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# Degradation of vinylidene chloride/methyl acrylate copolymers in the presence of amines [1]

B.A. Howell and H. Liu

*Center for Applications in Polymer Science and Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48859 (USA)*

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## Abstract

Because of the prominence of vinylidene chloride/methyl acrylate copolymers in barrier plastic packing applications the degradation of these materials continues to be the focus of much interest. The prominent degradation process at moderate temperatures (less than 200°C) is dehydrochlorination. This reaction is a typical radical chain process with distinct initiation, propagation and termination phases. A principal defect structure responsible for the initiation of degradation is unsaturation along the polymer backbone. Although most stabilization packages for these polymers contain basic components to absorb hydrogen chloride as it is generated, materials sufficiently basic to abstract hydrogen chloride might actually enhance the rate of degradation by introducing double bonds into the polymer structure. That this is the case has been established by the thermogravimetric examination of the degradation of a methyl acrylate (5 mol.%)/vinylidene chloride copolymer in the presence of amines of varying base strength. In general, the initiation rate constant $k_i$ for the degradation process is enhanced in the presence of amine.

## INTRODUCTION

Vinylidene chloride (VDC) copolymers display a number of superior characteristics including high crystallinity and good solvent resistance. However, the property which sets these materials apart from other vinyl polymers is their extremely low permeability to a wide variety of gases [1,2]. Because of this property these materials occupy a position of prominence in the barrier plastic packaging industry. Processing required for use in packaging applications exposes these polymers to thermal stress. Under

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*Correspondence to:* B.A. Howell, Center for Applications in Polymer Science and Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48859, USA.

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these conditions, the polymers undergo dehydrochlorination in the VDC sequences [3,4]. This degradative dehydrochlorination reaction is a typical radical chain process with distinct initiation, propagation and termination phases [5,6]. Initiation of degradation is strongly facilitated by the presence of unsaturation along the polymer backbone [7]. Such unsaturation may be introduced via interaction of the polymer with a variety of agents. Numerous process aids may be employed to minimize degradation [8]. Although most stabilization packages for these polymers contain basic components [3] to absorb hydrogen chloride as it is formed, materials sufficiently basic to abstract hydrogen chloride might actually enhance the rate of degradation by introducing double bonds into the structure. It is known, for example, that both pyridine [9] and inorganic base in the presence of cationic wetting agents [10] cause surface degradation of VDC polymers. To define further the impact of basic agents on the degradation, the thermal decomposition of a methyl acrylate (5 mol.%)/vinylidene chloride copolymer in the presence of amines of varying basicity has been studied by thermogravimetry.

## EXPERIMENTAL

### *Materials*

#### *Monomers and reagents*

Distilled vinylidene chloride and hydroxymethylcellulose (METHOCEL K4M cellulose ether) were provided by the Dow Chemical Company. The methyl acrylate (MA) used was commercial material from Hoechst Celanese and contained 200 ppm MEHQ (monomethyl ether of hydroquinone) as stabilizer. Azobisisobutyronitrile (AIBN; VAZO 64) was obtained from the Du Pont Chemical Company. The amines (1,4-diazobicyclo[2.2.2]octane (DABCO), 2,2,6,6-tetramethylpiperidine (TMP), triethylamine (TEA), trioctylamine (TOA) and 1,5-diazobicyclo[4.3.0]non-5-ene (DBN)) were obtained from Aldrich Chemical Company. Common solvents were obtained from Fisher Scientific Company.

#### *Polymerization*

Suspension polymerization was carried out to high conversion in a glass-lined reactor at 65°C. The aqueous phase contained 0.2 wt.% hydroxymethylcellulose as suspending agent. The initiator (AIBN; 0.5 wt.%, 0.3 mol.%) was dissolved in the monomer phase. A phase ratio of 1.5 : 1 (water mass to monomer mass) was maintained. The polymer generated was washed repeatedly with deionized water to remove residual monomer and suspending agent, collected by filtration at reduced pressure, and dried in an oven at 50°C.

## *Polymer characterization*

### *Size-exclusion chromatography*

Molecular weights were determined by size-exclusion chromatography relative to narrow-molecular-weight polystyrene standards (Polymer Laboratories, Inc.) using solutions in tetrahydrofuran (THF) and a Waters Associates modular chromatographic system which included a model M-6000 pump and a model 410 differential refractive index detector. Two 5 μm mixed-bed columns from Polymer Laboratories, Inc., (No. 5M-M-35-59, 60) were used in series. The polymer was of uniform molecular weight distribution with $M_n = 57000$, $M_w = 102000$ and $M_w/M_n = 1.79$.

### *Differential scanning calorimetry (DSC)*

Analysis by DSC was accomplished using a TA Instruments, Inc., 2100 Thermal Analyzer coupled to a model 2910 DSC unit equipped with a liquid nitrogen cooling accessory (LNCA). The cell was calibrated using an indium sample ($T_m$ onset, 156.21°C; $\Delta H_f = 29.24$ J g$^{-1}$). DSC plots (heat flow vs. temperature) were generated using a model 7440 Hewlett-Packard plotter supplied by TA Instruments. In general, 8–12 mg samples and closed aluminum sample pans were used. The cell was subject to a constant nitrogen purge. After equilibration at −40°C, the temperature was ramped to 200°C at 10°C min$^{-1}$. To observe a sharp glass transition temperature, samples were held at 185°C for 75 s and quench cooled in liquid nitrogen prior to analysis. The unannealed polymer displayed melting behavior characteristic of vinylidene chloride copolymers [4] with endotherms at 164.6 and 172.4°C. The melted/quench-cooled sample displayed a glass transition $T_g$ at 5.9°C, a crystallization exotherm $T_c$ at 68.4°C and a melting endotherm $T_m$ at 172.4°C. By making reference to a calibration plot of melting point vs. composition for vinylidene chloride/methyl acrylate copolymers for which the MA content had been determined rigorously by $^{13}$C NMR spectroscopy, it could be established that the polymer contained methyl acrylate at the intended 5 mol.% level.

### *Nuclear magnetic resonance spectroscopy (NMR)*

NMR spectra were recorded using solutions in THF-$d_8$ and a Nicolet NT-300 spectrometer. Carbon spectra were observed at 75.5 MHz with a pulse width of 18 μs (90°), a pulse delay of 10 s, an acquisition time of 0.41 s, gated decoupling without NOE, a sweep width of 20 kHz, and an acquisition size of 16K. The $^{13}$C NMR analysis [11] confirmed the random distribution of the methyl acrylate in the polymer and established that it had been incorporated at approximately the distribution in the initial monomer mixture.

### *IR spectroscopy*

IR spectra of both the initial polymer and degraded samples were obtained using a Nicolet 20 DXB FT instrument and dispersions in anhydrous potassium bromide.

### *Vinylidene chloride copolymer / amine blends*

In general the appropriate amount of amine was dissolved in hexane, the polymer was added, the suspension was stirred, the solvent was removed by evaporation at reduced pressure and the blend was dried at slightly above room temperature and reduced pressure. In a typical example, 5.00 g of DABCO was dissolved in 200 ml of hexane in a round-bottomed flask. Polymer (45.00 g) was added and the resulting mixture was stirred for 0.25 h at 40°C. The solvent was removed by rotary evaporation at reduced pressure and 40°C. The residual polymer/amine blend was transferred to a Pyrex boat and dried at approximately 20 Torr and 40°C for 24 h.

### *Thermal degradation*

The thermal degradation characteristics of both untreated polymer and samples containing 1–10 parts per hundred (pph) of an appropriate amine were examined by thermogravimetry using either a TA Instruments 2100 Thermal Analyzer coupled with a 2910 TGA unit or a Du Pont 1090 thermal analysis system coupled to a 951 TGA unit. Dynamic TGA experiments were carried out using either instrument. In a typical run the temperature was ramped at a rate of 5°C $\min^{-1}$ from 35 to 450°C. Most isothermal runs were conducted using the 951 unit. In these cases, the furnace was preheated to the desired degradation temperature, the sample chamber was inserted and data collection was started almost immediately [12]. In either case the TGA cell was swept with nitrogen at 40 ml $\min^{-1}$ during degradation runs and the sample, approximately 20 mg, was contained in a platinum sample pan. Decay plots, weight loss vs. time (or temperature), were generated by feeding the analyzer output (TA Instruments or Du Pont software was used for all data manipulation) to a model 7440 Hewlett-Packard plotter or, in the case of the 1090 instrument, to a MacIntosh personal computer for further manipulation and plotting. Plots of ln mass against time (ln $m$ vs. $t$) were generated using the MacIntosh. The initial slopes of these plots gave $k_i$ values, the rate constant for the initiation of degradation, while the slopes for longer run times provided the value for $k_p$ the degradation propagation rate constant [12].

## RESULTS AND DISCUSSION

The impact of the presence of amines of varying base strength on the thermal degradation of a vinylidene chloride/methyl acrylate copolymer (containing 5 mol.% methyl acrylate) has been examined using thermo-

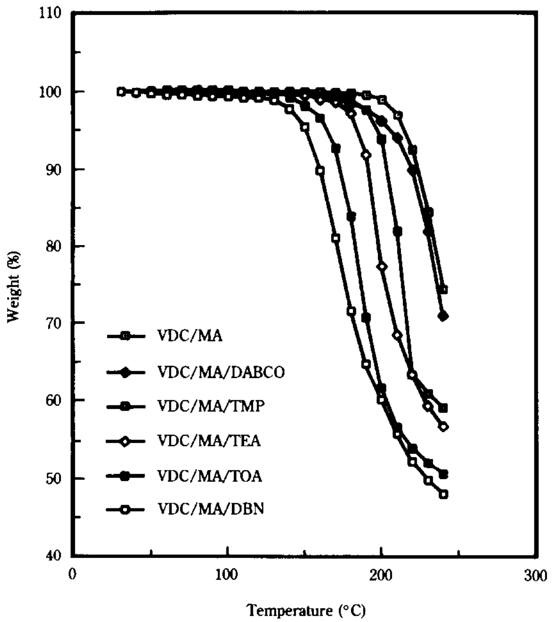

Fig. 1. Thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of 10 pph of selected amines: impact of amine basicity on the initiation of degradative dehydrochlorination.

gravimetric and spectroscopic techniques. Polymer samples containing 1, 5 and 10 pph of five amines of varying base strength were subjected to thermal degradation. The amines selected were 1,4-diazobicyclo[2.2.2]octane (DABCO), 2,2,6,6-tetramethylpiperdine (TMP), triethylamine (TEA), trioctylamine (TOA) and 1,5-diazobicyclo[4.3.0]non-5-ene (DBN). The presence of amines of basicity sufficient to abstract protons from the polymer backbone might be expected to introduce unsaturation via an E2 process and thus to increase the number of initiation sites for the thermal degradation [7]. This should be reflected in an enhanced rate of initiation for the degradation. As can be seen in Fig. 1, this was indeed the case for all the amines examined. In every instance the onset temperature for degradation of the polymer is lower in the presence of amine than in its absence (see Table 1). More significantly, the slope of the weight loss vs. temperature plot in the region in which initiation of degradation is occurring, changes dramatically with increasing basicity of the amine present. The slopes of the plots corresponding to greater weight loss where propagation of dehydrohalogenation is the prominent process are also altered but to a much lesser extent. Clearly, initiation of polymer degradation is enhanced in the presence of a compatible base. As was expected [13–16], DBN is the most effective amine for the base-promoted dehydrohalogenation. The introduction of unsaturation via amine interaction generates a

TABLE 1

Onset temperatures for the thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of amines

| Amine [a] | Degradation onset temperature (°C) [b] |
|---|---|
| None | 186 |
| 1,4-Diazobicyclo[2.2.2]octane (DABCO) | 175 |
| 2,2,6,6-Tetramethylpiperidine (TMP) | 161 |
| Triethylamine (TEA) | 158 |
| Trioctylamine (TOA) | 136 |
| 1,5-Diazobicyclo[4.3.0]non-5-ene (DBN) | 127 |

[a] All amines were present at 10 pph.

[b] Temperature at which detectable weight loss occurred.

polymer with many more defect sites (allylic dichloromethylene units) from which thermal degradation may be readily initiated.

A more quantitative reflection of the impact of the presence of amine on the degradation may be obtained by determining the rate constants for both the initiation and propagation phases of the dehydrochlorination reaction. As has been described previously [12], this could most conveniently be done using the Du Pont model 951 TGA unit. The furnace was equilibrated at the desired temperature for degradation, usually 120°C, with the sample chamber outside the furnace. When the furnace had come to the desired temperature, the sample chamber was slipped into the furnace and data collection was started almost immediately. In this way, meaningful data for the early portion of the degradation for which initiation is the prominent process could be obtained. A plot of ln $m$ vs. $t$ could

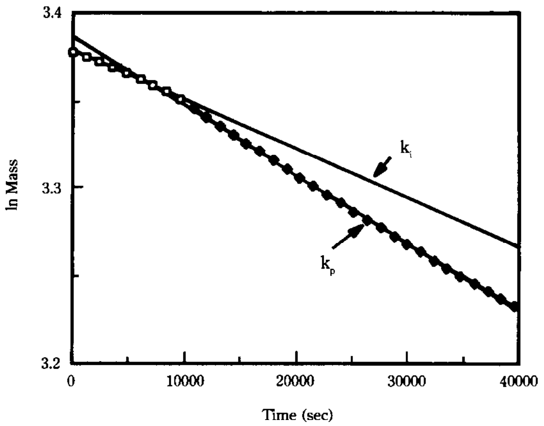

Fig. 2. Isothermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of 10 pph DBN at 120°c.

TABLE 2

Rate constants for the degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of 10 pph of selected amines at 120°C

| Amine present | $k_i \times 10^7$ ($s^{-1}$) | $k_p \times 10^7$ ($s^{-1}$) |
|---|---|---|
| None | 0.490 | 0.669 |
| DABCO | 5.51 | 2.84 |
| TMP | 6.34 | 4.04 |
| TEA | 9.66 | 3.26 |
| TOA | 14.6 | 6.44 |
| DBN | 28.1 | 39.4 |

then be used to obtain both $k_i$ and $k_p$, the initiation and propagation rate constants respectively. Such a plot for the decomposition of the polymer in the presence of DBN is shown in Fig. 2.

The rate constants obtained for polymer degradation in the presence of the five different amines are presented in Table 2. As can be seen, all the amines examined are effective in promoting the thermal degradation of the polymer. The overall effectiveness of a particular amine may be attributed to a combination of several properties including inherent basicity, degree of steric hindrance at the nitrogen, and compatibility with the polymer. DBN is unhindered, strongly basic and very weakly nucleophilic. It is, therefore, not surprising that it is most effective in promoting the dehydrohalogenation reaction.

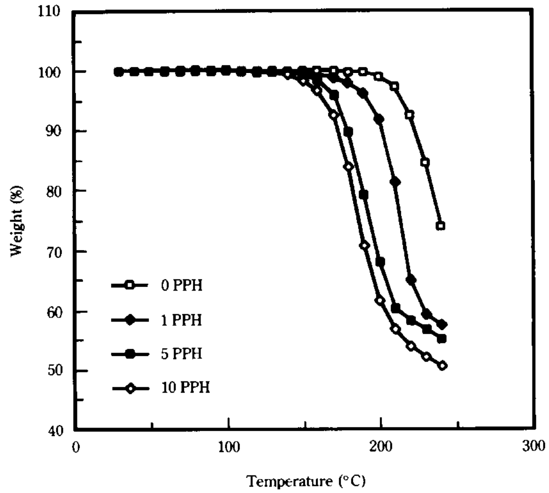

Fig. 3. Thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of increasing levels of trioctylamine: impact of amine loading on degradation initiation.

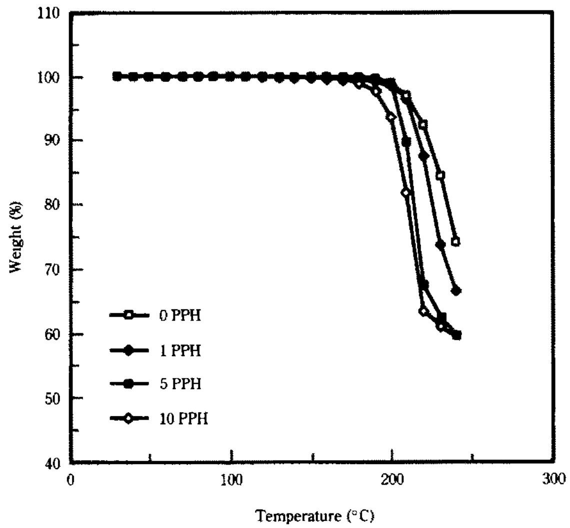

Fig. 4. Thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of increasing levels of 2,2,4,4-tetramethylpiperidine.

The effect of concentration and access of the amine nitrogen on the degradation process is demonstrated in Figs. 3 and 4. Figure 3 represents the thermal degradation of the polymer in the presence of 0, 1, 5 and 10 pph trioctylamine. As the level of amine loading is increased, the rate of initiation of degradative dehydrochlorination increases. This is indicated by both the initial slopes of the weight loss vs. temperature plots and by the onset temperature for degradation. Figure 4 provides similar information for the degradation of the polymer in the presence of TMP. Here again, increasing amine loading leads to an enhanced rate of initiation of degradation. However, the impact of an equivalent amount of TOA is much greater than that observed for TMP. TMP is a much more sterically hindered base than TOC and is correspondingly less effective in promoting the dehydrochlorination reaction.

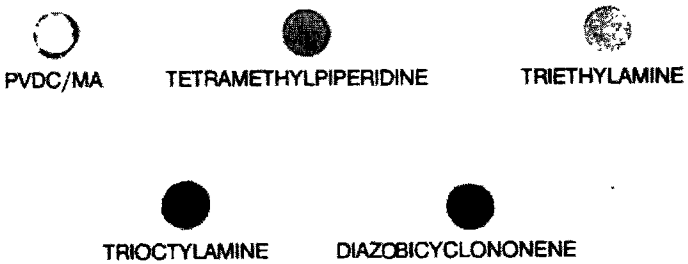

Fig. 5. Impact of the presence of amine on the color of a vinylidene chloride/methyl acrylate copolymer.

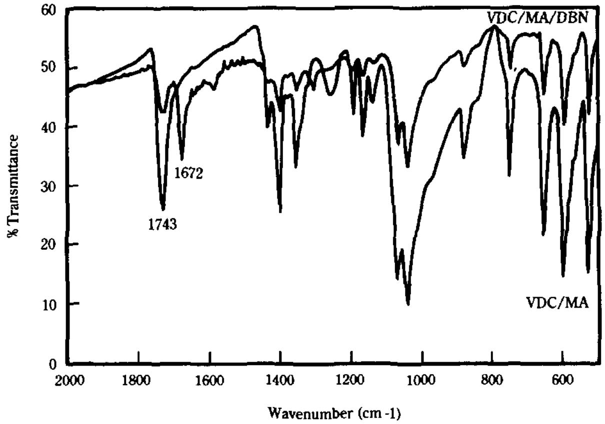

Fig. 6. IR spectra of a vinylidene chloride/methyl acrylate copolymer containing no amine additive, and of the same polymer containing 10 pph DBN.

That the amines are effective in introducing conjugated unsaturation along the polymer backbone is apparent in two ways. Firstly, as may be seen in Fig. 5, the polymer acquires a brown coloration in the presence of amine. The intensity of this coloration increases with increasing effectiveness of the amine in generating initiation sites for the thermal dehydrohalogenation reaction (see Table 2), i.e. there is a direct correspondence between the color induced and the magnitude of the rate constants for initiation of the thermal reaction. The effectiveness of the various amines in promoting color development in the polymer is as follows: TMP < TEA < TOA < DBN. Secondly, the IR spectra of the polymer after treatment with amine contain a prominent band at 1672 $cm^{-1}$ due to the presence of

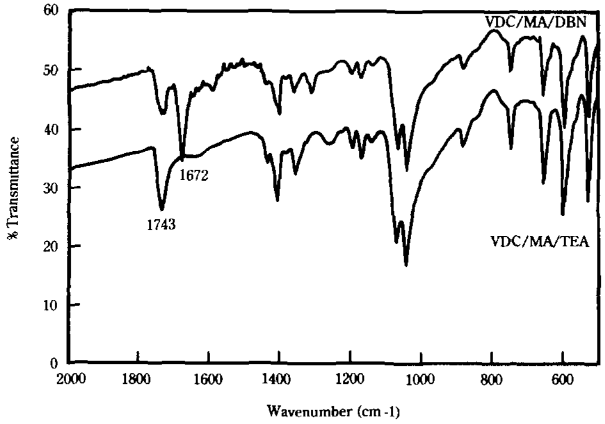

Fig. 7. IR spectra of a vinylidene chloride/methyl acrylate copolymer containing 10 pph DBN, and of the same polymer containing 10 pph TEA.

unsaturation. Figure 6 displays the IR spectra of both the untreated polymer and of that containing 10 pph DBN. The absorption due to the presence of unsaturation is prominent in the spectrum of the amine-treated polymer. The effectiveness of the various amines in promoting dehydrohalogenation is also apparent in the IR spectrum of the polymer containing amine. Figure 7 contains spectra of the polymer containing equivalent amounts of DBN and TEA. It is readily apparent that DBN is much more effective (intensity of the 1672 $\mathrm{cm}^{-1}$ band) in promoting double-bond formation than is TEA. Similar comparisons with spectra of the polymer containing the other amines examined clearly establish that DBN is the most effective in bringing about dehydrohalogenation of the polymer.

## CONCLUSIONS

The thermal degradation of a vinylidene copolymer is enhanced in the presence of amines. The amine functions as a base to remove hydrogen chloride and introduce unsaturation along the polymer backbone. Double bonds introduced in this manner serve as defect sites at which thermal degradation can be readily initiated. This is reflected as an increased rate of initiation for the thermal degradation process. The overall effectiveness of a particular amine for dehydrochlorination may be dependent upon several factors including inherent basicity, degree of steric hindrance at the nitrogen, and compatibility with the polymer.

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