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THE APPLICATION OF THERMOGRAVIMETRY FOR THE STUDY OF POLYMER DEGRADATION

B.A. HOWELL
Department of Chemistry and Michigan Polymer Consortium, Central Michigan University, Mt. Pleasant, MI 48859 (USA)

ABSTRACT

Polymer degradation continues to be of great theoretical and commercial, practical import. An understanding of the mechanism of degradation permits the projection of more suitable production/processing conditions, predictions of structural modifications which may extend use range, and more meaningful estimations of expected lifetime under a variety of conditions for a range of polymeric materials. Because of its simplicity and ease of application, thermogravimetry continues to be a convenient and attractive technique for the study of polymer degradation. However, the results to be obtained using this methodology are dependent upon a great many factors which must be controlled if the results are to be meaningful. Thermogravimetry is but one of a variety of techniques which may be applied to mechanism study and is most powerful when it is used in conjunction with techniques which permit the system under study to be well-defined.

INTRODUCTION

Most polymeric materials when subjected to sufficient thermal stress undergo degradation. Some polymers degrade randomly, some by chain depolymerization, and others suffer little chain scission but rather eliminate a low-molecular-weight fragment. This latter behavior is characteristic of poly(vinylidene chloride) (PVDC) and related vinyl polymers which generally undergo dehydrohalogenation at temperatures well below that required for significant chain scission. Since many degradation processes lead to loss of mass as the temperature is increased, thermogravimetry (TG) represents a convenient and popular method for studying these processes[1]. However, the mass loss profile observed upon thermal degradation is dependent upon a great many factors including the previous history of the sample (in particular, production variables and previous thermal stress may dramatically impact the nature and rate of decomposition observed), the physical state of the material during degradation, the environment in which the degradation is observed, the presence of processing aids, sample size, and several others. Further, for non-isothermal experiments, thermogravimetry is capable of rapidly providing information about reaction rates, reaction orders, energies of activation, and entropies of activation. Because of the ease with which numerical values for these quantities may be obtained, the temptation to record and report such values is often simply overwhelming. This is usually quite inappropriate since the degradation process may well not consist of a single well-defined reaction but rather may be complicated by the occurrence of several competitive reactions. As for any

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mechanism study the degradation process must be well-characterized for the TG results to be meaningful in any fundamental way. Such basic questions as: "what is the nature of the starting material?"; "what reactions occur upon thermal stress of the sample?"; "what are the identities of the volatile products of reaction?"; "what is the nature of the residue remaining after degradation is complete?" must be addressed for the power of TG methodology to be most properly utilized. Therefore, the utility of TG is greatest when it is used in conjunction with a variety of other techniques[2].

Because the method offers a simple and convenient approach for the evaluation of polymer stability, much effort has been directed toward the development of kinetic treatments based upon non-isothermal experiments using multiple heating rate techniques[3]. Perhaps the best of these is the Ozawa-Flynn-Wall method frequently referred to as the isoconversional method[4-7]. This approach does not require any assumptions with respect to the form of the kinetic equation and permits the determination of the apparent activation energy by plotting the log of the heating rate (β) versus the reciprocal of the absolute temperature (1/T) for fixed fractional weight loss values (α). However, even for this case, care must be exercised in the interpretation and application of the results obtained. These methods are somewhat more satisfactory for empirical lifetime predictions for polymeric materials[8]. However, even in this instance, the extrapolation from the experimental test conditions to actual service conditions may not be viable. Correlation of the test results with actual lifetime information is required to establish the validity of the method[9,10].

Despite the pitfalls associated with its use, TG can be a powerful asset in studies undertaken to establish the mechanism of degradation of polymeric systems[11]. In particular, the mode of degradation of poly(vinylidene chloride) and copolymers has been established using TG in conjunction with other instrumental and spectroscopic methods.

EXPERIMENTAL

Synthesis and Characterization

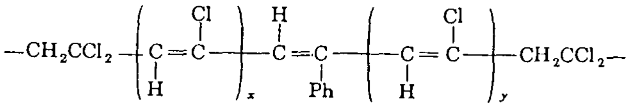
The synthesis and characterization of the polymers used in this work have been described elsewhere[12-16]. Four sets of materials which contain vinylidene chloride (VDC) as a major component were prepared and examined using thermogravimetric (TG) methods. The first was a series of vinylidene chloride/phenylacetylene (VDC/PA) copolymers containing small but varying amounts (0.0, 0.05, 0.1, 0.3, 0.5, 1.0 and 5.0 wt %) of phenylacetylene (to introduce a known concentration of unsaturation sites along the polymer chain), the second was a series of vinylidene chloride/methyl acrylate/ phenylacetylene (VDC/MA/PA) terpolymers containing a constant nine weight percent methyl acrylate and small but varying amounts of phenylacetylene, the third was a series of vinylidene chloride/methyl acrylate (VDC/MA) copolymers containing 0, 2, 5, 9, 12 and 20 weight percent methyl acrylate, and the fourth was a series of VDC oligomers of low molecular weight.

Degradation

Thermal degradation of the copolymers was examined thermogravimetrically using a DuPont model 951 TG unit coupled to the appropriate data handling accessories. The TG cell was swept with a nitrogen flow, 25 ml/min., during degradation runs, and the sample, approximately 30 mg, was contained in a platinum sample pan. To study decomposition propagation, samples were brought to 188°C (10 min were required for temperature equilibration) and weight loss was monitored as a function of time for at least two half-lives. To assess the impact of internal unsaturation on the rate of initiation of degradation, weight loss as a function of temperature was also examined. In a typical run, the temperature was ramped from 50 to 280°C at 5°C/min[12,13].

RESULTS AND DISCUSSION

Poly(vinylidene chloride) is the parent of a family of polymers which contain vinylidene chloride as a major component. The commercial advantage of these materials rests in their low permeability to both oxygen and flavor and aroma constituents[17]. Thus in food packaging applications oxygen transport into the container is prevented while flavor is maintained. These polymers are generally free of the defect sites characteristic of similar vinyl polymers, i.e., they are regular, head-to-tail, unbranched, highly crystalline polymers, yet they undergo degradation at relatively low temperatures. It might therefore be anticipated that internal double bonds introduced during the preparation and/or processing of these polymers are the sites responsible for the initiation of degradation. Accordingly, VDC polymers of approximately 100,000 weight-average molecular weight containing small but varying amounts of phenylacetylene as described above were prepared. The preparation of these materials was carried-out under controlled conditions at moderate (60°C) temperature. For all copolymers ^{13}C nmr analysis established that both phenylacetylene and methyl acrylate were randomly incorporated into the polymer and that the comonomers were incorporated at approximately the distributions in the initial monomer mixture[13-15]. In addition, it demonstrated that for the VDC/PA copolymers each phenylacetylene unit was contained within a polyene block of 7-8 units, i.e., the incorporation of phenylacetylene into a growing polymer chain had induced dehydrochlorination during the polymerization process such that structures of the following type had been formed[15].



$$-CH_2CCl_2-\left(\underset{H}{C}=\overset{Cl}{C}\right)_x-\overset{H}{C}=\underset{Ph}{C}-\left(\underset{H}{C}=\overset{Cl}{C}\right)_y-CH_2CCl_2-$$

Similar polyene blocks were also present in the VDC/MA/PA terpolymers except that the block length was somewhat shorter: 3-7 units. In both cases the number of polyene segments was equivalent to the amount of phenylacetylene incorporated, i.e., the number of unsaturation sites was directly reflected by the phenylacetylene incorporation Thus the purity, the thermal history, and the structure of all polymers was rigorously established prior to their use in degradation studies.

It has long been known that the degradation of poly(vinylidene chloride) and copolymers occurs in two distinct steps[18]. The first involves degradative dehydrochlorination via a chain process to generate poly(chloroacetylene) sequences. Subsequent Diels-Alder type condensation between conjugated sequences affords a highly crosslinked network which on further dehydrochlorination leads to the formation of a large surface area, highly absorptive carbon. The initial dehydrochlorination occurs at moderate temperatures (<200°C) and is a typical chain process involving distinct initiation, propagation, and termination phases[12]. It is this process which is of concern for most use applications and for which a detailed understanding was sought. It could be anticipated that the presence of unsaturation in polymers of this kind would lead to an enhanced rate of degradation. Introduction of a random double bond produces an allylic dichloromethylene unit activated for carbon-chlorine bond scission. Initiation by the thermally-induced cleavage of this bond followed by propagation by successive dehydrochlorination along the chain (the so called "zip" reaction) can then proceed readily. Rate constants for propagation of degradative dehydrochlorination for VDC/PA copolymers containing small but increasing amounts of unsaturation (induced by the presence of phenylacetylene in the polymer) were obtained by isothermal degradation of samples at 188°C and were found to be largely independent of the level of unsaturation present (the propagation rate constant for degradation of all samples was approximately 2 x 10^{-4} sec^{-1}). In contrast, the presence of unsaturation dramatically affects the rate of initiation for the dehydrochlorination reaction.

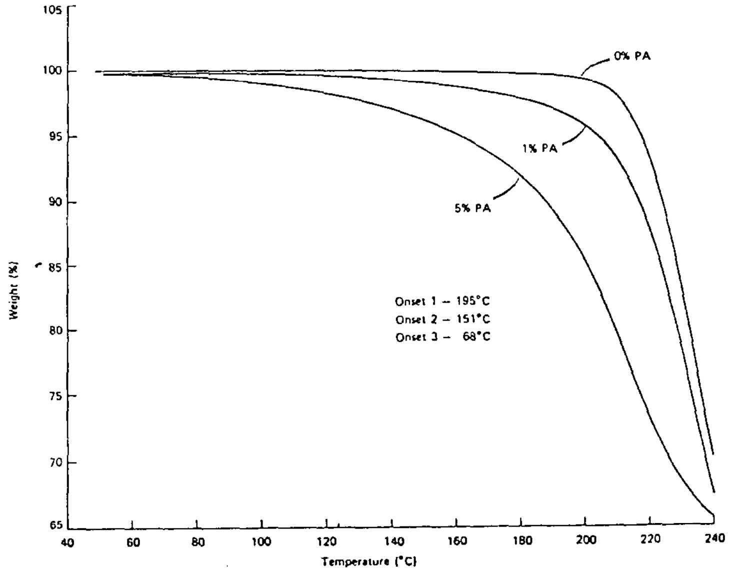


Figure 1. Weight loss for vinylidene chloride/phenylacetylene (VDC/PA) copolymers as a function of temperature: Impact of the presence of unsaturation on the initiation of degradative dehydrochlorination.

The data displayed in Figure 1 emphasize this observation and further indicate that with higher levels of unsaturation, the temperature at which degradation becomes prominent is lower. As evidenced by the point at which the plots (weight loss versus temperature) change slope (195°C for 0% PA, 151°C for 1% PA, 68°C for 5% PA), the onset of degradation is substantially earlier for copolymers containing higher levels of phenylacetylene. Further, as can be seen from the initial slopes of these plots, the rate of initiation increases markedly with increasing phenylacetylene content. As initiation is complete and propagation becomes the dominant process the slopes of the plots become quite similar.

The degradation of these copolymers in bibenzyl solution at 200°C provides further support for the description presented above and adds one vital observation. The impact of increasing phenylacetylene content was to increase the magnitude of the hydrogen chloride evolution during the initiation phase of the degradation. Rate constants for the propagation stage of the reaction were again effectively the same and independent of the level of unsaturation initially present in the polymer. Thus the degradation carried out in nonpolar solvent is very similar to that in the solid phase. Degradation in bibenzyl solution permits an assessment of the radical character of the reaction. Bibenzyl is an efficient scavenger which is converted to a product, stilbene, that can be readily quantified by GLPC. For these reactions the ratio of hydrogen chloride evolved to stilbene produced was ca. 35:1. This contrasts sharply with similar observations for the decomposition of various other materials which degrade by free-radical dehydrohalogenation in which the hydrogen halide/stilbene ratio often approaches the theoretical limit of 2:1. This suggests that the chlorine atom of the initially formed radical pair preferentially abstracts an adjacent hydrogen atom rather than interacting with solvent or that the radical component of the reaction is small. Much evidence has been accumulated to establish this radical nature of the reaction. Prominent components of this include slight inhibition of the reaction by certain radical scavengers and changes in the electron spin resonance (ESR) spectrum of a sample undergoing degradation.[18] Both suggest that radical intermediates are generated during the degradation. However, as was observed in this case, the concentration of "free" radical species (sufficiently free to interact with added scavenger molecules) is quite low.

The characterization of the residue from the degradative dehydrochlorination of these and related polymers (analogous results were obtained using the methyl acrylate copolymers) has been hampered by the fact that sufficient crosslinking occurs early in the reaction so that solubility in most solvents is lost. Since the structure of the degradation residue might be inferred from examination of the products which arise from the thermal decomposition of lower molecular weight analogs of these polymers, a series of oligomers were prepared by chlorine-atom-initiated telomerization of VDC monomer in carbon tetrachloride solution, subjected to thermal degradation and examined by nmr (^{1}H and ^{13}C) spectroscopy[16].

In total, the available evidence would suggest that random double bonds in the structure of VDC polymers are the principal defect sites responsible for the initiation of degradation and that propagation occurs via an allylic radical pair from which dehydrochlorination, i.e., abstraction of a hydrogen atom adjacent to the radical site, occurs far more rapidly than does dissociation of the radical components. The enhancement of VDC polymer degradation by metal ions, polar solvents, and other agents most probably occurs via the introduction of random double bonds into the polymer structure. Thus the mode of degradation of these polymers has been established using thermogravimetry as a basic technique. This was made possible by the availability of polymer samples of well-defined origin and purity, the ability to determine the total unsaturation present by ultraviolet spectroscopy, the ability to characterize the unsaturation by ^{13}C nmr spectroscopy, an assessment of the radical nature of the reaction by polymer decomposition in bibenzyl solution, an earlier determination that the only volatile product of degradation was hydrogen chloride, and spectroscopic examination of degradation residue.

CONCLUSIONS

As has been demonstrated, thermogravimetry can be a powerful tool for the study of the mechanism of polymer degradation. It is, however, but one technique and cannot alone be expected to provide a detailed understanding of thermal degradation processes. It is most useful in conjunction with other available techniques which permit the characterization of the transformations which occur during degradation.

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