

Thermal Stability and Decomposition Mechanism of Poly(*p*-acryloyloxybenzoic acid and Poly(*p*-methacryloyloxybenzoic acid) and Their Graft Copolymers with Polypropylene, Part II

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Received 4 June 2007; accepted 12 November 2007

DOI 10.1002/app.27659

Published online 28 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thermal stability and decomposition mechanism of poly(*p*-acryloyloxybenzoic) acid (PABA), *p*-methacryloyloxybenzoic acid (PMBA), and their graft copolymers of PP were studied by differential scanning calorimetry, direct pyrolysis mass spectrometry, and TG/IR system, combined thermogravimetric analyzer, and FTIR spectrometer. The homopolymers and corresponding grafts were found to be stable in nitrogen atmosphere but started to decompose under atmospheric conditions when heated above 230°C. PABA and PAPA-*g*-PP showed a better thermal stability compared to the other polymer. The degradation proceeded predominantly by decomposition of side

groups giving phenol, benzoic acid, hydroxybenzoic acid, carboxylic and carbonyl groups, and by decomposition of phenol into cyclodiene mainly. It was also seen that the degradation path did not greatly change whether the PABA or PMBA were homopolymers or grafted onto PP but the induction temperature of grafted polymers was seen at some 10–20°C higher. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 473–482, 2008

Key words: grafting; *p*-acryloyloxybenzoic acid; *p*-methacryloyloxybenzoic acid; polypropylene; thermal stability and decomposition

INTRODUCTION

The vinyl monomer, *p*-methacryloyloxybenzoic acid (MBA) has been polymerized by free radical initiation by Blumstein et al.^{1–3} The crystallinity and order in atactic poly(*p*-acryloyloxybenzoic acid) (PABA) and poly(*p*-methacryloyloxybenzoic acid) (PMBA) were studied in the later work of Blumstein et al.⁴ These polymers PABA and PMBA were obtained by thermal polymerization of the corresponding monomers at or above the melting points of monomers and by solution polymerization in dimethylformamide. In addition to the formation of crystals with long range lamellar (smectic) order, they reported that bulk polymerization by heating on a hot stage led to an isotropic *p*-acryloyloxybenzoic acid (ABA) melt, which formed a mobile, nematic schlieren texture out of which spherulites grow as the polymerization to PABA progresses.⁴ The development of spherulitic structures was more pronounced for PABA than for PMBA. The formation of mobile

nematic mesophase and the smectic phase were also reported by Menczel and Wunderlich⁵ in the study of phase transitions of PABA, in which the nematic mesophase was produced by melting of the crystals.

The polymerization of *p*-ABA was later reinvestigated by Menczel et al.⁶ in another study to resolve the questions such as the nucleation of the mesophase and transformation of the mesophase into solid by parallel use of optical microscopy and quantitatively thermal analysis. The research led to, however, the discovery of a much more complicated reaction instead of simple vinyl polymerization. It was assumed that the observed mesophase was not connected with *p*-ABA or PABA. The polymer was not involved in mesophase formation, but it seemed to cause solidification of spherulites, schlieren texture, and isomorphous material. It was proposed that after melting of ABA, which produced an isotropic phase, acidolysis produces acrylic acid and oligomers of poly(*p*-oxybenzoate), POB, and the oligomers of POB were the root of the mesophase formation. Polymerization of ABA without oligoester formation gave no intermediate mesophase.⁶

In our previous manuscript the polymerization and grafting process of both monomers were discussed.⁷ The monomers were polymerized in bulk at high *T*, and using an initiator (dicumyl peroxide) and also γ -irradiation in solution. The grafting was

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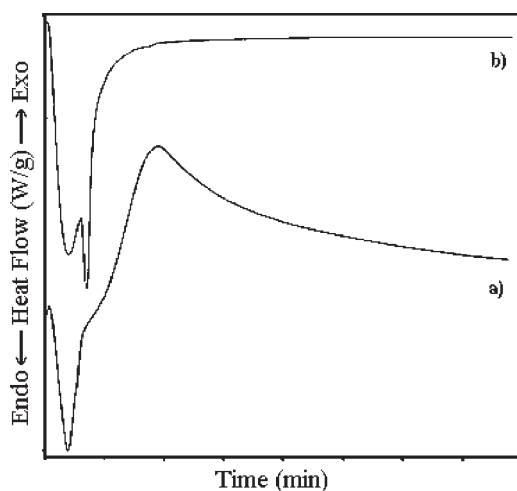


Figure 1 Isothermal experiments of DSC studies at 200°C for 15 min, of (a) PABA-g-PP (21% PABA) in air, (b) PABA-g-PP (7% PABA) in nitrogen.

carried out on irradiated powder PP, which contained active peroxides ready to initiate a radical reaction at various monomer and PP compositions and four different temperatures. Accordingly, it appears that thermal stability is also important for the processing not only homopolymers but also of the graft copolymers, PABA-g-PP and PMBA-g-PP. Therefore, it becomes necessary to clarify the thermal behavior of the polymers at the temperatures that the mesomorphic state is observed and to comprehend the optimum conditions at which the polymers are stable for processing.

In this work, thermal stability and decomposition mechanism of PABA, PABA-g-PP, PMBA, and PMBA-g-PP samples were studied by differential scanning calorimetry, direct pyrolysis mass spectrometry, and TG/IR system, which combined thermogravimetric analyzer and FTIR spectrometer.

EXPERIMENTAL

Materials

Poly(*p*-acryloyloxybenzoic acid), PABA was obtained by γ -irradiation induced polymerization and by bulk polymerization with dicumyl peroxide (DCP at 202°C) initiation, and the graft copolymers PABA-g-PP and PMBA-g-PP were produced by bulk melt polymerization as described in previous work.⁷ Poly(*p*-methacryloyloxybenzoic acid), PMBA was obtained only by bulk melt polymerization as it was reported in literature.⁴

Characterizations of the products

Isothermal DSC analyses of the polymers, PABA and PMBA, and the graft copolymers PABA-g-PP and

PMBA-g-PP were carried out with a TA-DSC 910S differential scanning calorimeter (New Castle, DE), under nitrogen atmosphere and in air, at constant temperature of 200°C for 15 min. Sample size was varied between 5 and 10 mg.

MS analyses of PABA, PABA-g-PP, PMBA, and PMBA-g-PP samples were carried out by a Hewlett-Packard 5973 Mass Spectrometer (Ringoos, NJ) equipped with metallized gold quadrupole mass filter and coupled with direct insertion probe. The samples were heated at a rate of 10°C/min between room temperature and 450°C. The mass data recorded under electron impact ionization energy of 70 eV at a scan rate of 2 scan/s and in the mass range of 16–600 amu.

TG/IR analyses of PABA, PABA-g-PP, PMBA, and PMBA-g-PP samples were carried out by a TG/IR system, which combined with a Perkin Elmer Pyris 1 TGA thermogravimetric analyzer and a Perkin Elmer Spectrum One FTIR spectrometer (Waltham, MA) (Central Research Laboratory, METU). Sample of about 10 mg were pyrolysed in the TG analyzer, and the evolved gases were led to the Perkin Elmer Spectrum One FTIR spectrometer directly through a connected heated gas line to obtain FTIR spectra of the gaseous pyrolysis products. The thermogravimetry test was performed in the air and nitrogen atmosphere in the temperature range from 25 to 600°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Beside the smectic form of PMBA^{3,4} and PABA,⁴ monoclinic and nematic phases were also reported for PABA,^{4,5} where mobile nematic mesophase was produced by melting of the crystals. These works, however, state some conflicting results on the thermal behavior of both polymers. One of them⁶ mentioned a fast decomposition of PABA without given any fur-

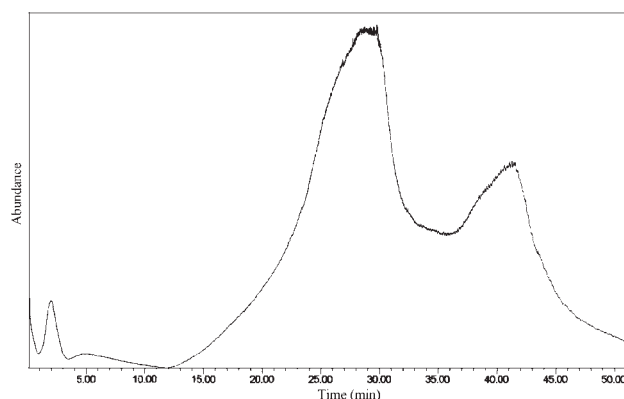


Figure 2 The total ion current of the pyrolysis of PABA (initiated by DCP at 202°C) with the heating rate of 10°C/min.

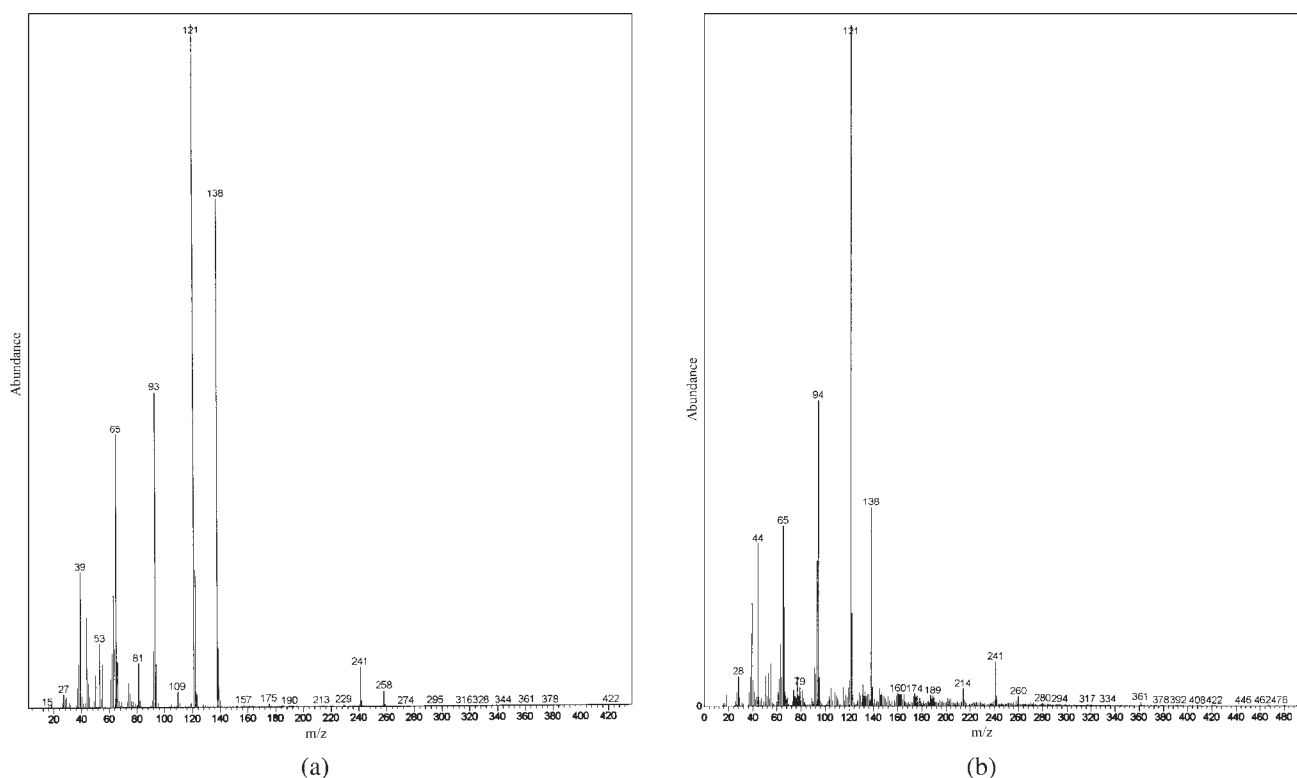


Figure 3 The mass spectra of PABA (initiated by DCP at 202°C) taken at (a) 29.1 and (b) 41.5 min, with the heating rate of 10°C/min.

ther information. There exists no study on the decomposition mechanism of both PABA and PMBA. Roman et al.⁸ studied the thermal degradation of poly(*o*-methacryloyloxybenzoic acid) by dynamic and isothermal thermogravimetric analysis and infrared spectroscopy. The degradation was explained by release of salicylic acid from isotactic sequences and by the formation of six membered cyclic structures of the glutaric anhydride type in the temperature range 140–220°C. At higher temperatures loss of salicylic groups to form polyanhydride compound (220–330°C), and degradation of the main chain (above 330°C) were reported. Without MS analysis, however, it is questionable to suggest these results.

The thermal properties of graft copolymers of PABA-*g*-PP and PMBA-*g*-PP were presented previously.⁷ We have detected that PABA and PMBA started to decompose before completing the melting endotherm in grafted samples. A simple test was carried out with PABA to experience the reported nematic mesophase by polarizing microscope with hot stage. A small amount of PABA was put in a small flattened glass tube, sealed under vacuum, and heated to above the melting (230°C). No mesomorphic behavior was seen in the melt state. In addition, sublimation products covered the walls of the tube. These were apparently possible decomposition products of

PABA. Furthermore, the isothermal experiments of DSC studies on PABA-*g*-PP samples were carried out at the temperature 200°C for 15 min. Although there was not any heat flow in the experiments carried out in nitrogen atmosphere, an endothermic change was seen when it was performed in the presence of air at the same isotherm temperature, 200°C, which was well below the melting point of PABA, Figure 1. This

TABLE I
The Characteristics of the Peaks Present in the Pyrolysis Mass Spectra Corresponding to the Degradation Products of PABA Produced by Initiation of DCP Recorded at 29.1 min (291°C) with the Heating Rate of 10°C/min

m/z	Assignment	m/z	Assignment
27	C ₂ H ₃	81	C ₄ HO ₂ , C ₆ H ₉
38	C ₃ H ₂	92	C ₆ H ₅ O—H
39	C ₃ H ₃	93	C ₆ H ₅ O
44	CO ₂	94	C ₆ H ₅ OH
45	CO ₂ H	109	C ₂ H ₂ COC ₂ H ₃ CO, C ₂ H ₂ CO ₂ C ₃ H ₃
53	C ₂ HCO	121	C ₆ H ₅ CO ₂
55	C ₂ H ₃ CO	122	C ₆ H ₅ CO ₂ H
63	C ₅ H ₃	138	C ₆ H ₅ CO ₂ HOH
64	C ₅ H ₄	139	(C ₂ H ₃ CO ₂) ₂ CH, C ₂ HCO ₂ C ₂ H ₂ CO ₂
65	C ₅ H ₅	241	C ₂ HCO ₂ C ₆ H ₅ C ₂ HCO ₂ C ₂ H ₂
66	C ₅ H ₆	258	C ₂ HCO ₂ C ₆ H ₄ CO ₂ C ₂ HCO ₂ , CHCO ₂ C ₆ H ₅ C ₂ H ₂ CO ₂ C ₂ H ₂ CO

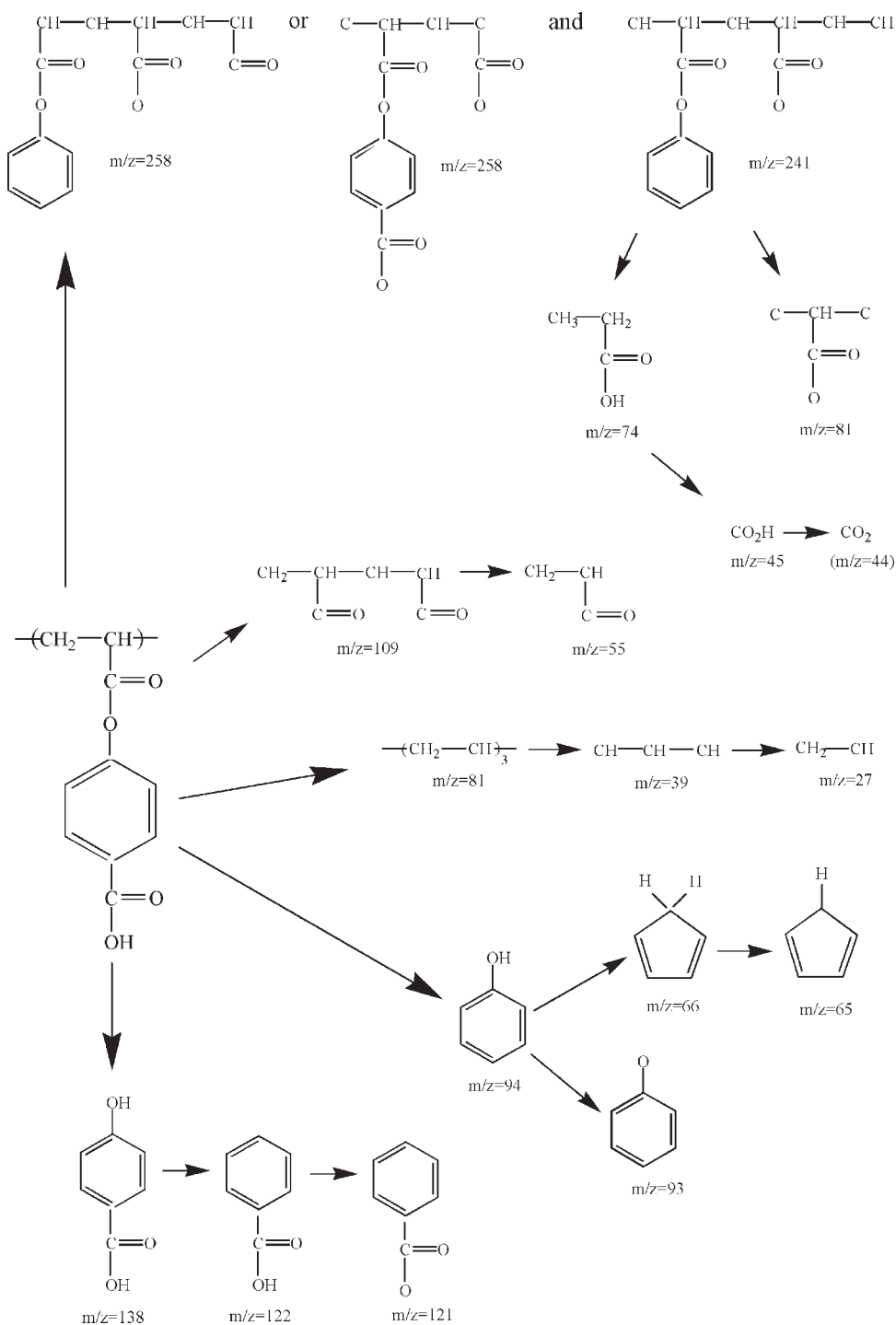


Figure 4 Possible degradation mechanism of PABA based on the MS and FTIR results.

showed that PABA was thermally rather stable in nitrogen atmosphere at 200°C [Fig. 1(b)], but displayed obvious decomposition when it was done in the presence of air [Fig. 1(a)]. A similar observation was found to be valid for PMBA almost at the same temperature. After this preliminary study aforementioned the homopolymers were studied first then their corresponding grafts.

Characterization of PABA and PABA-g-PP by MS and TG/IR

The thermal degradation of PABA produced by DCP initiator starts at early times of the heating, and takes place in a broad temperature range as measured in MS, Figure 2. The MS spectrum of the degradation products (on the total ions current, TIC) were taken at 29.1 (291°C) and 41.5 min (415°C) with the heating

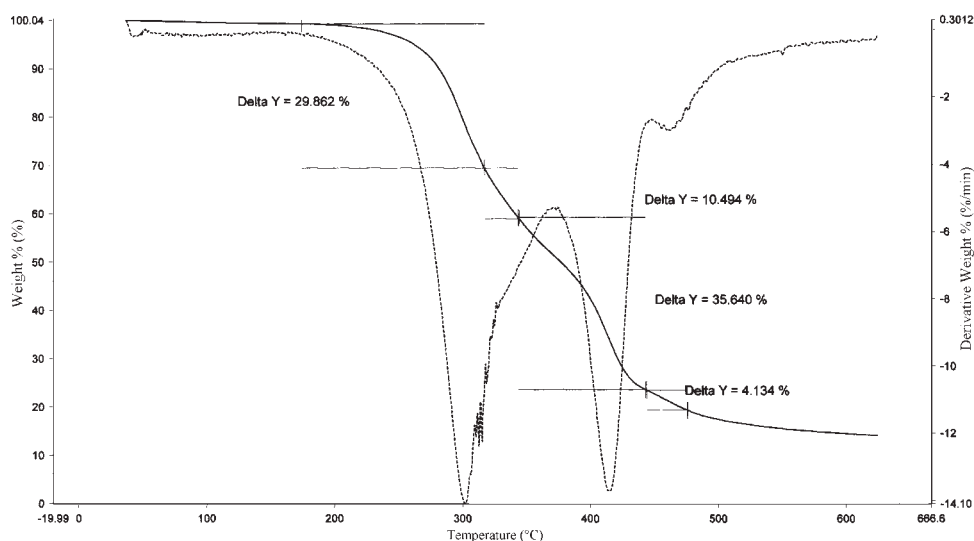


Figure 5 TGA thermogram of PABA produced by DCP initiator taken with the heating rate of 20°C/min in air.

rate of 10°C/min, Figure 3(a,b). The degradation products with m/z values of 27, 39, 44, 53, 65, 74, 81, 93, 109, 121, 138, 241, and 258 were mainly observed at the time scale of 29.1 min (291°C). The corresponding possible products derived from MS spectrum were given in Table I. The same degradation peaks continued to appear in the spectrum taken at 41.5 min but with lower intensity, Figure 3(b). Therefore, it can be easily stated that the same products were present even at high temperatures. These results showed that PABA broke up mainly by forming hydroxybenzoic acid, benzoic acid, phenol, carboxylic and carbonyl group containing compounds. The decomposition of phenol into cyclodiene was also observed clearly. The small peaks observed at higher temperature, 415°C, are probably due to the degradation of the main chain of PABA. Then, a possible degradation mechanism was proposed on the basis of these results as given in Figure 4.

Thermogravimetric analysis of PABA produced by DCP initiator, in the presence of air, revealed that the weight loss due to decomposition started above 200°C and continued to 450°C with showing a step around 400°C, Figure 5. The decomposition gas products were also simultaneously analyzed by FTIR spectrometer combined with the thermogravimetric analyzer. The same decomposition products were observed at all stages of heating, Figures 6 and 7. No extra IR absorption was observed with increasing temperature where the temperature was increased from 288°C (Fig. 6) to 394, 404, and 454°C (Fig. 7) but increased the intensity of absorption peaks in FTIR spectra. These results supported the decomposition products observed in MS analysis. In general IR absorption peaks were found to be very sharp and could be easily assigned to some major characteristic

groups. The formation of carbon dioxide was detected with the C=O stretching bands at 2361 cm^{-1} at early times, and it appeared in all stages of heating. The other absorption bands observed due to the decomposition started at about 200°C. In the FTIR spectrum taken at 200°C phenolic and carboxylic O—H stretching bands at 3643 and 3582 cm^{-1} , aromatic C—H stretching band at about 3050 cm^{-1} , carboxylic C=O stretching band at 1756 cm^{-1} , aromatic C=C stretching band at about 1606 and 1512 cm^{-1} , phenolic O—H in plane bending at about 1360 cm^{-1} , and C—O stretching bands at about 1264, 1187, 1163 and 1078 cm^{-1} corresponded to phenol, benzoic acid, and *p*-hydroxybenzoic acid, respectively.

The decomposition mechanism of PABA produced by γ -radiation was found to be identical to PABA initiated by DCP with the first maximum of the total ion current giving almost the same degradation products. However, it was observed on the total ion current that the decomposition took place at earlier times.

Furthermore, the decomposition of PABA tested under nitrogen atmosphere showed the same decomposition mechanism in TGA experiments but it started at higher temperatures, above 250°C, with respect to that of observed in the presence of air.

We found no considerable difference in degradation products in the first maximum of the total ion current for PABA-*g*-PP samples in comparison to pure homopolymer PABA. This shows that at early stages the degradation proceeds predominantly by breaking up of grafting polymer PABA. Carboxylic, aromatic, and carbonyl groups rather than that of the main chain of PP, and the decomposition of the phenol formed during degradation into cyclodiene were still observed clearly. TIC and the mass spectrum taken at 25.4 min (254°C) were given in

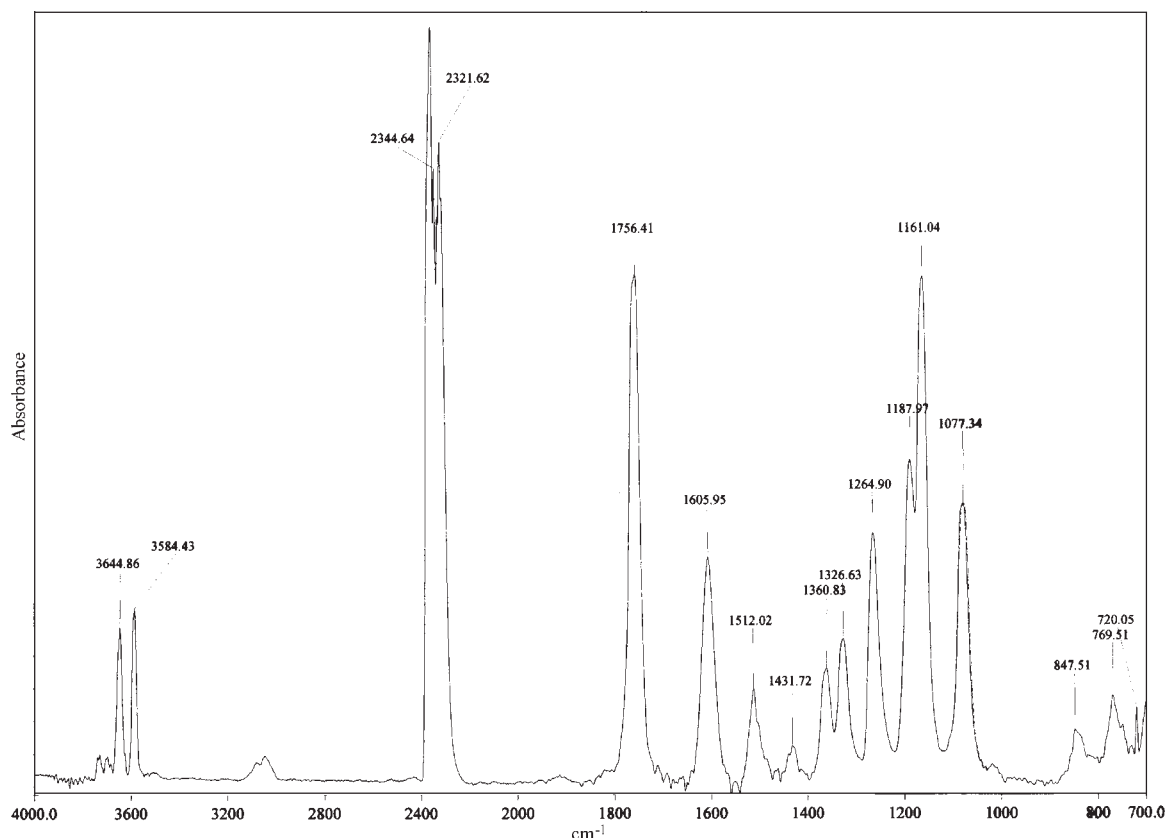


Figure 6 The FTIR spectrum of the gaseous products formed at 14.4 min (288°C) of the TGA heating of PABA with the rate of 20°C/min in air.

Figures 8 and 9. Furthermore, the mass spectrum became more complicated at 41.8 min (418°C) as a result of combined decomposition of main chain of PP and grafted polymer PABA, Figure 10. Indeed, after 35 min (350°C) the higher intensity in abundance compared with Figure 2 indicated the main backbone PP started to break apart.

TGA analyses of the PABA-g-PP revealed the decomposition mechanism observed in MS analysis. The similar decomposition and trend of TGA figure were observed in the samples as seen in homopolymer PABA. The decomposition temperature in air was found about 240°C while under nitrogen atmosphere PABA-g-PP started to decompose at a higher temperature 270°C. In both cases the thermal degradation of PABA appeared to be retarded when it was grafted. This may be attributed to the protective activity of PP.

Characterization of PMBA and PMBA-g-PP by MS and TG/IR

The thermal degradation of PMBA and PMBA-g-PP samples, in analogous manner to PABA, started at early times of heating, and continued in a wide range of temperature. The degradation products with the m/z values of 39, 44, 53, 65, 74, 81, 93, 110,

121, and 138 were commonly observed in almost all mass spectra. This also indicated that the degradation occurred prevalently by decomposition of side groups. The total ion current of pyrolysis of PMBA and the peaks of the degradation products at 27.3 minutes (273°C) were given in Figures 11 and 12, respectively. Comparing TIC of PABA (Fig. 2) with

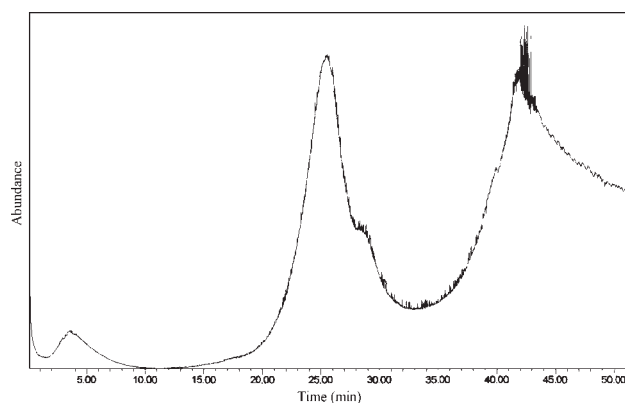


Figure 7 The FTIR spectrum of the products formed at 19.7, 20.2, and 22.7 min (corresponding to 394, 404, and 454°C) of the TGA heating of PABA with the rate of 20°C/min in air.

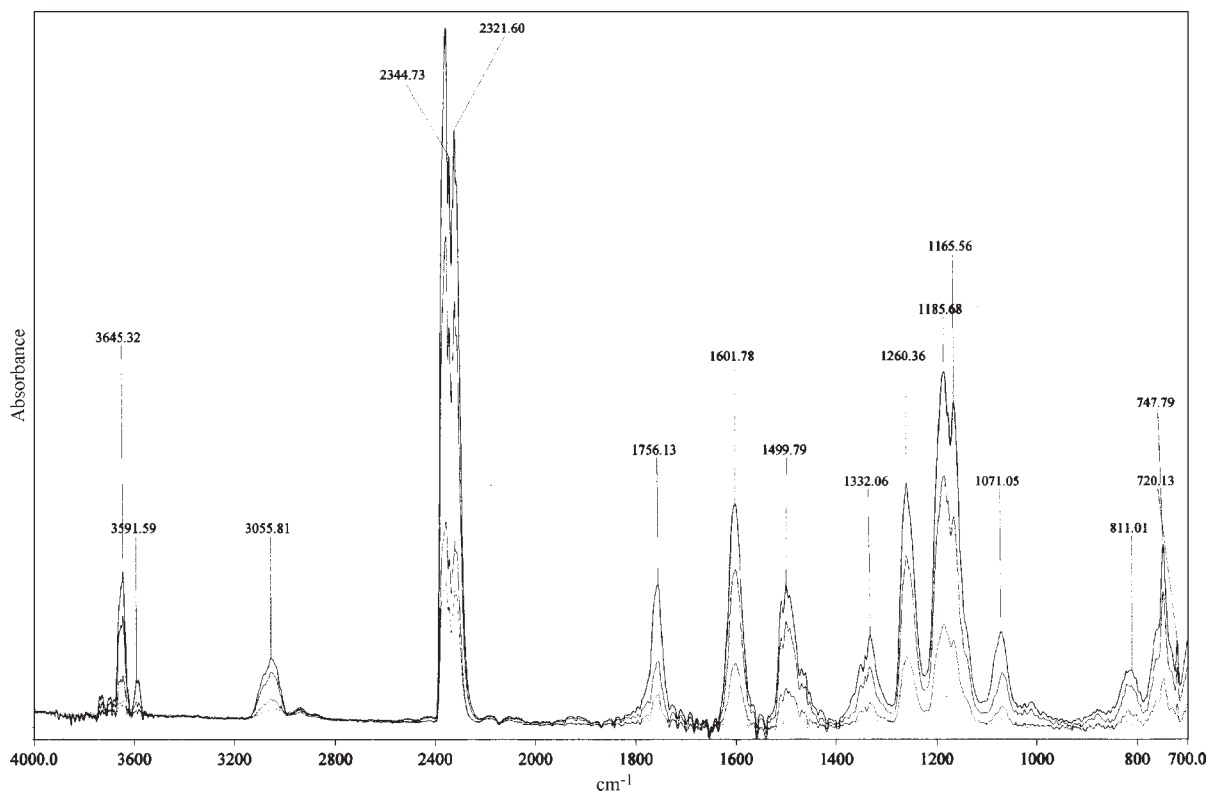


Figure 8 The total ion current during the pyrolysis of PABA-g-PP (47.5% PABA) with the heating rate of 10°C/min.

TIC of PMBA (Fig. 11) they were basically seemed to be the same but PMBA showed a sharper TIC, and earlier and faster decomposition peak, especially the

second peak. Conclusively, this indicates that degradation starts at lower temperatures in PMBA but the same products were produced.

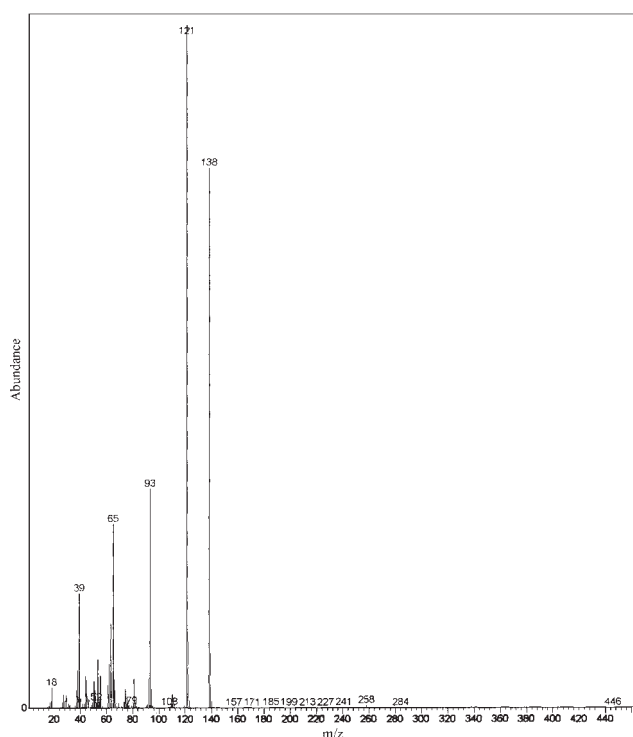


Figure 9 The mass spectrum of PABA-g-PP (47.5% PABA) taken at 25.4 min (254°C).

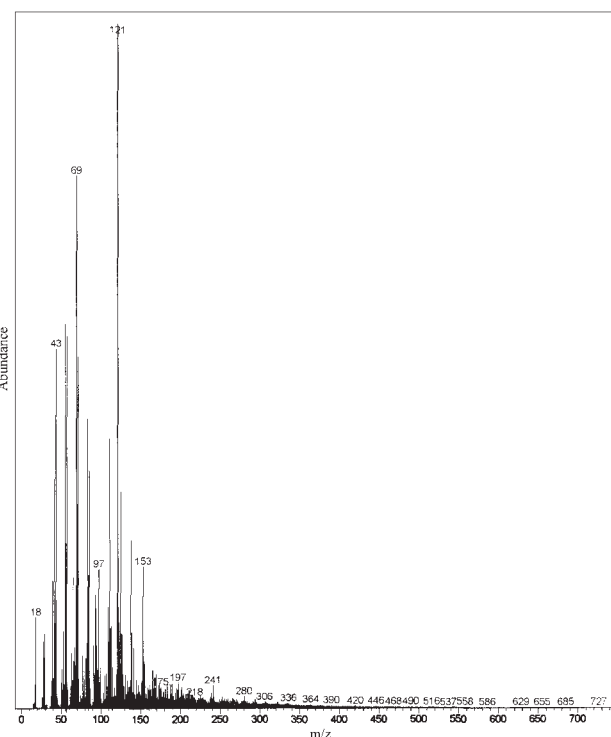


Figure 10 The mass spectra of PABA-g-PP (47.5% PABA) taken at 41.8 min (418°C).

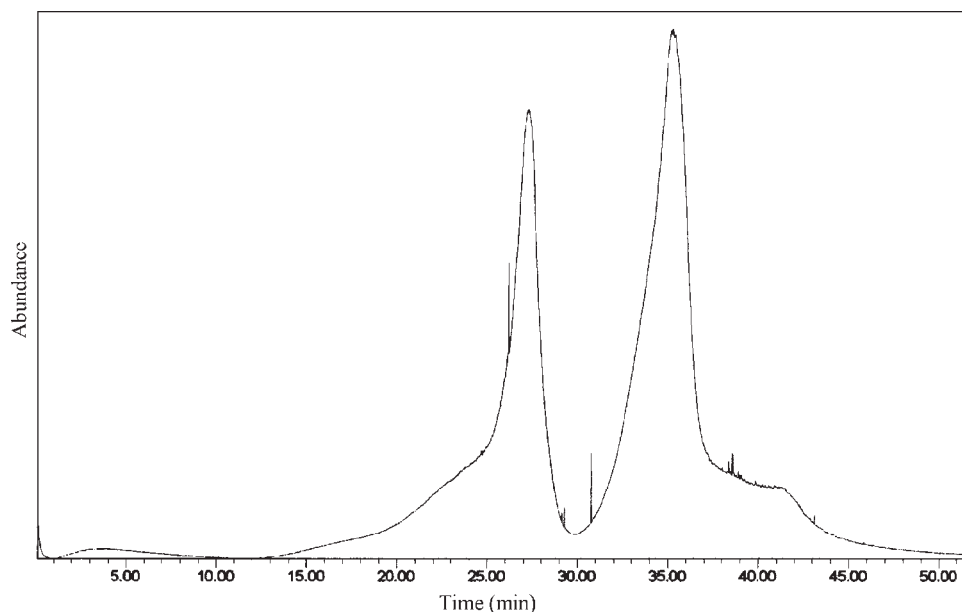


Figure 11 The total ion current of the pyrolysis of PMBA taken with the heating rate of $10^{\circ}\text{C}/\text{min}$.

Thermogravimetric analysis of PMBA-g-PP carried out in the presence of air, which was found to be distinctly different compared with that of PABA and its graft (Fig. 5) was given in Figure 13. The first weight loss was seen above 200°C and followed by two steps with the weight losses 8% at about 306°C and 17.5% at about 360°C , and the material showed very fast weight loss due to completion of the decomposition. However, FTIR analysis of the gas decomposition products of PMBA indicated that at initial stage of decomposition the products similar to those observed in PABA, which was verified by

the absorption bands corresponding to phenol, benzoic acid, hydroxybenzoic acid, and carbon dioxide in the FTIR spectra. Furthermore, the decomposition products observed in MS spectra were also supported by FTIR spectra of the products formed in thermogravimetry. In addition to the bands mentioned previously, C—H stretching bands of CH_2 and CH_3 were detected at about 2966 and 2925 cm^{-1} . The alkenyl C=C stretching band at 1649 cm^{-1} and C—H out of plane bending band at 890 cm^{-1} corresponding to cyclo diene observed in MS spectra with the molecular weight of 65 were

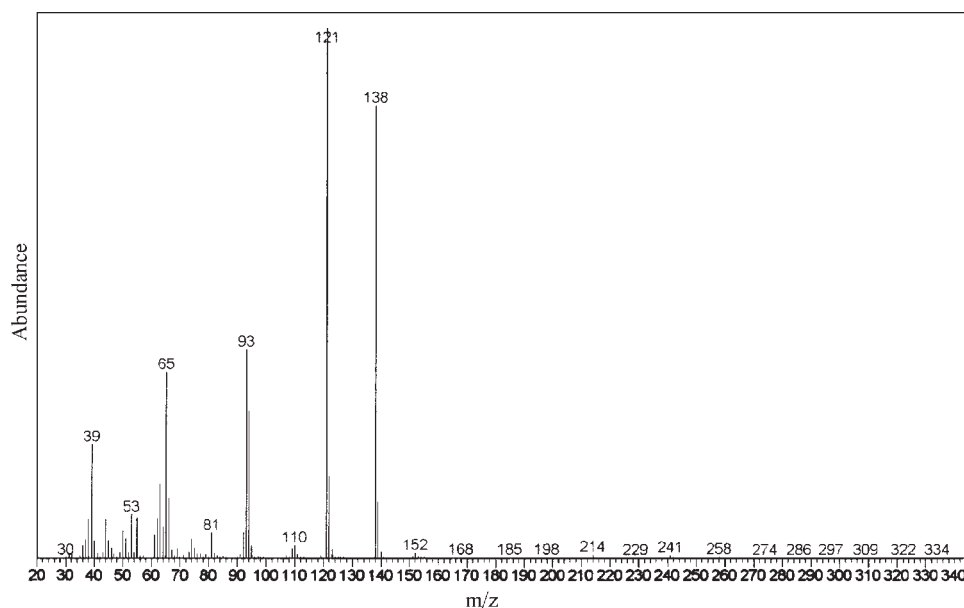


Figure 12 Mass spectrum of PMBA taken at 27.3 min (273°C), with the heating rate of $10^{\circ}\text{C}/\text{min}$.

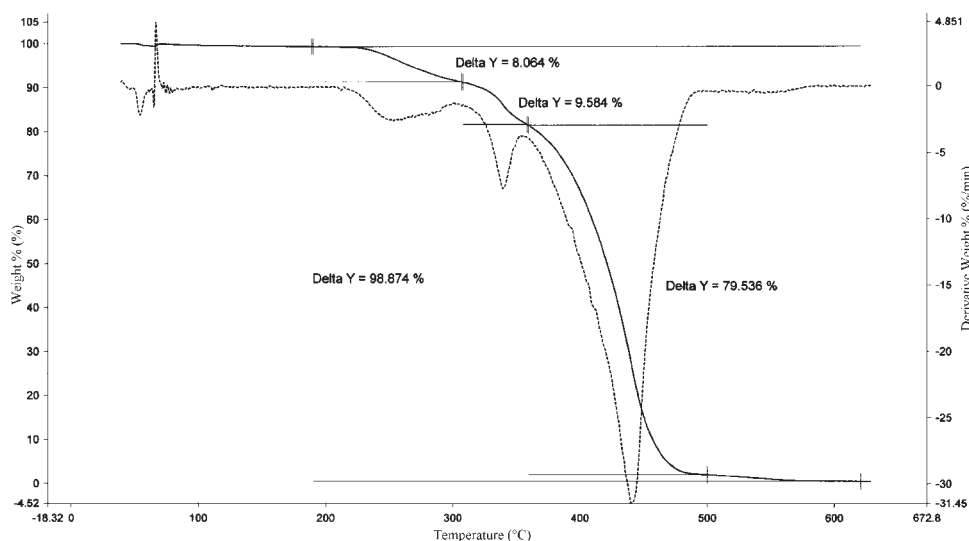


Figure 13 TGA thermogram of PMBA-g-PP (30.68% PMBA) taken with the heating rate of 20°C/min in air.

detected above 340°C. As the temperature increased above 340°C, however, undefined peaks started to form beside the observed peaks. It seemed that at higher temperatures the phenol and carboxylic acid formed by decomposition diminished, and then after 400°C almost only the groups of CO₂, CH₂, and CH₃ were detected indicating that the polymer completely pyrolysed, Figure 14.

The PMBA-g-PP was also tested in nitrogen. The results indicated that the decomposition took place at slightly higher temperatures about 15°C, but

almost with the same mechanism and trend observed in air.

CONCLUSIONS

MS and TG/IR characterization revealed that PABA and PMBA and their graft coproducts of PP were very sensitive to thermal degradation. At early stages the thermal degradation proceeds predominantly by breaking up of the side groups into carbonyl, carboxylic, and aromatic groups, and decom-

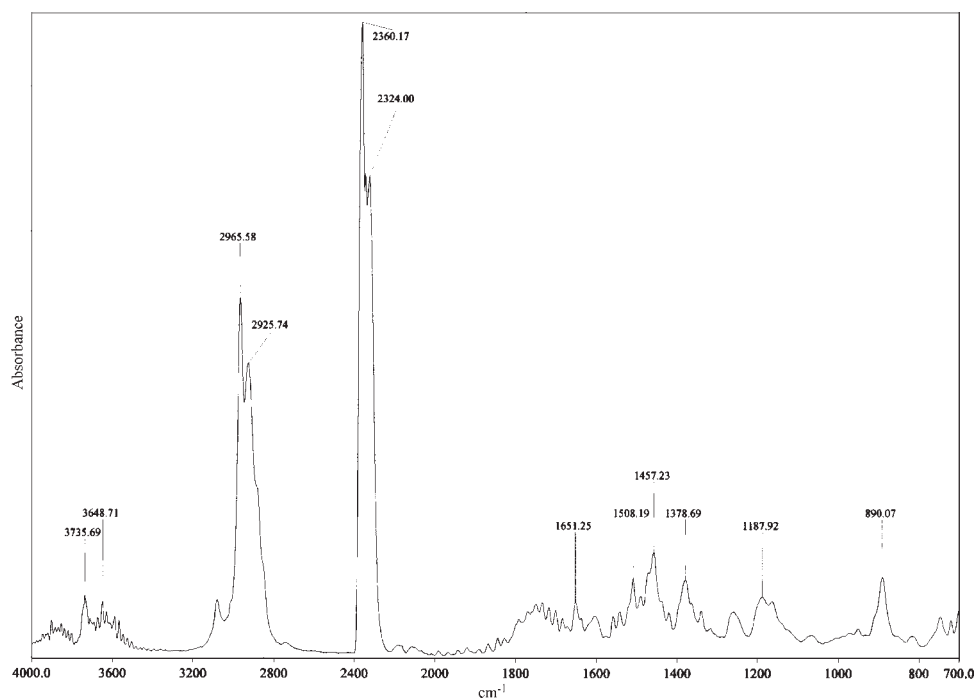


Figure 14 FTIR spectrum of the products formed during the heating of PMBA-g-PP (30.68% PMBA) taken at 19.8 min (396°C) with the rate of 20°C/min in air.

position of the phenol into cyclodiene. At high temperatures (prolong time of heating) smaller hydrocarbon peaks also started to appear in lower m/z regions because of decomposition of main chain of PABA and PMBA, and PP of the PABA-*g*-PP or PMBA-*g*-PP decomposition.

The degradation behavior of these graft polymers are particularly important because a high temperature processing may inevitably cause an extensive degradation of the grafted polymers of PABA and PMBA. Furthermore, both homo and grafted polymers were seemed to have better stability under a neutral atmosphere, that is, nitrogen, compared to air. Indeed, when heated in air showed sudden color change (yellowing then darkening to brown) close to their melting point. In addition in the second run of DSC studies we did not observe any indication of T_m of grafted polymers if the temperature was increased over the melting point of PABA or PMBA in the first run.⁷ Therefore, it could be stated that the presence of oxygen strongly fastens the decomposition of these polymers but the aliphatic backbone, PP, might act as a protective material especially become very useful during melt processing. Further-

more and finally the reported nematic mesophase of PABA⁵ conflicts with its degradation behavior studied in this work since PABA was found to decompose when heated close or just above its melting point.

The authors thank Prof. Dr. J. Hacaloglu for providing her laboratory for the MS analyses and METU Central Research Labs for the TGA-FTIR studies.

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