

# THERMAL DEGRADATION OF VINYLIDENE CHLORIDE/[4-(*t*-BUTOXYCARBOXYLOXY)PHENYL]METHYL ACRYLATE COPOLYMERS

B. A. Howell\*, D. A. Spears and P. B. Smith

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859-0001, USA

Vinylidene chloride polymers containing comonomer units capable of consuming evolved hydrogen chloride to expose good radical-scavenging sites might be expected to display greater thermal stability than similar polymers containing simple alkyl acrylates as comonomer. Incorporation of a comonomer containing the phenyl *t*-butyl carbonate moiety into a vinylidene chloride polymer has the potential to afford a polymer with pendant groups which might interact with hydrogen chloride to expose phenolic groups. Copolymers of vinylidene chloride with [4-(*t*-butoxycarboxyloxy)phenyl]methyl acrylate have been prepared, characterized, and subjected to thermal degradation. The degradation has been characterized by thermal and spectroscopic techniques. The degradation of vinylidene chloride/[4-(*t*-butoxycarboxyloxy)phenyl]methyl acrylate copolymers is much more facile than the same process for similar copolymers containing either [4-(isobutoxycarboxyloxy)phenyl]methyl acrylate or methyl acrylate, a simple alkyl acrylate, as comonomer. During copolymer degradation, [4-(*t*-butoxycarboxyloxy)phenyl]methyl acrylate units are apparently converted to acrylic acid units by extensive fragmentation of the sidechain. Thus, the phenyl *t*-butyl carbonate moiety does function as a labile acid-sensitive pendant group but its decomposition in this instance leads to the generation of a phenoxybenzyl carboxylate capable of further fragmentation.

**Keywords:** acid-labile pendant groups, acrylate acid scavengers, degradative dehydrochlorination, stabilization of vinylidene chloride barrier resins

## Introduction

Vinylidene chloride copolymers are important specialty polymers. These materials display several unique properties [1]. Principal among these is the extremely low permeability of oxygen and flavor and aroma constituents of common food items in polymers of high vinylidene chloride content [2, 3]. For this reason, these polymers occupy a place of prominence in the barrier plastic packaging industry. A major processing variable which must be attended for the utilization of these materials is the propensity, under thermal stress, to undergo dehydrochlorination in the vinylidene chloride sequences [4, 5]. If unchecked, sequential dehydrochlorination along the polymer mainchain leads to the formation of polyene segments of sufficient length to absorb in the visible portion of the electromagnetic spectrum and to impart color to the polymer. Although the development of color occurs well before any diminution of the physical or mechanical properties of the polymer is observed, the color itself is objectionable in some applications. Therefore the development of vinylidene chloride copolymers containing stabilizing features has been the focus of much effort. This propensity for degradation might be controlled by the incorporation into the polymer of comonomer units containing

functionality that can 1) absorb a mole of hydrogen chloride and 2) do so in such a manner that good radical-scavenging sites are exposed. The presence of groups capable of reaction with evolved hydrogen chloride would prevent its interaction with metal components of process equipment to form metal halides which are known to facilitate the dehydrochlorination reaction [6]. The presence of effective radical-scavenging sites might be expected to disrupt propagation of the dehydrochlorination reaction and provide stabilization for the polymer. It has previously been shown that vinylidene chloride polymers containing either styrene [7] or acrylate [8] comonomer units bearing 3,4-dihydroxyphenyl groups masked as the cyclopentanone ketal do not display enhanced stability with respect to that exhibited by the homopolymer. In the first instance chain scission at benzylic sites on the mainchain apparently competes with dehydrochlorination. In either case, the reaction of evolved hydrogen chloride with the ketal functionality is insufficiently facile to expose phenolic groups with the efficiency necessary for effective stabilization. In this instance, the degradation of vinylidene chloride/[4-(*t*-butoxycarboxyloxy)phenyl]methyl acrylate copolymers containing the acid-sensitive phenyl *t*-butyl carbonate moiety has been examined by thermogravimetry and spectroscopic methods.

\* Author for correspondence: bob.a.howell@cmich.edu

## Experimental

The necessary copolymers were prepared from vinylidene chloride and the appropriate acrylate monomer using suspension techniques as previously described [4, 9]. These materials were characterized by chromatographic, thermal, and spectroscopic methods. Differential scanning calorimetry (DSC) was carried out at a heating rate of  $5^{\circ}\text{C min}^{-1}$  using a TA Instruments Inc. model 2100 thermal analysis system equipped with a model 2910 DSC cell. The sample compartment was exposed to a constant purge of dry nitrogen at  $50\text{ mL min}^{-1}$ . Size exclusion chromatography (SEC) was accomplished using solutions in tetrahydrofuran, microstygel columns, and linear poly(styrene) calibration. Nuclear magnetic resonance (NMR) spectra were obtained using a General Electric NT-30 spectrometer and samples dissolved in tetrahydrofuran (THF) [10]. The data acquisition parameters for  $^{13}\text{C}$  NMR spectra obtained at 75.5 MHz were a pulse width of  $90^{\circ}$ , a delay time of 10 s, a size of 16 K, an accumulation time of 0.41 s, a sweep width of 20 KHz, exponential apodisation, 5-Hz line broadening, and gated decoupling without NOE. Polymer stability was assessed by thermogravimetry (TG) using a TA Instruments Inc. model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The sample (4–10 mg) was contained in a platinum sample pan and the TG cell was swept with nitrogen at  $50\text{ mL min}^{-1}$  during degradation runs. The temperature was ramped at  $2\text{--}10^{\circ}\text{C min}^{-1}$ .

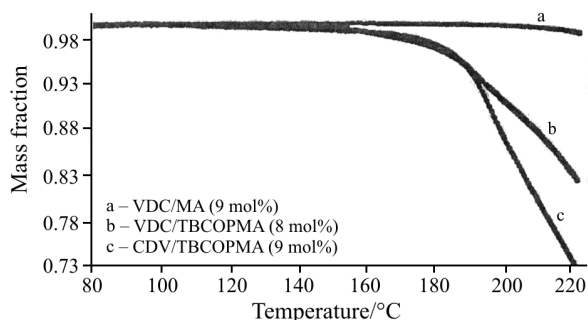
## Results and discussion

High vinylidene chloride content copolymers are high-value, specialty materials important to the packaging industry. Thermally-induced dehydrochlorination during processing of these materials must be controlled to prevent the formation of conjugated polyene sequences and consequent color development. The dehydrochlorination reaction is a typical chain process with distinct initiation, propagation, and termination phases [4]. Initiation most readily occurs at an allylic dichloromethylene unit introduced during polymerization, drying, etc. Initial homolytic fragmentation of a carbon-chlorine bond generates an allylic carbon chlorine radical pair. The chlorine atom abstracts a hydrogen atom at the adjacent methylene in strong preference to other possible modes of reaction [4]. This produces a mole of hydrogen chloride, introduces a second chloroacetylene unit, and generates another allylic dichloromethylene unit. Rapid repetition of this process represents propagation of the dehydrochlorination reaction and generates a conjugated polyene sequence, often of sufficient size to impart color to the polymer. Copolymers containing units

capable of consuming a mole of hydrogen chloride to expose a good radical scavenger (to trap chlorine atoms and other radical species) might be expected to exhibit considerably greater stability than copolymers of simple alkyl acrylates. Monomers containing the *t*-butyl phenyl carbonate moiety might be good candidates for use in the preparation of such copolymers. The *t*-butyl phenyl carbonate group is known to be quite sensitive to the presence of acid and to degrade with the expulsion of carbon dioxide and the concomitant exposure of phenolic functionality [11]. An acrylate monomer containing this grouping was synthesized from commercially-available 4-hydroxybenzaldehyde. Generation of the carbonate at the phenolic site followed by reduction of the aldehydic group afforded an alcohol which could readily be converted to the acrylate ester. In order to prepare copolymers containing less-reactive carbonate groupings, the analogous esters containing both isobutyl and *n*-butyl carbonate substituents were prepared by similar methods.

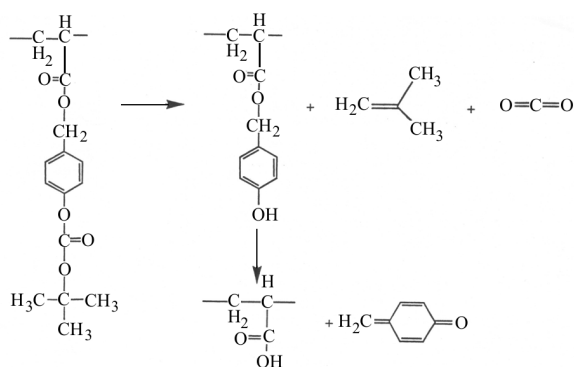
Copolymers of vinylidene chloride (VDC) with [4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate (TBCOPMA), [4-(isobutoxycarbonyloxy)phenyl]methyl acrylate (IBCOPIA), and methyl acrylate were prepared by suspension techniques as previously described [4]. These materials were characterized by SEC, DSC and  $^{13}\text{C}$  NMR. All the copolymers, containing acrylate at approximately 9 mol%, were typical VDC polymers with  $M_n$  of approximately 20000 and  $M_w$  of 42000. All displayed a glass transition at approximately  $15^{\circ}\text{C}$  and a melting endotherm at  $170^{\circ}\text{C}$ . Analysis by  $^{13}\text{C}$  NMR established that the acrylate was randomly incorporated into the copolymer and at approximately the level in the monomer feed in all cases [10].

The stability of the copolymers was determined by thermogravimetry. Figure 1 contains a comparison of the thermal degradation characteristics of a VDC/MA (9 mol%) copolymer (as reference) with those of two VDC/TBCOPMA (8 and 9 mol%, respectively) copolymers. As can readily be seen, the rate of initiation of degradation is much greater for the TBCOPMA copolymers than for the simple acrylate copolymer.



**Fig. 1** Thermal degradation of vinylidene chloride/[4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate (8 and 9 mol%) copolymers

That this behavior is peculiar to the *t*-butoxycarbonyloxy polymer is apparent from the comparison with the degradation of the analogous polymer containing [4-(isobutoxycarbonyloxy)phenyl]methyl acrylate. The degradation behavior of the VDC/IBCOPMA copolymer is quite similar to that of the VDC/MA copolymer. The behavior of both is typical of that expected for a VDC copolymer containing 9 mol% alkyl acrylate comonomer units. In contrast, the VDC/TBCOPMA copolymer is much less thermally-stable than either. Initiation of degradation for this polymer is quite facile with an onset temperature of approximately 115°C. Thus, while the phenyl *t*-butyl carbonate moiety in this polymer is sensitive to the presence of acid and readily degrades, it does not do so to generate a stable phenolic pendant group (Scheme 1).



**Scheme 1** Mode of degradation of the *t*-butyl carbonate moiety in a VDC copolymer

In contrast the phenyl isobutyl carbonate group is not cleaved by evolving hydrogen chloride during the degradation of the VDC/IBCOPMA copolymer and that polymer behaves very much as does a VDC copolymer containing an equivalent amount of a simple alkyl acrylate.

## Conclusions

Incorporation of [4-(*t*-butoxycarbonyloxy)phenyl]methyl acrylate into a vinylidene chloride polymer does not enhance the stability of the polymer. In fact, the thermal degradation of VDC/TBCOPMA copolymers is much more facile than that observed for

VDC/IBCOPMA copolymers containing the isomeric phenyl isobutyl carbonate moiety or for VDC/MA copolymers containing simple carboxymethyl pendant groups. While the phenyl *t*-butyl carbonate grouping does undergo facile fragmentation during polymer degradation this fragmentation does not generate a stable phenolic unit, instead more extensive decomposition occurs to place a carboxy group pendant to the polymer mainchain.

## Acknowledgements

Partial support of this work by the Dow Chemical Company (DAS) and funding from the Michigan Research Excellence Fund for the establishment of the Center for Applications in Polymer Science are gratefully acknowledged.

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DOI: 10.1007/s10973-005-7481-2