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THERMAL DEGRADATION OF VINYLIDENE CHLORIDE/4-VINYLPYRIDINE COPOLYMERS

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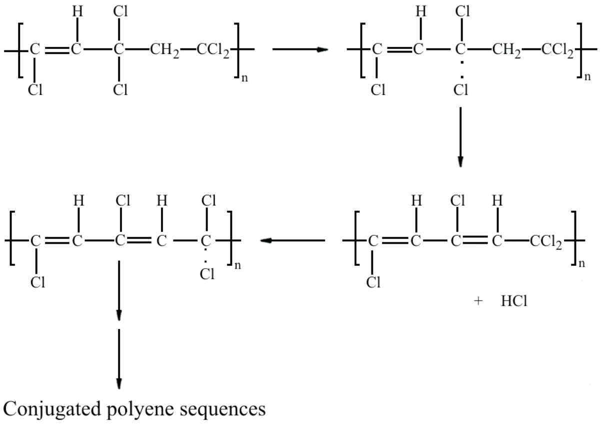
Vinylidene chloride polymers are prominent in the barrier plastics packaging industry. They display good barrier to the transport of oxygen (to prevent spoilage of food items) and flavor and aroma constituents (to prevent ‘scalping’ on the supermarket shelf). However, these polymers undergo thermal dehydrochlorination during processing. This can lead to a variety of problems including the evolution of hydrogen chloride which must be scavenged to prevent its interaction with the metallic walls of process equipment. Such interaction leads to the formation of metal halides which act as Lewis acids to facilitate the degradation. A potentially effective means to capture hydrogen chloride generated might be to incorporate into the polymer a mild organic base. Accordingly, copolymers of vinylidene chloride and 4-vinylpyridine have been prepared and subjected to thermal aging. Results suggest that the pyridine moiety is sufficiently basic to actively promote dehydrochlorination in the vinylidene chloride segments of the polymer.

Keywords: *barrier polymers, NMR spectroscopy, stabilization, vinylidene chloride copolymers*

Introduction

Permeation of a variety of compounds in vinylidene chloride polymers is extremely slow. This property has placed these materials in a position of prominence in the barrier plastics packaging industry [1]. Packaging containing these polymers as a functional component prevents the ingress of oxygen which would lead to the spoilage of food items and at the same time prevents the loss of flavor and aroma compounds such that the attractiveness and palatability of packaged food items are not diminished during periods of storage. The polymers are used both as monolithic structures in flexible packaging applications, e.g., as wraps for meat and dairy products, and as a central component of rigid multilayer structures (bottles, tubs, jars, etc.). While these polymers have very desirable properties for the construction of packaging they must be processed with care at relatively low temperatures (150–170°C) in specially designed equipment. This limitation arises from the propensity for these polymers to undergo thermally-induced degradative dehydrochlorination at the melt temperature [2].This process has two deleterious effects which must be controlled. If unchecked, successive dehydrochlorination along the polymer mainchain will lead to the formation of polyene sequences large enough to absorb in the visible portion of electromagnetic spectrum and impart color to the material (Scheme 1).

A second impact of this degradation is the evolution of hydrogen chloride which can interact with the walls of process equipment to form metal halides, particularly iron chlorides, which act as Lewis acid catalysts to strongly promote the dehydrochlorination reaction [3]. To prevent this a passive base capable of absorbing hydrogen chloride must be present in the polymer melt either as an additive or as an integral part of the polymer.



Scheme 1 Mode of degradation of vinylidene chloride polymers

Experimental

Methods and instrumentation

Polymers were characterized by spectroscopic, thermal, and chromatographic methods [4]. Differential scanning calorimetry (DSC) was carried out at a heating rate of 5°C min^{-1}, using a TA Instruments Inc.

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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 mL min^{-1}. Size exclusion chromatography (SEC) was accomplished using solutions in tetrahydrofuran, microstyrogel 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). The data acquisition parameters for ^{13}C NMR spectra obtained at 75.5 MHz were a pulse width of 90°, 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.

Polymers

Copolymers of vinylidene chloride and 4-vinylpyridine containing varying levels of 4-vinylpyridine were prepared by suspension polymerization using AIBN as initiator and methods previously described [2].

Assessment of polymer thermal stability

To assess the thermal stability of various vinylidene chloride/4-vinylpyridine copolymers samples of approximately 0.5 g in mass were oven aged at elevated temperatures (100–150°C) for times ranging from 0.1 to 2.0 h. The level of dehydrochlorination induced by the thermal treatment was qualitatively apparent from the intensity of the discoloration of the sample. A quantitative reflection of the level of degradation was obtained from the ^{13}C NMR spectra of the degraded samples. With increasing length of time at a particular elevated temperature, the intensity of absorption due to the presence of unsaturated carbon atoms in the polymer increased in a regular fashion.

Results and discussion

Vinylidene chloride copolymers undergo degradative dehydrohalogenation at process temperatures. To scavenge hydrogen chloride formed, the stabilization system for these polymers generally contains a passive base. Often this is a maingroup metal oxide or a polyvalent oxyanion salt. The presence of these inorganic stabilizers may contribute negatively to the clarity of the finished product. For this reason organic stabilizers which would be compatible with the polymer, which would effectively absorb evolved hydrogen chloride, and which would not actively promote the dehydrochlorination reaction have been sought. Amines, even highly hindered amines, have been found to be too basic to function as satisfactory stabilizers [5, 6]. The incorporation of a comonomer containing a basic site into these polymers could eliminate the need for a stabilizing additive. In this case copolymers of vinylidene chloride (VDC) and 4-vinylpyridine (VP) have been prepared, characterized, and subjected to oven aging to assess their thermal stability. Initial experiments established that degradation of copolymers containing various levels of 4-vinylpyridine was exceedingly facile at temperatures approaching those required for melt processing. For example, one hour at 150°C was sufficient to convert most of the samples to carbon. A polymer containing 12 mol% 4-vinylpyridine was selected for greater study. A series of six samples of this polymer of approximately 0.5 g were aged at 150°C. The results were presented in Table 1.

As can be seen the loss of hydrogen chloride at 150°C is rapid. Twelve percent of the polymer mass is lost in only five minutes at this temperature. The polymer held at 150°C for 0.5 h has lost almost a full mole of hydrogen chloride, i.e., first-stage degradation is nearly complete at this point. As would be expected all samples rapidly decolored at 150°C. Even that heat treated for the shortest period of time was essentially black in color. The samples after heat treatment were insoluble in THF.

In order to better characterize the degradation, oven aging was carried out at 100°C. At this temperature the rate of degradation was lower and the samples of partially degraded polymer were soluble in THF so that analysis by NMR spectroscopy was possible. The ^{13}C NMR spectrum of a sample heated at 100°C for 20 min is shown in Fig. 1. Compositional changes were monitored using the VDC dichlorinated carbon atom sequences. The VVV (VDC-VDC-VDC) triad resonance appears at δ 84.7, that from the VVP

Table 1 Oven aging of a vinylidene chloride/4-vinylpyridine (12 mol%) copolymer at 150°C

Sample	Initial mass/g	Time/min	Final mass/g	Change/g	Change/mass%
1	0.4926	5	0.4342	0.0584	11.86
2	0.5293	10	0.4062	0.1201	23.26
3	0.5221	15	0.3768	0.1453	27.83
4	0.5242	20	0.3676	0.1566	29.87
5	0.5668	25	0.3835	0.1833	32.34
6	0.5685	30	0.3783	0.1902	33.46

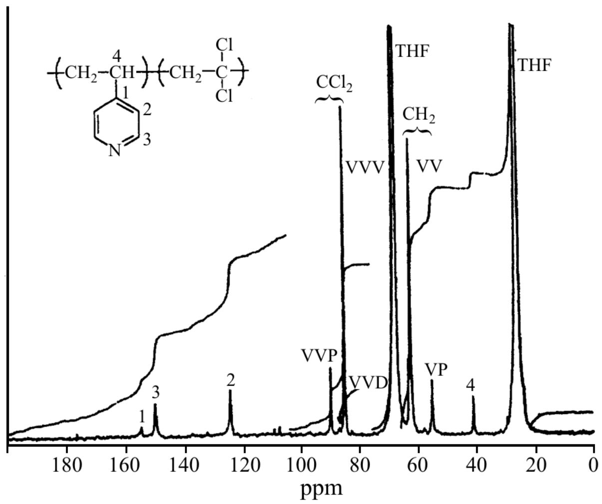

Fig. 1 The ^{13}C NMR spectrum of a vinylidene chloride/4-vinylpyridine (12 mol%) copolymer held at 100°C for 20 min

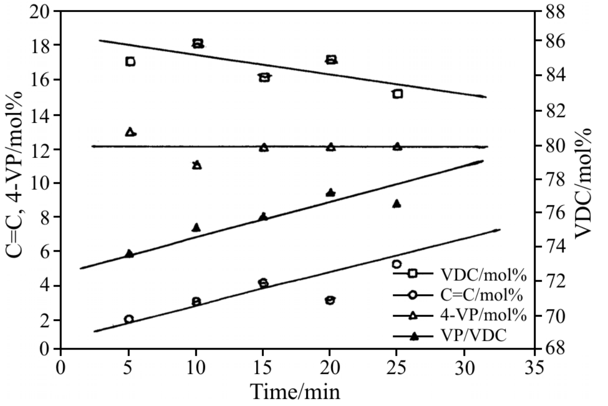

Fig. 2 Time dependence of the composition of a vinylidene chloride/4-vinylpyridine (12 mol%) copolymer undergoing thermal degradation at 100°C

(VDC-VDC-VP) triad at δ 89.5, and that from the VVD (VDC-VDC-C=C) triad at δ 86.3. The most obvious change in the spectrum as the degradation proceeds is the growth of the VVD triad resonance. The time dependence of the level of these three species during the degradation is displayed in Fig. 2. The ratio of VP/VDC determined from the areas of the VP methine resonance at δ 40.4 and that for VVV triad is also shown there. The data presented in Fig. 2 clearly show that the level of VDC in the copolymer is being depleted and that correspondingly the level of unsaturation (C=C) is increasing as the degradation proceeds. The fact that the degradation is so facile at a relatively modest temperature (100°C) suggests that the pyridine moiety is sufficiently basic so as to promote E2 elimination in VDC sequences to generate initiation sites (internal unsaturation; allylic dichloromethylene units) for the thermal dehydrochlorination.

Conclusions

Vinylidene chloride/4-vinylpyridine copolymers undergo facile thermally-promoted degradative dehydrochlorination. The pyridine moiety in the comonomer units of the polymers is sufficiently basic so as to actively strip hydrogen chloride from vinylidene chloride units to generate initiation sites for the thermal reaction.

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