropriate Sampling Temperatures

Optimal charring temperatures were determined using TGA. The thermal decomposition curve resulting from TGA of poly(vinyl alcohol) with an average molecular weight of 2 × 10^3 g/mol and 22 × 10^3 g/mol are shown in Figure 1. The curve shown in inset 1B indicates that higher-average-molecular-weight polymers can be modeled using the lower molecular weight analogue. TGA-MS experiments confirmed the evolution of water and acetaldehyde reported in previous studies.[8] Higher molecular weight species such as crotonaldehyde and benzaldehyde, however, were not observed. In addition, TGA-MS results indicate that those volatile products

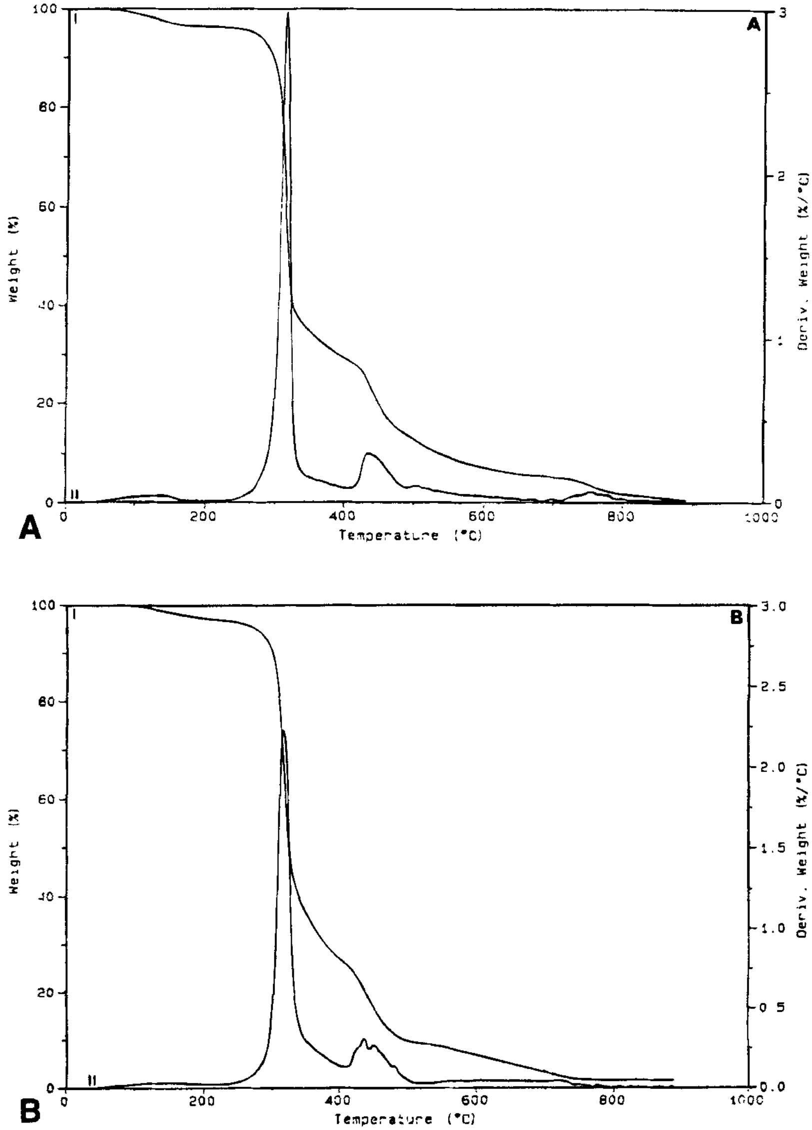

FIGURE 1 (A) High resolution thermogravimetric analysis curve of poly(vinyl alcohol) with $M_w = 2000$ g/mol.; (B) High resolution thermogravimetric analysis curve of poly(vinyl alcohol) with $M_w = 22{,}000$ g/mol.

formed during thermal decomposition are independant of the average molecular weight of the polymer sample.

Liquid thermal decomposition products were collected at three temperatures for this study. The first charring temperature, 325°C, corresponds to the maximum of the first derivative of weight loss. The second sampling temperature, 400°C, occurs between the two weight loss transitions in the TGA. The final temperature, 480°C corresponds to the final weight loss transition. TGA and TGA-MS results indicate that no volatile materials were produced at temperatures less than 300°C. This was confirmed experimentally. Samples collected at temperatures greater than 480°C did not vary significantly from those collected at 480°C.

GC-MS Analysis of PVA Pyrolysates

The total ion chromatogram (TIC) of the liquid pyrolysates evolved at 325°C is shown in Figure 2. Structural identification of these materials indicates several compounds are produced during pyrolysis of PVA that have not been previously identified as products of this reaction. Furthermore, additional steps are occurring in the degradation mechanism that must be addressed.

Identification of the decomposition products at 325°C reveals the presence of aromatic carbonyls, alcohols and ethers. Polycyclic aromatic derivatives are also found in this mixture. Although cyclization of the residues can be predicted by resonance considerations, the presence of carbonyl groups indicates that dehydration is inhibited by delocalization of electrons through extended conjugation. The presence of aliphatic substituents, attached to the aromatics, possibly provides further evidence that the C-O and C = O bonds are stabilized by delocalization due to extended conjugation rather than through aromatic resonance stabilization. In addition, the presence of napthalene derivatives suggests that unknown reaction pathways determine the extent of dehydration prior to cyclization. The pictorial representation shown in Figure 3 contrasts the accepted mechanism[10] with additional steps suggested by our results. This figure indicates that primary degradation, most likely, occurs via the accepted pathway, however, some additional reactions are occurring that need to be considered to give a complete description of the thermal degradation pathway. The literature pathway (Fig. 3A) describes only dehydration and subsequent activation of adjacent hydroxyls leading to extended conjugation. In contrast, our

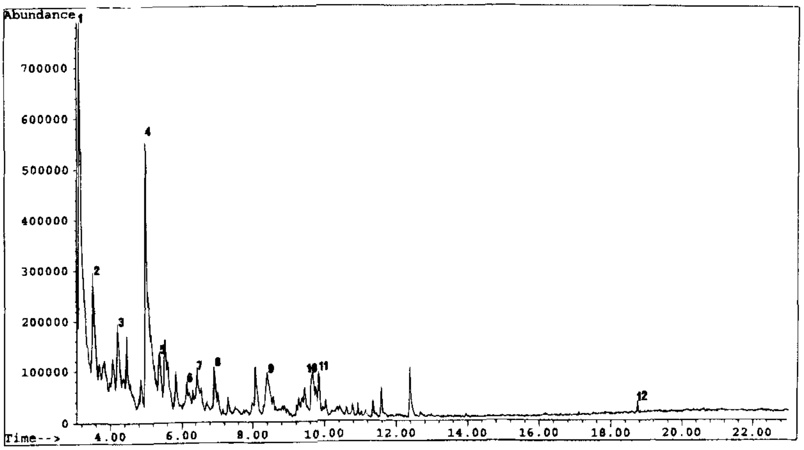

FIGURE 2 Total ion chromatogram of pyrolysis products collected from PVA charring experiment at 325°C temperature program 100 °C (1 min) to 280°C at 10°C/min; (1) phenyl ethanone; (2) methoxy-methyl benzene; (3) 4-methyl benzene methanol; (4) phenyl butanone; (5) 3-phenyl-2-propenal; (6) phenyl butanone; (7) 4-phenyl-3-buten-2-one; (8) dimethyl napthalene; (9) napthalenecarboxaldehyde; (10) 1-napthalenyl ethanone; (11) diphenyl methanone; (12) bis(2-ethylhexyl)-1,2-benzenedicarboxylic acid (present in the blank). Unlabeled peaks have not been unambiguously identified.

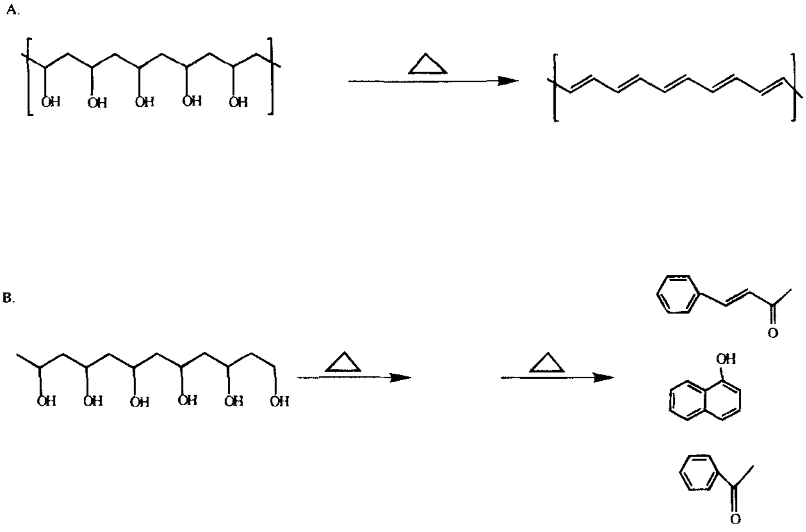

FIGURE 3 Structural comparison of (A) the accepted literature thermal decomposition[9] contrasted with (B) possible additional steps suggested from the experimental results.

results, as indicated in Figure 3B, show cyclization, aromatization, and electron transfer to pendant hydroxyls. It is not possible to confirm, at this point, whether deprotonation occurs as a concerted step along with electron transfer to the oxygen, or rather a cationic intermediate is formed.

As would be predicted by TGA, the total ion chromatogram of semi-volatiles produced at 400°C (Fig. 4) appears to contain the same compound classes as found in Figure 2. In the TGA curve of PVA with $M_w = 2000$ g/mol (Fig. 1A), very little weight loss occurs between approximately 350°C and 425°C. Differential scanning calorimetry confirms that no significant processes occur in this temperature region. Some of the observed differences may be explained by considering the boiling points of the individual components. Phenanthrene (peak 11, Fig. 4) has a boiling point of 340°C. This is slightly above the collection temperature for Figure 3. Changes in relative intensities between Figures 3 and 4 may or may not have similar origins.

As the collection temperature is increased to 480°C, significant changes occur. The total ion chromatogram for the GC-MS analysis of the semi-volatile mixture, collected at this temperature, can be seen in Figure 5. Although many of the early peaks are derived from the same compound classes as found in Figures 2 and 4, a much higher percentage of the peaks

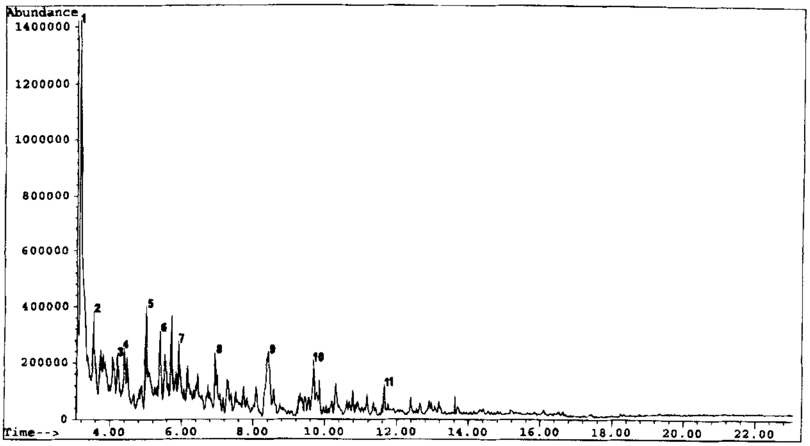

FIGURE 4 Total ion chromatogram of pyrolysis products collected from PVA charring experiment at 400°C; temperature program 100°C (1 min) to 280°C at 10°C/min; (1) 1-phenyl ethanone; (2) methoxy methyl benzene; (3) 4-methyl benzene methanol; (4) napthalene; (5) 3-phenyl-2-butanone; (6) 4-phenyl-2-butanone; (7) 1-methyl napthalene; (8) 1-ethyl napthalene; (9) naphalenecarboxaldehyde; (10) 1-napthaleneyl ethanone; (11) phenanthrene.

are due to derivatives of polycyclic aromatic hydrocarbons (PAH's). In addition, these PAH's contribute structural isomers many of which cannot be unambiguously identified. Peaks (9) and (10) (Fig. 5), for example, correspond to structural isomers of dimethyl napthalene. The region of the chromatogram between twelve and fourteen minutes contains peaks corresponding to substituted-phenanthrene type compounds. The shift of component types from substituted benzenes at 325 and 400°C to substituted PAH's at 480°C indicates an important shift in the degradation reaction. In addition, a relatively large percentage of the identifiable peaks in Figure 5 do not contain oxygen, compared with those found in Figures 2 and 4.

CONCLUSIONS

Off-line pyrolysis GC-MS has proven to be a useful method for studying the semi-volatile products of thermal degradation from PVA. TGA results indicate that very high average molecular weight polymer samples can be

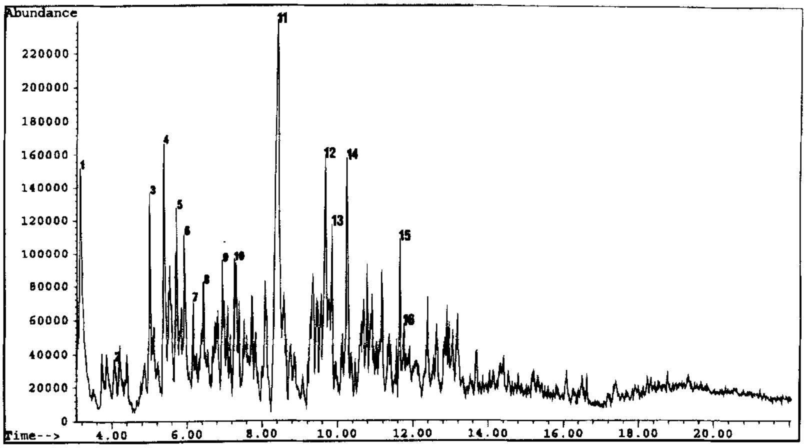

FIGURE 5 Total ion chromatogram of pyrolysis products collected from PVA charring experiment at 480°C; temperature program 100°C (1 min) to 280°C at 10 °C/min; (1) 1-phenyl ethanone; (2) 3-ethyl-phenol; (3) phenyl butanone; (4) 3-phenyl-2-propenal; (5) 1-methyl napthalene; (6) 2-methyl napthalene; (7) phenyl butanone; (8) 4-phenyl-3-buten-2-one; (9) dimethyl napthalene; (10) dimethyl napthalene; (11) napthalene carboxaldehyde; (12) 1-napthenyl ethanone; (13) diphenyl methanone; (14) cyclopentyl phenylmethanone; (15) phenanthrene (16) anthracene.

effectively modeled using a low-molecular-weight analogue. Furthermore, TGA can be used to provide a suitable framework for experimental design in pyrolysis studies. Analysis of the semi-volatile products reveals the presence of aromatic derivatives which can be predicted from the accepted mechanism. Further comparison on the basis of collection temperature can also be made. Product mixtures collected at 325°C and 400°C are very similar. This is consistent with TGA data. The sample collected at 480°C shows marked changes however. Determination of the identities of the components in the mixtures indicates that the accepted thermal degradation mechanism for poly(vinyl alcohol) is not complete.

Acknowledgments

Financial support for this work has been provided, in part, by the Ashland Oil Foundation (RTP), the Stephen Harris Cook Memorial Fellowship (KLA), the KY NASA EPSCoR Program and the NSF EPSCoR Program. The authors would like to thank Professors Meier, Selegue and Toreki for allowing us to use their instruments and for their helpful discussion.

References

[1] Conley, R. T. and Malloy, R. (1970). In: *Thermal Stability of Polymers;* R.T. Conley, Ed.; vol. 1; pp. 223–258 (Marcel Dekker: New York).
[2] Smith, C. G., Smith, P. B., Pasztor, A. J., McKelvy, M. L., Meunier, D. M. and Froelicher, S. W. (1995). *Anal. Chem.*, **67**, 97R.
[3] Brown, M. E. (1988). *Introduction to Thermal Analysis: Techniques and Applications*, 1st ed., pp. 211 (Chapman and Hall: New York).
[4] Arnold, F. E., Cheng, S. Z. D., Hsu, S. L.-C., Lee, C. J., Harris, F. W. and Lau, S.-F. (1992). *Polymer*, **33**, 5179.
[5] Scanlan, F. P. and Houriet, R. (1991). *J. Trace Microprobe Tech.*, **9**, 177.
[6] Ohreach, K.-H., Radhoff G. and Kettrup, A. (1985). *Thermochemica Acta*, **85**, 403.
[7] Yalcin, T., Akbulut, U. and Suzer, S. (1993). *Macromol. Reports*, **A30**, 55.
[8] Ettre, K. and Varadi, P. F. (1963). *Anal. Chem.*, **35**, 69.
[9] Gilbert, J. B. and Kipling, J. J. (1962). *Fuel*, **12**, 249.
[10] Futama, H. and Tanaka, H. (1957). *J. Phys. Soc. (Japan)*, **12**, 433.
[11] Saunders, K. J. (1973). *Organic Polymer Chemistry*, (Chapman and Hall: London).
[12] Chatterjee, N., Sudhapada, B., Palit, S. K. and Maiti, M. M. (1994). *J. Polym. Sci.: Part A: Polymer Chem.*, **32**, 1225.
[13] Hawkins, W. L. (1984). *Polymer Degradation and Stabilization*, (Springer-Verlag: Berlin).
[14] Marvel, C. S. and Denoon, C. E. (1938). *J. Am. Chem. Soc.*, **60**, 1045.
[15] Boon, J. J. (1992). *Int. J. Mass Spectrom. Ion Proc.*, **118/119**, 755.