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Thermal degradation of poly{[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate}

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Abstract

Comonomers contraining the phenyl *t*-butyl carbonate moiety have previously been incorporated into acid-producing polymers to act as traps for acid evolved and thereby lend stability to the polymer. To better understand the thermal fragmentation of such materials, a homopolymer, poly**{**[4-(*t*-butyoxycarbonyloxy)phenyl]methyl acrylate**}**(PBPMA), has been prepared, fully characterized, and subjected to examination by thermogravimetry (TGA). In the main, this polymer undergoes multistep degradation to evolve isobutylene and carbon dioxide, to extrude a quinoid aryl fragment and to form a residue of poly(acrylic acid) which may degrade further with the evolution of water, carbon dioxide, and carbon monoxide.

Keywords: Thermogravimetry; PBMA; Monomer

1. Introduction

Vinylidene chloride copolymers display outstanding barrier to the transport of oxygen and other small molecules as well as flavor and aroma constituents. Because of this rather unique property, vinylidene chloride polymers are widely used in the barrier plastic packaging industry. A serious drawback for the use of these materials is their tendency to undergo degradative dehydrochlornation at process temperatures. If severe this can lead to the formation of polyene sequences sufficiently long so as to absorb visible light and cause streaking in the polymer film. This is esthetically displeasing in many applications and, consequently, the degradation must be controlled. This is most often accomplished by addition of one or more stabilizing agents during the mixing phase of the processing operation.

A potentially quite useful approach to the stabilization of these polymers which has received much recent attention has been incorporation into the polymer of a comonomer which contains a substitutent group capable of reaction with evolved hydrogen chloride to expose a phenolic group potentially capable of scavenging chlorine atoms [1–4]. A particularly interesting pendant group is the benzyl *t*-butyl carbonate moiety. This grouping readily undergoes decomposition in the presence of acid and might be expected to be a good scavenger of hydrogen chloride produced during degradation of vinylidene chloride polymer sequences. Indeed, a copolymer containing a benzyl acrylate bearing a *t*-butoxycarbonyloxy group in the 4-position of the phenyl nucleus undergoes thermal degradation to evolve several volatile products in addition to hydrogen chloride [3]. Infrared analysis of the decomposing polymer suggested that the acrylate units were

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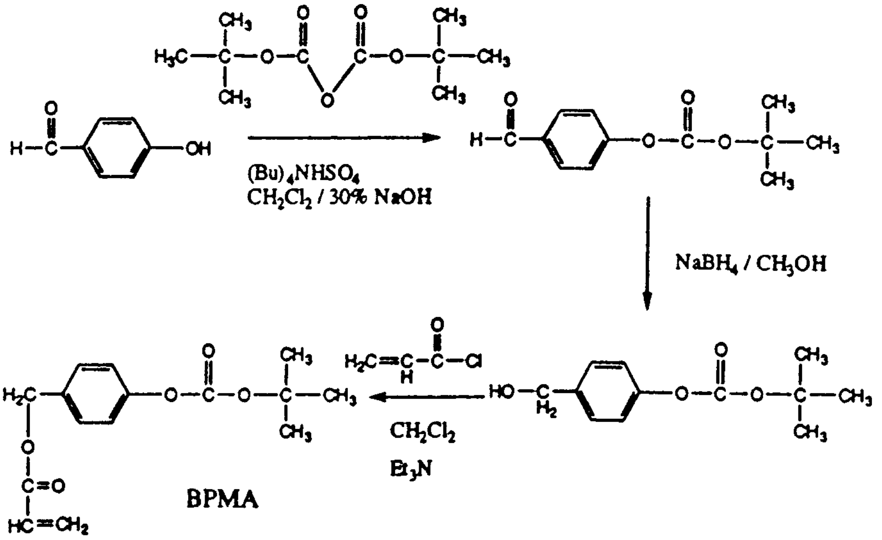


Scheme 1. Synthesis of [4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate.

being converted to acrylic acid units, i.e., that the polymer was being converted to a copolymer of vinylidene chloride and acrylic acid. The goal of this work was to establish the details of the purely thermal degradation of the benzyl *t*-butyl carbonate grouping. This required the synthesis of the homopolymer, poly{[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate} and an examination of its thermal degradation properties.

2. Experimental

The monomer, [4-(*t*-butoxycarbonyloxy)phenyl]-methyl acrylate, was prepared in a three-step sequence from 4-hydroxybenzaldehyde (available from the Aldrich Chemical Company) as previously described [3]. The polymer was prepared by solution polymerization using AIBN as initiator. The polymer was

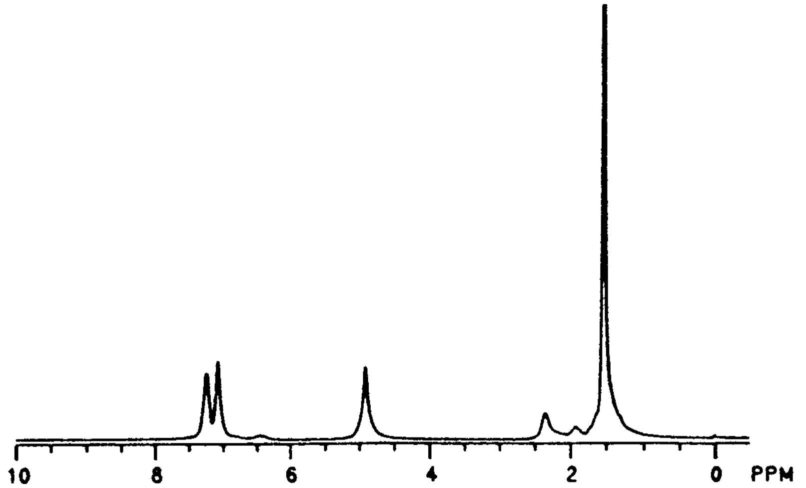
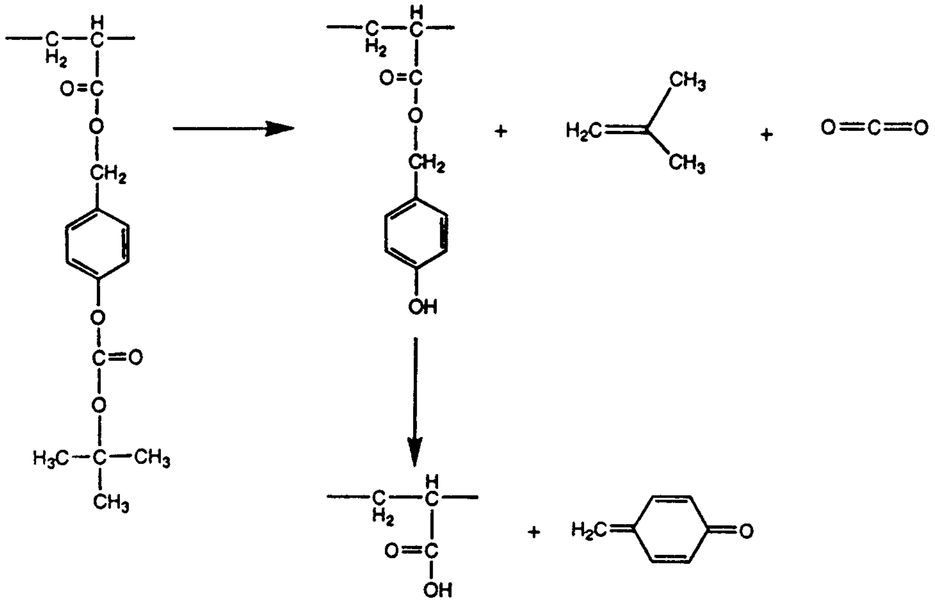


Fig. 1. Proton NMR Spectrum of poly{4-*t*-butoxycarbonyloxy)phenyl]methyl acrylate}.



Scheme 2. Mode of thermal degradation of poly{[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate}.

characterized by spectroscopic, thermal, viscometric and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained using dilute solutions in deuterochloroform and a General Electric QE-300 spectrometer. Chemical shifts are reported in parts per million (δ) with respect to internal tetraxnethylsilane. Infrared spectra were obtained using solid solutions (1%) in anhydrous potassium

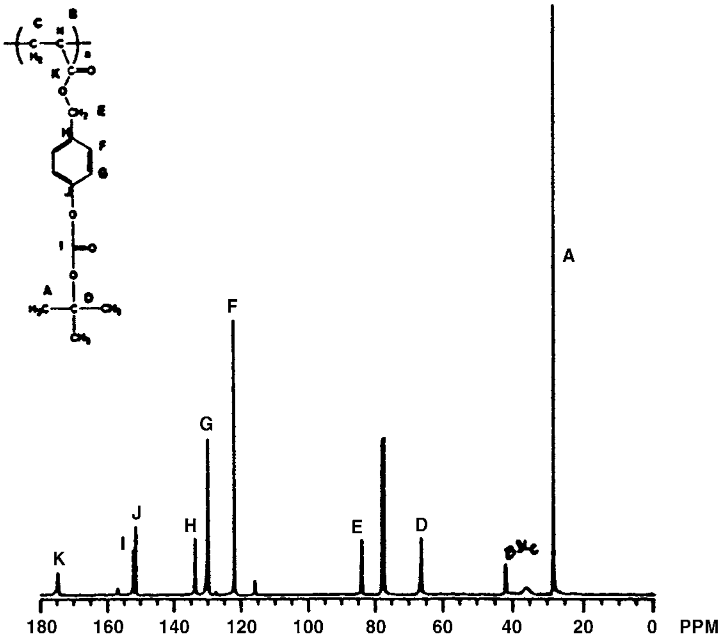
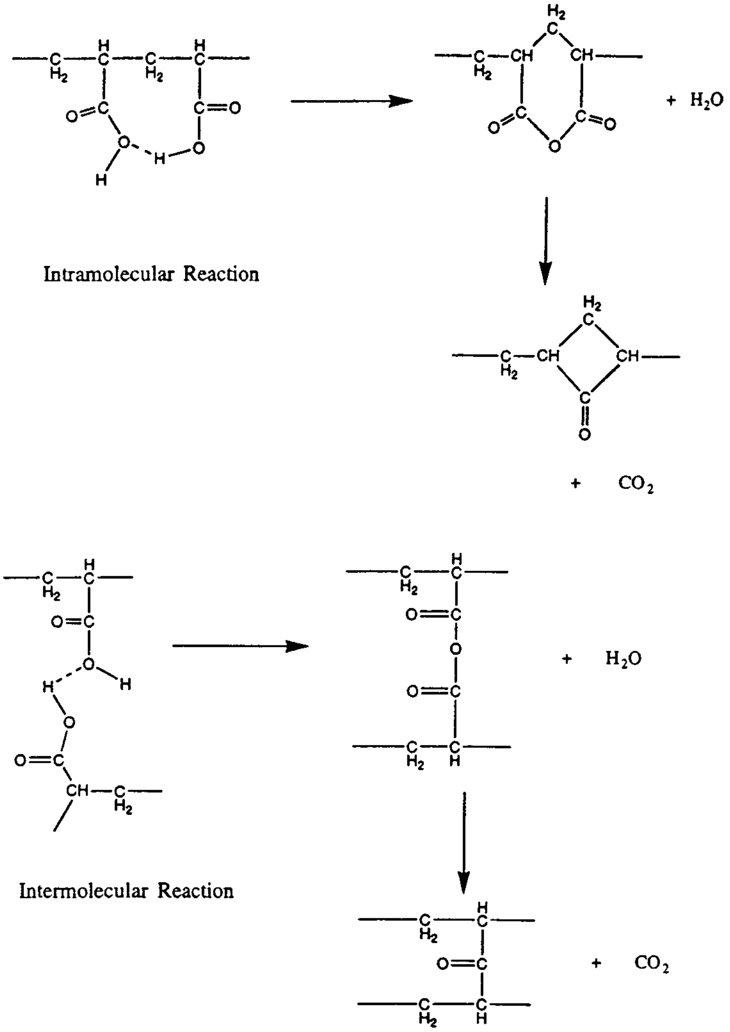


Fig. 2. Carbon-13 NMR Spectrum of poly{[4-*t*-butoxycarbonyloxy)phenyl]methyl acrylate}.

bromide (as pellets) or thin films between sodium chloride discs and a model 1600 Perkin-Elmer FTIR instrument. Differential scanning calorimetry (DSC) was carried out at a heating rate of 10°C/min using a TA Instruments Thermal Analyst 2100 system equipped with a model 2910 DSC cell. The sample compartment was subjected to a constant purge of dry nitrogen at 50 ml/min. Viscosity was determined at 35°C using dilute solutions in 2-butanone and a Schott-Gerate AVS 450 viscometer equipped with a Ubbelohde capillary. The thermal degradation characteristics of poly{[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate} were determined by thermogravimetry using a TA Instruments model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TGA cell was swept with nitrogen at 50 ml/min during degradation runs and the sample, approximately 10 mg, was contained in a platinum sample pan. The temperature was ramped at a rate of 5°C/min from 30 to 600°C.

3. Results and discussion

The monomer, [4-(*t*-butoxycarbonyloxy)phenyl]-methyl acrylate (BPMA), was obtained by synthesis



Scheme 3. Thermal degradation of residual poly(acrylic acid).

from 4-hydroxylbenzaldehyde as shown below in Scheme 1.

Polymerization of [4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate was accomplished by heating a solution in benzene at 65°C in the presence of azobisisobutronitirile (AIBN) as initiator. The polymer was repeatedly precipitated from benzene (or THF) with excess methanol to effect purification and was then dried at 20 Torr and 50°C for 48 h. The NMR spectra, ^{1}H and ^{13}C, are both fully consistent with the expected structure. Differential scanning calorimetry (DSC) disclosed an apparent glass transition at 24°C and a melting endotherm at 48°C. Thermogravimetric analysis (TGA) of the polymer revealed two major decompositions at 160 and 420°C, respectively. A residue remaining at 600°C corresponded to approximately 25% of the initial sample mass. An intrinsic viscosity for the polymer determined in 2-butanone solution was 13.4 ml/g at 30°C and 9.27 ml/g at 35°C. Analysis of the polymer by size exclusion chromatography (SEC; GPC) using a mixed-bed column (Polymer Laboratories) with THF as eluant and polystyrene calibration indicated a number average molecular weight (M_n) of 27,000 with a polydispersity of 2.74.

A TGA thermogram for the decomposition of the polymer is shown below in Fig. 1. As noted above, two major events characterize the degradation. The first occurs at 160°C and corresponds to a loss of 35.5±0.7% of the mass initially present. This reflects almost perfectly the loss of isobutylene and carbon dioxide from each repeat unit. The second occurs at 420°C and corresponds to a loss of 40.1±4.5% of the initial mass present. The error in the measurement of the second loss is rather large because the residue [poly(acrylic acid)] is itself not stable and undergoes dehydration at temperatures greater than 150°C. In both cases the values reported are the averages of three runs. The second loss reflects the expulsion of 3-oxo-6-methylene-1,4-cyclohexadiene. The residue accounts for 24.4±4.5% of the initial mass and is nearly that (25.5%) expected for the formation of poly(acrylic acid). The decomposition of the polymer may be formulated as shown below (Scheme 2, Fig. 2).

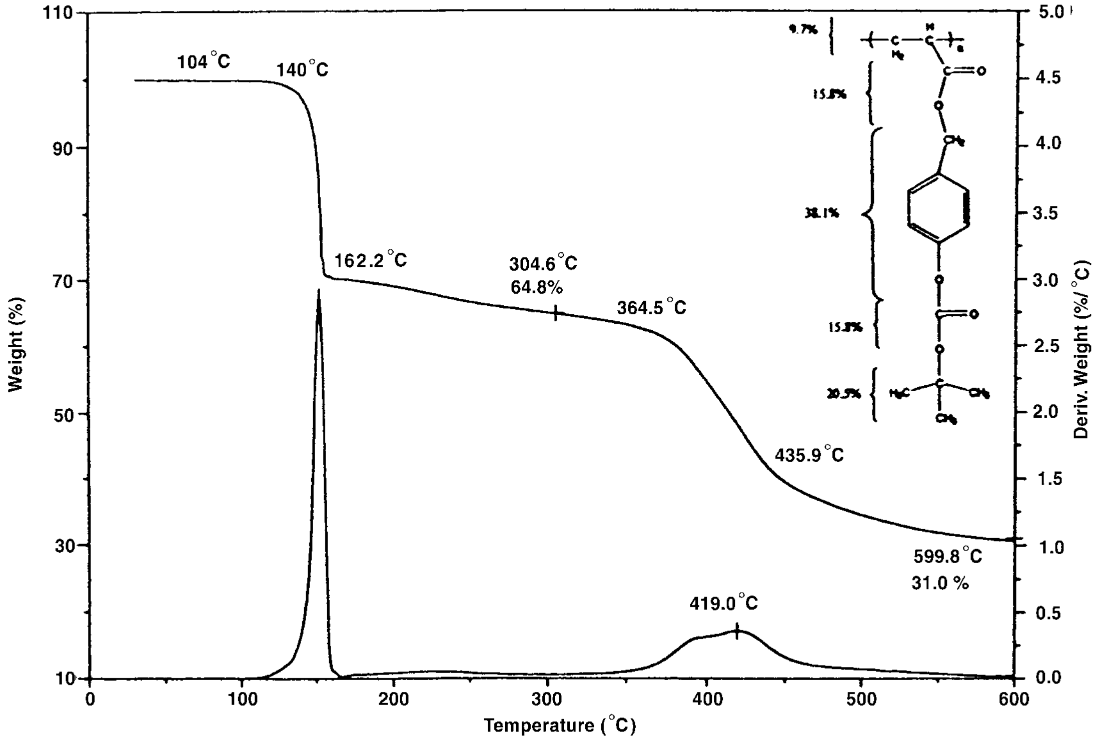


Fig. 3. Thermal decomposition of poly{[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate}.

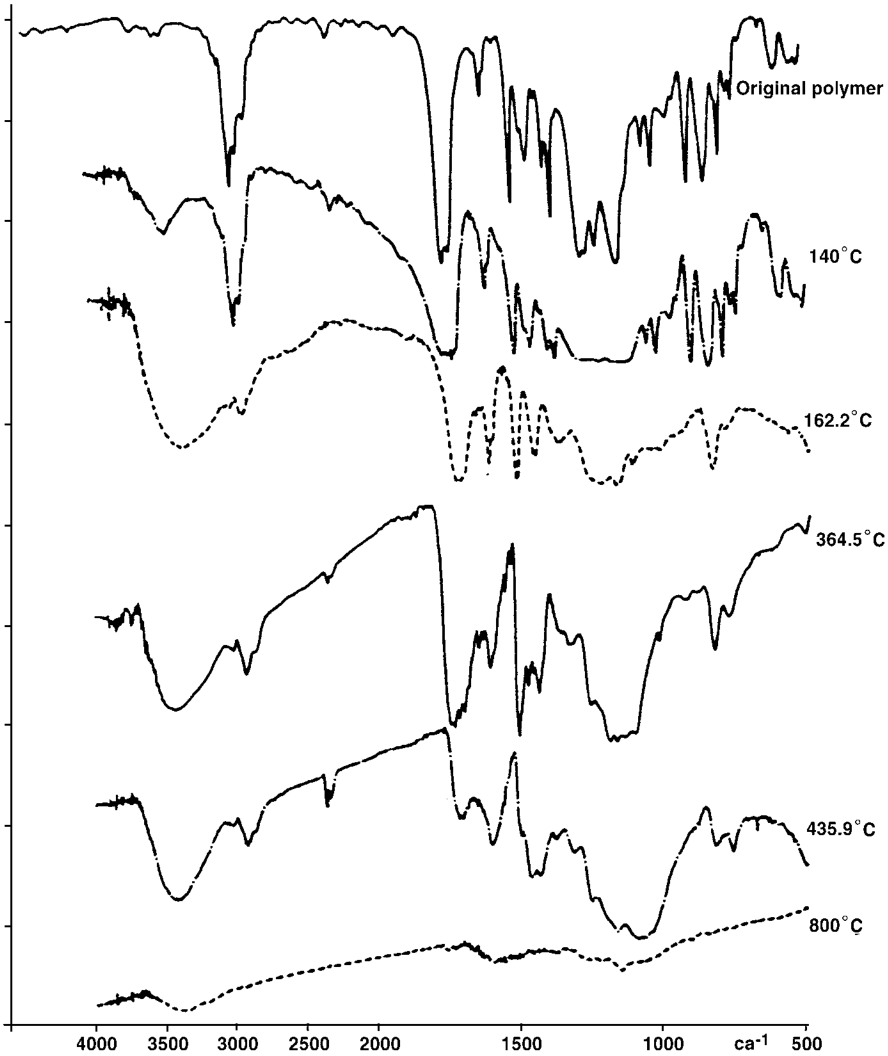


Fig. 4. Infrared spectra for samples removed from degradation of poly[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate}.

The polymer sample undergoing degradation was also examined by infrared spectroscopy. Portions of the sample were removed at 140, 162, 365, 436, and 800°C and subjected to analysis by FTIR. Prior to degradation the polymer displays carbonyl absorption at 1739 cm^{-1} (acrylate) and 1757 cm^{-1} (carbonate). As the temperature increases there is a continual decrease in the intensity of first the band at 1757 cm^{-1} and then the band at 1739 cm^{-1} with concomitant formation of a broad band at 3300–3500 cm^{-1} (phenol and carboxyl). The sample removed at 436°C contained new carbonyl absorption at 1710 cm^{-1} presumably due to the formation of ketone from decomposition of residual poly(acrylic acid) [5] (Scheme 3, Figs. 3 and 4).

4. Conclusions

Poly{[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate} undergoes thermal degradation in two distinct steps reflecting the decomposition of the pendant benzyl *t*-butyl carbonate moiety. The initial fragmentation occurs at 160°C and corresponds to the loss of isobutylene and carbon dioxide from the *t*-butyl carbonate grouping. A second fragmentation occurs at 420°C and corresponds to the loss of the 4-hydroxybenzyl moiety as a quinoid-type molecule. The residual poly(acrylic acid) is thermally unstable at the temperature of formation and undergoes further degradation to form anhydride and ketone structures.

Acknowledgements

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