Available online at www.sciencedirect.com
ScienceDirect
J. Anal. Appl. Pyrolysis 79 (2007) 323–326
JOURNAL of ANALYTICAL and APPLIED PYROLYSIS
www.elsevier.com/locate/jaap

Precise compositional analysis of liquid crystalline aromatic polyesters containing aromatic amide linkages by thermally assisted hydrolysis and methylation-gas chromatography

Hajime Ohtnai [a,*], Noriaki Sugimoto [b], Michiko Hirano [b], Toshiaki Yokota [c], Kohichi Katoh [c]

[a] *Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*
[b] *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan*
[c] *Polyplastics Co., Ltd., Fuji 416-8533, Japan*

Received 22 June 2006; accepted 9 November 2006
Available online 18 December 2006

Abstract

Multi-component liquid crystalline aromatic polyesters (LCPs) containing 4-aminophenol (PAP) units to form amide linkages were characterized by thermally assisted hydrolysis and methylation-gas chromatography (THM-GC). Under the given THM conditions (300 °C; in the presence of 25 wt% tetramethylammonium hydroxide in methanol), the aromatic amide linkages in the LCP chains were only methylated but hardly cleaved, whereas the ester bonds almost quantitatively decomposed into methyl esters and methyl ethers. Thus dimeric and trimeric products consisting of PAP and another monomer unit linked through methylated amide linkage(s) were observed in the THM chromatograms along with dimethyl derivatives of the monomer units other than PAP. The compositions of the LCP samples containing PAP units were then determined from the relative peak intensities observed in the THM chromatograms, and showed quite good agreement with the original monomer compositions in feed with superior reproducibility; less than 1% relative standard deviation.

Keywords: Thermally assisted hydrolysis and methylation; THM-gas chromatography; Liquid crystalline aromatic polyester; Tetramethylammonium hydroxide; Amide linkage; *p*-Aminophenol; Compositional analysis

1. Introduction

Fully aromatic liquid crystalline polyesters (LCPs) have been recognized as amongst the most promising high performance engineering plastics, especially in the fields where ever increasing thermal stability and mechanical strength required. Commercially available LCPs are usually copolymer type including 4-hydroxybenzoic acid (PHB) and 2-hydroxy-6-naphthoic acid (HNA) units to modify the processability [1]. Precise compositional analysis is often required for quality control. However, not only ordinary spectroscopic analytical methods such as NMR and IR but also conventional pyrolysis-gas chromatography (Py-GC) have their shortcoming for providing sufficient information on LCPs as they are intractable materials.

On the other hand, thermally assisted hydrolysis and methylation-gas chromatography (THM-GC) using tetramethylammonium hydroxide (TMAH) [2] was successfully applied to the characterization of the LCP samples [3–5]. The THM reaction of LCP under the optimized conditions results in the almost quantitative formation of the methyl derivatives of the constituent units in the copolyesters, which enables us to carry out rapid and precise compositional analysis of the LCP samples [3,4]. Moreover, the trace amounts of branching and cross-linking structure in LCPs formed during its thermal treatment were also characterized in detail by this technique [5].

Recently, LCPs containing amide linkages as well as ester bonds, which are prepared by the copolymerization of 4-acetylaminophenol (APAP), have been developed as the superior polymeric material with higher mechanical strength induced by the additional hydrogen bonding at the amide linkages [6,7]. In this work, the THM reactions of the LCPs with amide linkages were briefly examined and then their

---

* Corresponding author. Tel.: +81 52 735 7911; fax: +81 52 735 7911.
E-mail address: ohtani.hajime@nitech.ac.jp (H. Ohtnai).

0165-2370/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jaap.2006.11.003

precise compositional analysis was achieved on the basis of the observed THM chromatograms.

2. Experimental

2.1. LCP samples

The LCP samples were prepared in laboratory scale through successive acetylation/polycondensation of the corresponding monomeric compounds [6,7]. Scheme 1 shows the formation pathway of the LCP sample. Here five kinds of monomeric materials such as HBA (ca. 90 g), HNA (ca. 120 g), isophthalic acid (IA) (ca. 70 g), 4,4′-dihydroxybiphenyl (BP) (ca. 0–60 g) and APAP (ca. 15–70 g) were mixed with acetic anhydride (ca. 200 g) and potassium acetate (23 mg) as a polymerization catalyst, and heated at 140 °C for 1 h and then raised to 200 °C in 1 h under nitrogen atmosphere in a sealed vessel to cause the acetylation at the hydroxyl groups in the monomeric materials. The acetylated mixture was further heated in the same vessel to higher temperature around 330 °C in 2.5 h to promote polycondensation with eliminating acetic acid formed, excess acetic anhydride and the other low-boiling point fractions. The condensation reactions between carboxyl groups and acetoxy or acetylamino groups were finally completed at 330 °C under the reduced pressure (down to 1330 Pa in 15 min) to form multi-component LCP samples containing amide linkages. Four kinds of LCP samples with various compositions were prepared where molar contents for HBA, HNA and IA were fixed as HBA/HNA/IA = 30/30/20 while the balance between APAP and BP was changed between APAP/BP = 5/15 and 20/0, and then subjected to THM-GC measurement.

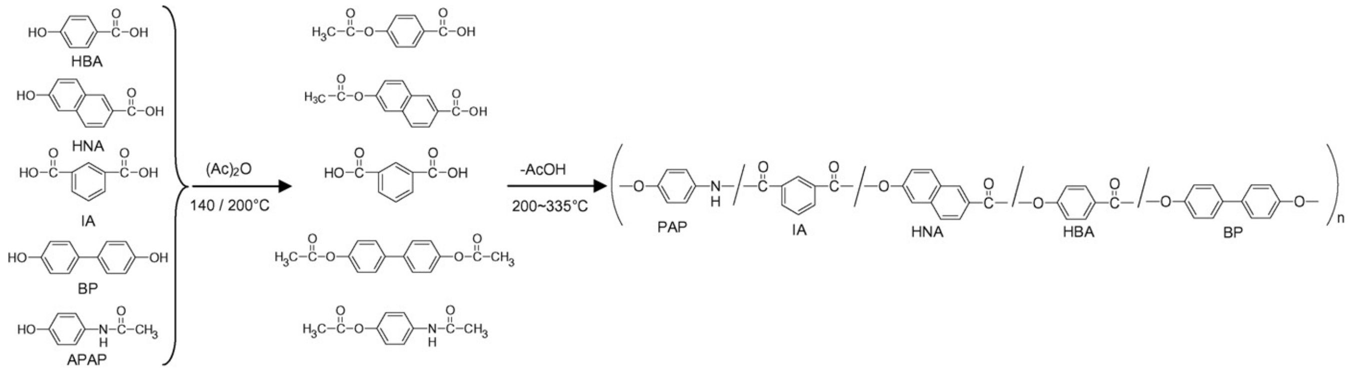
2.2. Conditions for THM-GC measurements

The THM-GC system used in this study was basically the same as described in our previous papers [8–10]. A microfurnace pyrolyzer (Frontier Lab, PY-2020D) was attached to a GC (HP 5890) equipped with a flame ionization detector (FID). About 50 μg of the cryo-milled polymer sample taken in a platinum sample cup together with 2 μl of TMAH solution (25 wt% in methanol, Aldrich) was dropped into the center of the pyrolyzer heated at 300 °C under a helium carrier gas flow (50 ml min^{-1}). The THM temperature and the amount of the reagent were empirically optimized; the lower temperature might cause incomplete cleavages of the ester bonds while the higher temperature led the scission of the amide linkages to some extent. As for the amount of TMAH, the shortage of the reagent often brings about the insufficient THM reactions whereas too much amount of the reagent often contaminates the pyrolyzer mainly due to backflash caused by its explosive evaporation. A part of the flow (1 ml min^{-1}) reduced by a splitter was introduced into a metal capillary separation column (Frontier Lab, Ultra ALLOY^{+}-5; 30 m long × 0.25 mm i.d.) coated with immobilized 5%diphenyl–95%dimethylpolysiloxane (0.25 μm film thickness). The column temperature was programmed from 50 to 320 °C at a rate of 5 °C min^{-1}. For peak identification the pyrolyzer was also attached to a gas chromatography–mass spectrometry (GC–MS) system (JEOL, AM-II 150) with an electron impact ionization (EI) at 70 eV.

3. Results and discussion

Fig. 1 shows a typical THM chromatogram of the LCP sample containing amide linkages (feed composition; APAP/IA/HNA/HBA/BP = 10/20/30/30/10 [mol%]) detected by FID. After the elution of methanol and trimethylamine originating from the TMAH reagent, eight major peaks are observed in the chromatogram, of which assignments are listed in Table 1. Among these products, peaks 1–4 were identified as the dimethyl derivatives of HBA, TA, HNA and BP, respectively, which should be formed through THM reaction at the ester bonds in the LCP sample. On the other hand, peaks 5–8 were attributed to the products containing PAP unit(s).

Fig. 2 shows the mass spectrum of peak 5 observed by THM-GC/MS measurement. This spectrum indicates the molecular ion at *m*/*z* 271 and some fragments ions typical to the methylated PHB unit such as *m*/*z* 135 (base ion) and *m*/*z* 107. This peak was thus identified as a methyl derivative of a dimeric product consisting of PHB and PAP linked with a methylated amide group. In a similar manner, peaks 6 and 7 were identified as the dimeric products of IA and PAP, and HNA and PAP, respectively, from the corresponding mass spectra. Furthermore, the mass spectrum of peak 8 shown in Fig. 3 illustrated that this product was identified as a trimeric compound



Scheme 1.