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# CONFIRMING THE DESIGNED THERMAL DEGRADATION OF A POLYCARBONATE BY TGA/FT-IR

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**Key Words:** Polycarbonate; Thermodecomposable; TGA/FT-IR; Degradation

## ABSTRACT

Integrated thermogravimetric analysis/Fourier transform infrared spectroscopy (TGA/FT-IR) was applied to study the thermal degradation of an aliphatic polycarbonate based on 2,5-dimethyl-2,5-hexanediol and 1,4-cyclohexanediol. A single experiment confirms that the polymer decomposes as designed to the expected products. Carbon dioxide, 1,4-cyclohexanediol, and isomeric hexadienes were thus detected and identified by comparison of their vibrational spectra with those of pure compounds in the spectral library. Some mechanistic implications are discussed.

## INTRODUCTION

Polycarbonates displaying enhanced depolymerization are well known, having been designed, synthesized, and tested by Fréchet et al. [1–4] several years ago. The application of these polymers in various imaging technologies is also well established, including patents [4–6]. However, the initial research [1–3] required the use of both integrated gas chromatography-mass spectroscopy (GC/MS) and thermogravimetric analysis (TGA) to identify the products as well as to ascertain the

polymer's thermal stability, respectively. Recently, integrated thermogravimetric analysis/Fourier transform infrared spectroscopy (TGA/FT-IR) has been developed [7-10] as an effective and extremely convenient technique to simultaneously provide both data sets, leaving no ambiguities that can otherwise arise due to the difference in reaction conditions that are a consequence of the fact that while TGA is performed under a nitrogen atmosphere, GC/MS is done under vacuum [10]. Herein, a typical thermally decomposable polycarbonate is synthesized, and its decomposition behavior is verified in a single experiment.

## EXPERIMENTAL

### Materials

1,1'-Carbonyldiimidazole, 2,5-dimethyl-2,5-hexanediol (DMHD), 1,4-cyclohexanediol (CHD), and 18-Crown-6 were used as received from Aldrich Chemical Company. Potassium carbonate, obtained from J. T. Baker Inc., was ground to a fine powder immediately prior to use. Tetrahydrofuran (THF) was Baker reagent grade and was distilled from sodium benzophenone ketyl prior to use. Baker reagent grade ethyl acetate, dichloromethane, and methanol were used without further purification.

### Synthesis

#### 2,5-Dimethylhexane-2,4-di(oxy carbonylimidazole)

The diurethane was made by the method of Houlihan et al. [3a]. A solution of 2,5-dimethyl-2,5-hexanediol (8.00 g, 54.7 mmol) in dry THF (80 ml) was treated with fresh cut potassium (0.210 g, 5.37 mmol) under nitrogen. The mixture was heated at reflux until the potassium had dissolved (~1 hour). The solution was cooled slightly and transferred to an additional funnel. This solution was slowly added to a stirred suspension of 1,1'-carbonyldiimidazole (17.7 g, 10.9 mmol) in THF (40 mL). After the addition was complete, the solution was heated at reflux for 1 hour. The mixture was then cooled to room temperature and transferred with ethyl acetate (150 mL) to a separatory funnel. The solution was washed three times with water and once with saturated brine, and the product was dried over anhydrous magnesium sulfate. The solution was filtered and reduced, and the crude residue was taken up in methylene chloride and washed three times with water and once with brine, and the solution was dried over anhydrous magnesium sulfate. The filtered solution was reduced, and the product was dried in vacuo to yield 14.3 g (78.5%) as a white solid:  $^1\text{H NMR}$ :  $\delta$  8.1 (s, 2 H), 7.3 (s, 2 H), 7.0 (s, 2 H), 2.0 (s, 4 H), 1.5 (s, 12 H).

### Polycarbonate

A solution of diurethane (3.00 g, 8.97 mmol) and 1,4-cyclohexanediol (1.05 g, 9.00 mmol) in methylene chloride (5 mL) was stirred under nitrogen, and powdered potassium carbonate (6.4 g, 46.3 mmol) was added. To the stirred suspension was added 18-Crown-6 (0.154 g, mmol). The mixture was stirred for 10 minutes at room temperature, and then heated at reflux overnight. The reaction mixture was cooled

and diluted with fresh methylene chloride (50 mL) and stirred for an additional 5 hours. The mixture was vacuum filtered, and the remaining solid was washed several times with methylene chloride. The filtrate was reduced, and the residue was dissolved in methylene chloride (10 mL). The solution was poured into methanol (200 mL) to precipitate the polymer. The polymer was isolated and precipitated a second time into methanol. The polymer was isolated once again and dried to constant weight (1.81 g, 64%):  $^1\text{H NMR}$ :  $\delta$  4.4–4.5 (m, 2 H), 1.4–2.0 (m, 8 H), 1.7 (s, 4 H), 1.4 (s, 12 H).

## Characterization

### NMR

Spectra were obtained in deuterated chloroform on a Bruker AC 300 spectrometer. Tetramethylsilane was used as an internal standard.

### DSC

Thermal analysis was performed on a DuPont 912 differential scanning calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$ .

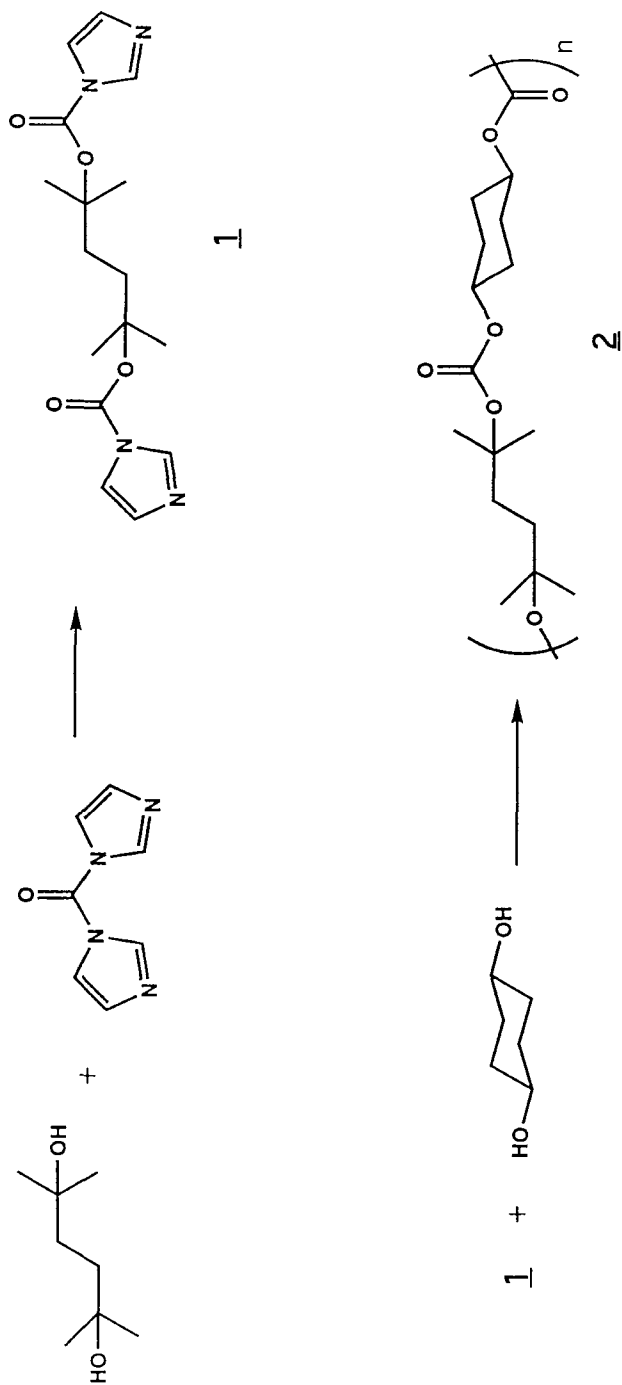
### TGA/FT-IR

Experiments were performed using a BIORAD FTS-45 TGA/FT-IR system consisting of a Digilab FTS-45 Fourier Transform Infrared Spectrophotometer with a broad band MCT detector (set at  $4\text{ cm}^{-1}$  resolution) coupled to a PL Omnitherm TGA 1000. Specific details of this integrated system are discussed elsewhere [7, 8]. Sample sizes for these studies were  $\sim 2\text{ mg}$ . Under a nitrogen purge, a heating rate of  $5^\circ\text{C}/\text{min}$  was used to scan samples from 30 to  $350^\circ\text{C}$ . The heated line that transfers evolved gases from the TGA to the FT-IR was maintained at  $220^\circ\text{C}$ ; the IR cell was held at  $230^\circ\text{C}$ . Spectral searches were done with Search32 (Version 5.00) software supplied with the system using Sadtler and EPA libraries.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The bis(carbonylimidazole) of DMHD was prepared in a manner (Scheme 1) identical to that used by Houlihan et al. [3a]. The reaction product was confirmed by NMR but it was also clear that the product was contaminated with imidazole. Pure material was easily isolated using dichloromethane as an organic extraction medium, since imidazole has little solubility in this solvent. The preparation of the desired polycarbonate proceeded as described in the literature to yield a white powder. This material shows no melting point by DSC below  $200^\circ\text{C}$ . At this temperature, thermal decomposition occurs (*vide infra*), analogous to the thermal depolymerization of linear aliphatic polycarbonates investigated by Fréchet [3].



SCHEME 1. Synthesis of poly(DMHD-CHD)carbonate.

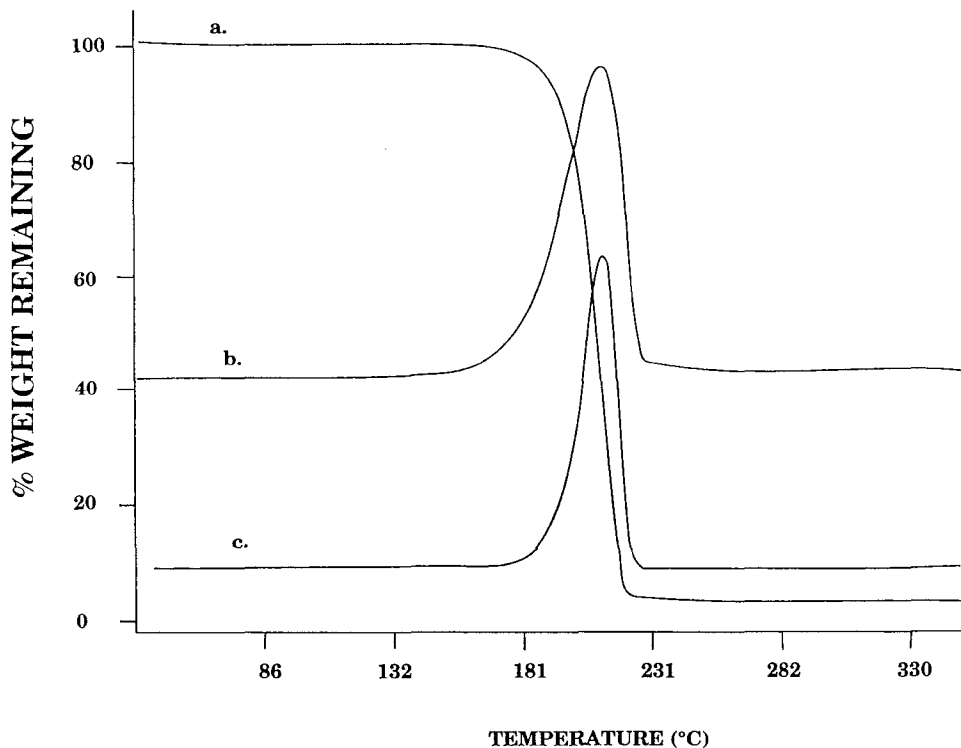


FIG. 1. TGA/FT-IR curve. Heating at 5°C/min: (a) weight loss, (b) evolved gas profile, (c) first derivative of weight loss.

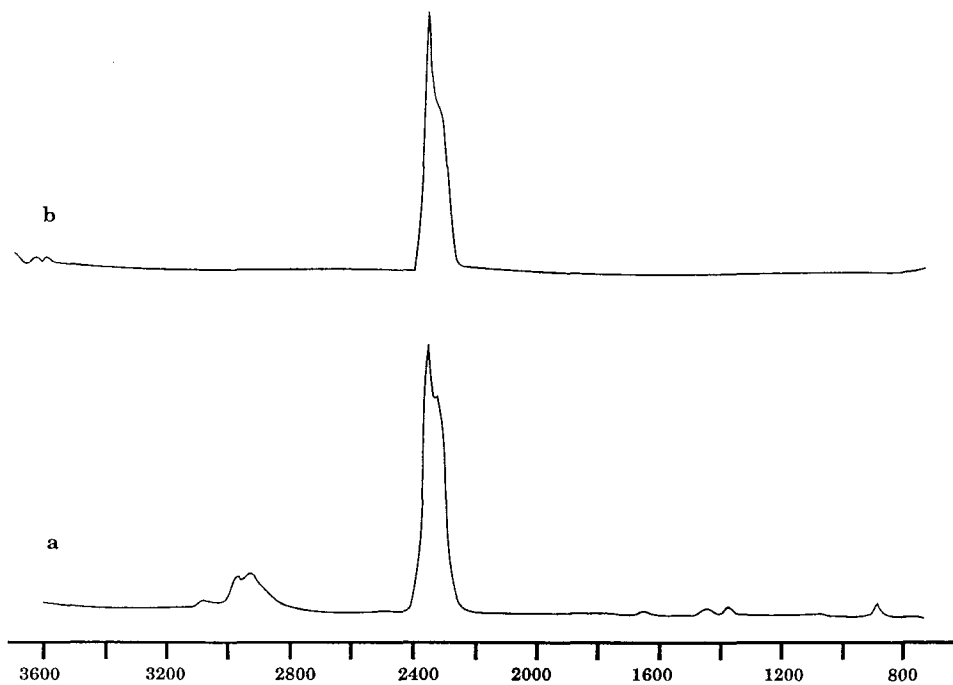


FIG. 2. FT-IR spectrum (a) observed at 200°C and (b) its match to a carbon dioxide spectrum from the Sadtler Library.

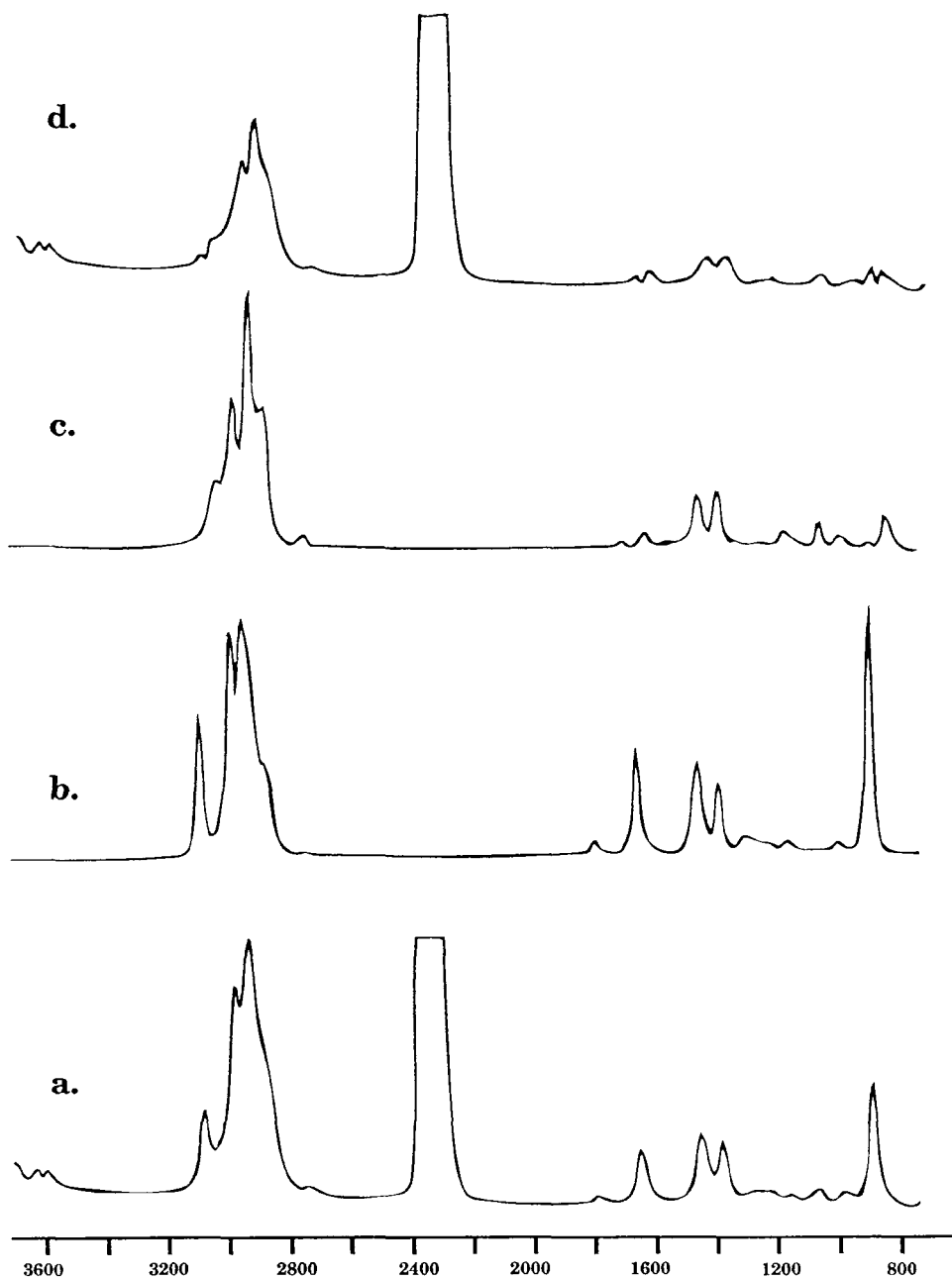


FIG. 3. FT-IR spectrum (a) of TGA effluent at 213°C, (b) Sadtler Library spectrum for 2,5-dimethyl-1,5-hexadiene, (c) Sadtler Library spectrum for 2,5-dimethyl-2,4-hexadiene, (d) difference spectrum from subtracting spectrum of (c) from that of (a).

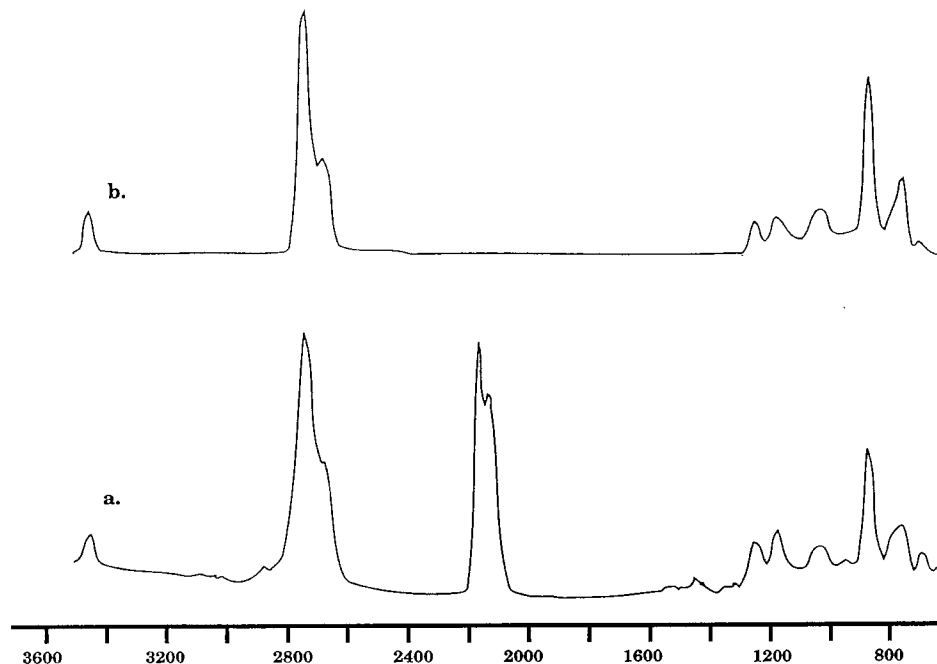


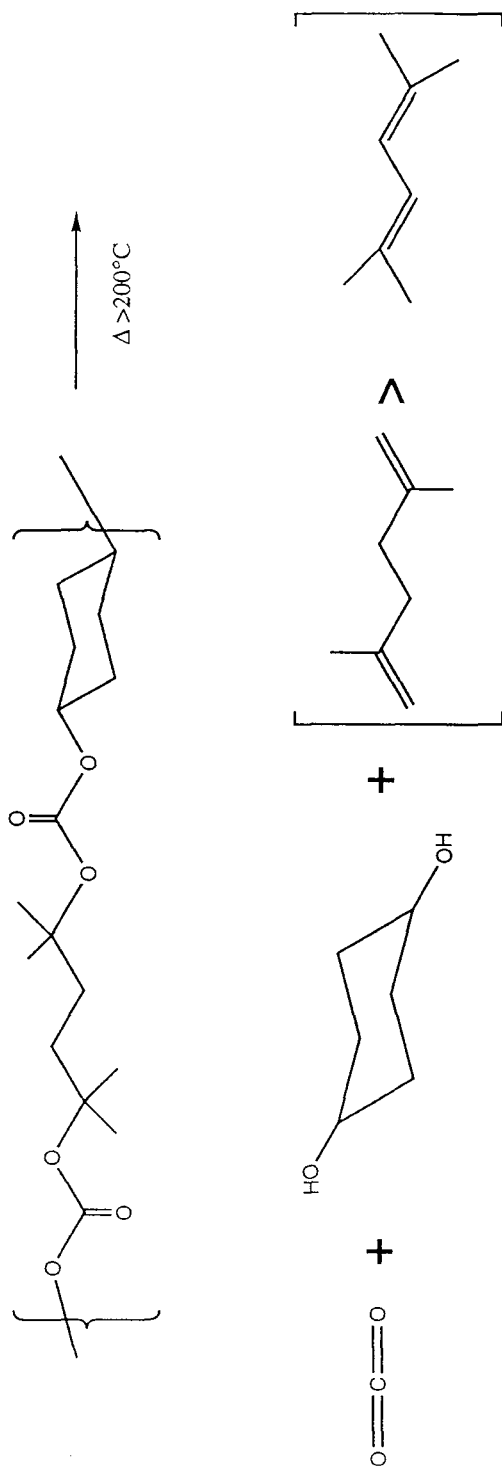
FIG. 4. FT-IR spectrum (a) observed at 230°C and its match (b) to a 1,4-cyclohexanediol spectrum from the Sadtler Library.

### TGA/FT-IR Analysis

Figure 1 displays the TGA curve for the synthesized polymer. It exhibits a sharp single step degradation at  $\sim 200^\circ\text{C}$ , similar in thermal stability to materials previously investigated [1–3]. From the derivative curve and the evolved gas profile, the latter of which represents the total IR absorbance of all the species present, it is apparent that the degradation occurs in a single step. However, the observed spectrum monitored during this transition varies with increasing temperature, thus clearly demonstrating that the resulting products do not all evolve simultaneously. One can easily search the library for their identities. It is very clear (Fig. 2) that carbon dioxide is the first and apparent major product observed, the latter being a consequence of its large extinction coefficient. After performing a spectral subtraction, the resulting spectrum (Fig. 3a) was searched once again in the Sadtler Library. The best logical (structurally possible due to conservation of carbon atoms) hits are the two isomeric alkenes displayed in Figs. 3(b) and 3(c). By looking at the relative peak heights in the hydrocarbon region ( $2800\text{--}3200\text{ cm}^{-1}$ ), it is clear that a mixture is probably present. 2,5-Dimethyl-1,5-hexadiene (Fig. 3b) appears to be the major product, although if one subtracts that spectrum from that experimentally observed (Fig. 3a), the result (Fig. 3d) clearly shows that the 2,5-dimethyl-2,4-hexadiene (Fig. 3c) is also apparently present. Since our library lacks data for 2,5-dimethyl-1,4-hexadiene, its presence could not be confirmed; significant quantities of this isomer may be present [3a].

At higher retention temperatures, concurrent with carbon dioxide evolution, is the evolution of 1,4-cyclohexanediol (Fig. 4). This retardation effect is probably





SCHEME 2. Scheme for the thermal decomposition of the polycarbonate.

not due to mechanistic effects; we would still tend to think that the three products are generated almost simultaneously as indicated in Scheme 2. However, the boiling point of the 1,4-cyclohexanediol (bp 150°C/20 mm) is much higher than that of the carbon dioxide, 2,5-dimethyl-1,5-hexadiene (bp 114°C) or 2,5-dimethyl-2,4-hexadiene (bp 132–134°C) [11]. Indeed, using a pressure-temperature nomograph, it extrapolates to above 200°C, which is above the degradation temperature, whereas those of the hexadienes are below that of the degradation temperature and thus they are much more easily volatilized once generated.

Two aspects of the thermal decomposition products of this polymer are noteworthy. First, no cyclohexene products are seen among the olefins from the decomposition. Cyclohexene compounds would be the necessary products of elimination of the hydroxyl group from the ring of the cyclohexanediol portion of the polymer. The lack of such products contrasts with the observation of benzene as product during the decomposition of a similar class of polymers containing 2-cyclohexene-1,4-diol subunits [12]. For such polymers, both the formation of a stabilized allylic intermediate and the high thermodynamic stability of benzene are clearly driving forces for such a decomposition mechanism. In our case the resulting cyclohexene offers neither a stabilized intermediate nor a comparably thermodynamically stable product; consequently, there is no breaking of the carbon-oxygen bond directly on the ring to create unsaturation.

Second, the olefinic products formed predominantly possess terminal (Hofmann-type) double bonds. Houlihan et al. [3a] noted this result as well, and they suggested that the reaction is kinetically controlled. Such a product geometry is similar to that seen in eliminations of alkyl xanthates ("Chugaev reaction") [13]. Therefore, a similar mechanism thus appears to be operative.

## CONCLUSIONS

By being an integrated technique, TGA/FT-IR is useful in elucidating the structure of thermal degradation products as they are being produced. It is far more reliable than conventional methodology in verifying the identity of products and mechanistic nuances of degradation chemistry, since there is no variation in "atmospheric" conditions as exists when one independently applies both the techniques of TGA and GC/MS. In previous work, such an experimental combination resulted in observable differences in detected products [10]. Although Fréchet et al. [1-3] were able to confirm the expected products using GC/MS, TGA/FT-IR provides a more automated analysis that can be easily applied to directly detect a wide variety of compounds in order to best select the material of choice for a given application.

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