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UTILIZATION OF THERMOGRAVIMETRY IN THE STUDY OF REACTION MECHANISM

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Thermogravimetry is often used to study polymer degradation. Most often the information obtained may have some practical application but is of limited value for the determination of fundamental processes which may be occurring. A kinetic expression or activation parameters for a complex process which may involve consecutive or parallel reactions provides almost no information about any of the reactions that might be occurring. However, for single, well-defined processes, thermogravimetry, in conjugation with other analytical methods, can be effectively utilized in the determination of reaction mechanism. The thermal degradation of vinylidene chloride barrier polymers corresponds to the elimination of hydrogen chloride initiated at an allylic dichloromethylene unit in the mainchain. This process is uncomplicated by competing reactions.

Thermogravimetry may be utilized to obtain meaningful rate constants and activation parameters for the degradation. This in conjunction with mass spectral analysis of evolved gas, characterization of both the polymer and degradation residue by ultraviolet, infrared and ^{1}H and ^{13}C NMR spectroscopy, and the study of model compounds has permitted a detailed description of the degradation process. General purpose poly(styrene) is a commodity polymer widely used in the food packaging industry as well as many others. If processed at excessively high temperature, it undergoes thermal degradation to expel styrene monomer which can impart negative flavor and aroma characteristics to packaged food items. The degradation reaction has been fully detailed using thermogravimetry in conjugation with evolved gas analysis, size exclusion chromatography and NMR spectroscopy.

Keywords: *barrier polymers, chromatographic characterization, defect structures, degradative dehydrochlorination, evolved gas analysis, spectral characterization, thermal degradation*

Introduction

The thermal degradation of polymeric materials is much studied. The degradation characteristics of a particular material may largely define its use range. Thermogravimetry is often utilized to examine the degradation of polymeric materials. Most often degradation as a function of increasing temperature is monitored. While this approach is useful for determining the response of the material to thermal stress it yields almost no information about the fundamental processes responsible for degradation. Multiple processes often contribute to degradation and these change as a function of temperature. While it is common practice to extract ‘global’ activation parameters for polymer degradation these quantities have no fundamental significance. In fact, the recorded activation energy may vary as a function of temperature since the nature of the reactions occurring change as the temperature changes. The ‘activation energy’ obtained is not a reaction parameter at all but rather is a composite to which many processes may contribute. In contrast, for cases in which degradation corresponds to a single, well-defined process, thermogravimetry can provide sound data that may be utilized in the establishment of reaction mechanism. Two such cases are the thermal degradation of vinylidene chloride barrier polymers and the decomposition of atactic poly(styrene) produced by conventional radical techniques. However, even in these ‘best case’ situations it is necessary to use other techniques in conjunction with thermogravimetry to fully characterize the structural and chemical changes which correspond to degradation. In particular, chromatographic and spectroscopic techniques are often essential for characterization of both the substrate and the nature of volatile fragments formed as the degradation proceeds.

Experimental

Polymers

Vinylidene chloride/acrylate copolymers were prepared by AIBN-initiated suspension polymerization [1]. Atactic general purpose poly(styrene) was obtained by azo initiated radical polymerization of styrene in benzene at 60°C [2, 3]. Head-to-head poly(styrene) was obtained by hydrogenation of poly(2,3-diphenyl-1,3-butadiene) [2]. Fully head-to-tail poly(styrene) containing no head-to-head units was

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obtained by nitroxyl-mediated radical polymerization of styrene followed by reductive removal of the nitroxyl and groups [3]. Poly(styrene) produced by anionic polymerization was purchased from Showa Denko K.K.

Methods

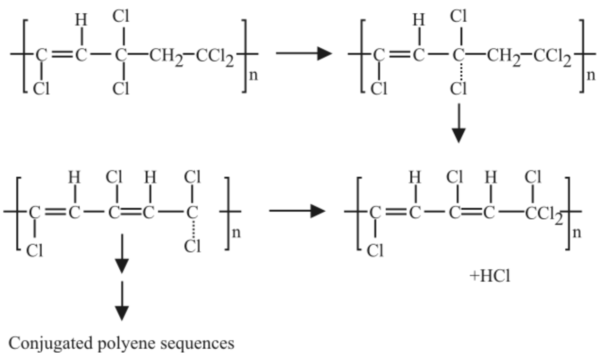
Polymers were characterized by spectroscopic, thermal and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained in deuterochloroform using a General Electric QE-300 spectrometer. Infrared spectra were obtained using solid dispersions (l%) in anhydrous potassium bromide (as pellets) or thin films between sodium chloride discs using a model 560 Nicolet MAGN-IR spectrophotometer. Molecular masses of the polymers were routinely determined by size exclusion chromatography (SEC) using solutions in THF, miscrostyrogel columns, and linear poly(styrene) calibration. For branching studies, solutions were prepared at a concentration of 1 mg mL^{-1} in THF and filtered through a 0.2 μm PTFE filter. The injection volume was 50 mL. THF was used as eluant at 1 mL min^{-1}. Separation was accomplished with three mixed bed columns (Polymer Laboratories) in series. For detection a Viscotek model H-502 differential viscometer was used in series with a Waters 2410 differential refractive index detector. Columns and detectors were held at 35°C. Narrow distribution poly(styrene) standards were used to generate the universal calibration curve. Polystyrene 1683, a broad, linear poly(styrene) standard was used to verify system performance.

The glass transition temperatures (T_g) of polymers were determined using differential scanning calorimetry (DSC) at a heating rate of 10°C min^{-1}, using a TA Instruments Inc., Thermal Analyst model 2100 system equipped with a model 2910 MDSC cell. The sample compartment was subject to a constant purge of dry nitrogen at 50 mL min^{-1}. The thermal degradation characteristics were examined by thermogravimetry using a TA instruments model 2950 TG unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs. The sample size was approximately 5–10 mg in a platinum sample pan. The temperature was ramped at a rate of 2 or 10°C min^{-1}.

For isothermal kinetic studies the temperature was held at a specific temperature between 170 and 350°C. Mass loss was recorded as a function of time. Evolved gas analysis was accomplished using a Thermo Cahn TG-2131 microbalance in conjunction with a Thermo Finnigan TRACE GC/MS instrument. Approximately two mg of sample contained in platinum sample pan was placed in the furnace. The furnace compartment was purged with helium at a flow rate of 50 mL min^{-1} for 20 min prior to analysis. The temperature of the furnace was ramped from 25°C to the set point (280, 320, 350°C) at 10°C min^{-1} and held at the set temperature for 60 min. For the TG/MS analysis, the TG transfer line was maintained at 250°C in the GC oven. The mass spectrometer was operated in the electron impact mode using 70 eV electrons for ionization. The detector was maintained at 400 V. During the TG/MS experiment, a portion of the volatiles were collected in a cryotrap which was maintained at –100°C. After the TG/MS experiment was complete, the GC oven was cooled to ambient temperature and analysis of the mixture of volatiles in the cryotrap initiated. The column used was a Restek Corporation RTX-5MS of 15 m length and 0.25 mm internal diameter with a film thickness of 0.25 micron. The temperature program used was 40°C for 2 min and then 40 to 330°C at 10°C min^{-1}. Programmed flow was used for the helium carrier gas. The flow was maintained at 4.5 mL min^{-1} for the first 4.5 min to maximize the amount of analyte pushed onto the column from the cryotrap. After that, the flow was reduced to 1.5 mL min^{-1} for the remainder of the analysis.

Results and discussion

Because of their importance in the barrier plastic packaging industry the degradation of vinylidene chloride polymers has been extensively studied [4–6]. The commercial prominence of these polymers is a consequence of low permeability of oxygen and flavor/aroma constituents such that food quality is maintained in packaging prepared from these materials [7–9]. These polymers are generally free of the defect sites characteristic of similar vinyl polymers, i.e., they are regular head-to-tail, unbranched and highly crystalline polymers [10]. However, when subjected to thermal stress, these polymers undergo degradative dehydrochlorination. This thermal dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination phases [10]. Unsaturation in these polymers appears to be a principal defect structure (allylic dichloromethylene units) responsible for degradation [10, 11]. Thermal homolysis of an allylic carbon-chlorine bond generates a tight carbon chlorine radical pair. The chlorine atom most generally abstracts an adjacent hydrogen atom to extend the unsaturation by one unit, to regenerate an allylic dichloromethylene group, and to propagate the dehydrochlorination reaction. This outlined below in Scheme 1. The consequence of



Scheme 1 Mode of degradation of vinylidene chloride polymers

sequential dehydrochlorination is the formation of conjugated polyene sequences of sufficient size to absorb in the visible portion of the electromagnetic spectrum. This leads to the development of color which may be aesthetically unpleasing in an item of packaging. For this reason degradation during processing must be controlled. Effective stabilization strategies depend on a detailed understanding of the degradation mechanism. A profile for the evolution of hydrogen chloride accompanying the degradation of a typical vinylidene chloride polymer is displayed in Fig. 1. This reaction is ideally suited for study by thermogravimetry since the only process occurring at modest temperatures (120–200°C) is the loss of hydrogen chloride, i.e., no other volatile products are formed at these temperatures [12]. Therefore, the rate of change of sample mass accurately reflects the rate of degradation. A curve for degradation of a typical vinylidene chloride polymer as a function of temperature is shown in Fig. 2. As can be seen degradation becomes prominent as the temperature approaches 200°C and occurs smoothly to reflect the loss of hydrogen chloride from each vinylidene chloride mer unit in the polymer. The curve for isothermal degradation of the same polymer at 180°C is displayed in Fig. 3. Both the initiation and propagation phases of the degradation are apparent in this plot. These regions are even more obvious in a plot of $\ln[(w_\infty - w_0)/(w_\infty - w_t)]$ *vs*. time where w_∞ is the mass of the sample at infinite time (t_∞) taken as that mass remains after 37.62% of the initial vinylidene chloride component mass (corresponding to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the polymer) has been lost; w_0 is the mass at time zero (t_0), i.e., the time at which the first data

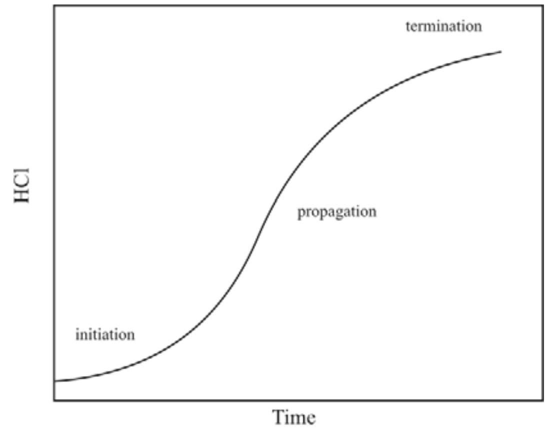


Fig. 1 Hydrogen chloride evolution for the thermal degradation of a typical vinylidene chloride polymer

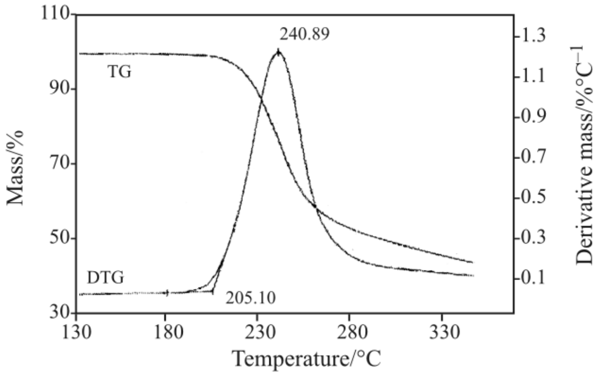


Fig. 2 TG/DTG curves for the degradation of a typical vinylidene chloride polymer

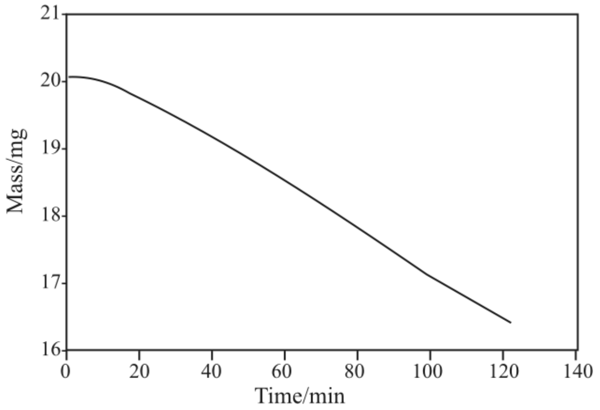


Fig. 3 Degradation of a typical vinylidene chloride polymer at 180°C

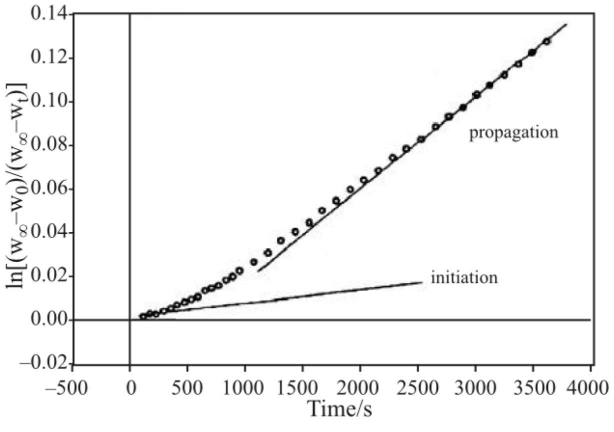


Fig. 4 Thermal degradation of a typical vinylene chloride polymer at 180°C

Table 1 Rate constants for the thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer

$k_i \cdot 10^5$/s^{-1} [a,c]	$k_p \cdot 10^5$/s^{-1} [b,c]	Temperature/°C
1.56±0.05	2.24±0.10	170
3.32±0.16	4.15±0.01	180
6.26±0.12	8.91±0.09	190
14.56±0.58	17.75±0.16	200

[a] Rate constant for the initiation of degradation.
[b] Rate constant for the propagation of degradation.
[c] Average of three determinations accompanied by the average deviation

point was recorded and w_t is the mass at any time t, during the run. This is illustrated in Fig. 4.

Rate constants for both initiation (k_i) and propagation (k_p) may be obtained from the appropriate linear portions of this plot. This is illustrated in Figs 5 and 6 in which portions of the data presented in Fig. 1 are replotted. It might be noted that an excellent least squares fit is obtained in both cases. In practice, data for multiple runs are plotted and the average reported as the rate constant. This permits a ready assessment of the uncertainty in the value for the rate constant. Reproducibility is typically excellent. Determination of rate constants at several temperatures (e.g., 170, 180, 190, 200°C) provides the data needed for the construction of a plot of ln(k/T) *vs.* $1/T$ (where k is the rate constant and T is the corresponding Kelvin temperature) and the extraction of the enthalpy of activation ($\Delta H^{\ddagger}$) [1, 3]. This is illustrated below for the degradation of a vinylidene chloride/methyl acrylate (five mole percent) copolymer. Rate constants for the degradation at several temperatures are displayed in Table 1.

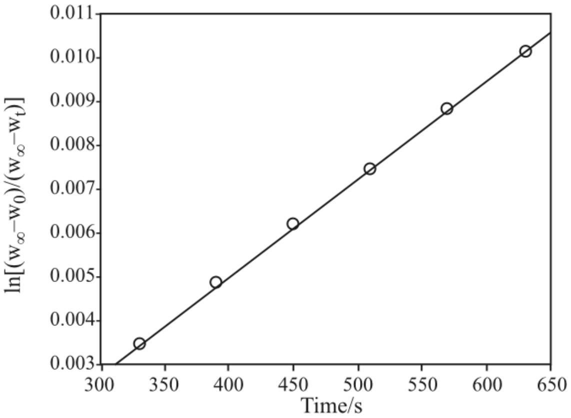


Fig. 5 Initiation rate constant (k_i) for the thermal degradation of typical vinylidene chloride polymer 180°C

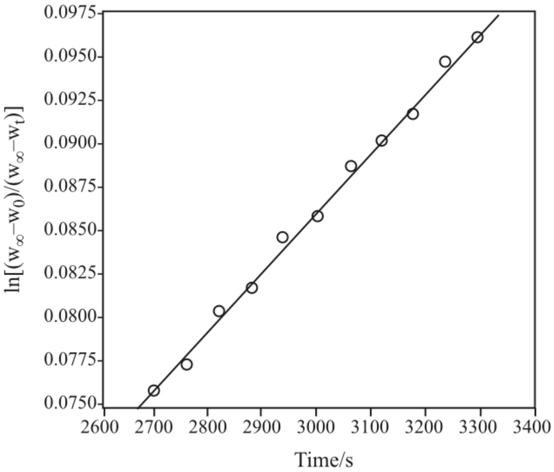


Fig. 6 Propagation rate constant (k_p) for the thermal degradation of typical vinylidene chloride polymer 180°C

The corresponding activation parameters are contained in Table 2. These parameters, both the activation enthalpy and activation entropy, serve to define the degradative dehydrochlorination reaction [13]. Thus fundamental information about the reaction may be obtained from thermogravimetry. These data combined with the observation that the rate of reaction is retarded in the presence of radical scavengers, spectroscopic monitoring of poly(ene) formation in the degrading polymer, and analysis of the evolved gas by mass spectrometry and titrimetry provide strong support for the mechanism of reaction depicted in Scheme 1.

The thermal degradation of poly(styrene) often limits the processing window for the polymer and can lead to the introduction of unacceptable levels of monomer in finished articles, particularly those used in food packaging. Although the degradation has been much studied, a full understanding of the processes which occur has not been available owing, in the main, to the decomposition being examined as a function of increasing temperature or at high temperature (>300°C). Under either of these conditions many processes occur simultaneously. To better understand the degradation several poly(styrene)s have been

Table 2 Activation parameters for the degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer

Initiation of degradation		Propagation of degradation	
$\Delta H_i^{\ddagger}$/kcal mol^{-1} [a]	$\Delta S_i^{\ddagger}$/cal mol^{-1} °C^{-1}; 200°C	$\Delta H_p^{\ddagger}$/kcal mol^{-1} [a]	$\Delta S_p^{\ddagger}$/cal mol^{-1} °C^{-1}; 200°C
29.60	–14.45	28.14	–17.14

[a] Based on the uncertainty in the values for rate constants and the temperature control (±0.2°C) possible with the TG unit, the estimated uncertainty in activation values is less than 0.5 kcal mol^{-1}.
[b] Calculated from the expression: $\Delta S^{\ddagger}/R = \ln k - 23.760 - \ln T + \Delta H^{\ddagger}/R$ using the experimental activation enthalpy

examined by thermogravimetry (TG) with the volatile effluent from the decomposition being analyzed by gas chromatography/mass spectrometry (GC/MS). These include general purpose atactic poly(styrene) produced by conventional radical polymerization, a fully head-to-head poly(styrene) generated by hydrogenation of poly(2,3-diphenyl-1,3-butadiene), poly(styrene) containing no head-to-head units generated by nitroxyl-mediated radical polymerization of styrene followed by reductive removal of the nitroxyl end groups, and poly(styrene) produced by anionic techniques. The latter two polymers contain no head-to-head units as a consequence of the means of polymerization. The material from conventional radical polymerization contains one head-to-head unit as a consequence of polymerization termination by radical coupling [14]. The remaining polymer contains only head-to-head units.

A kinetic plot for the thermal degradation of general purpose poly(styrene) at 280°C is shown in Fig. 7. As may be noted two major processes are apparent. An initial early process is followed by a second which is much more rapid. Data for the early portion of degradation are replotted in Fig. 8.

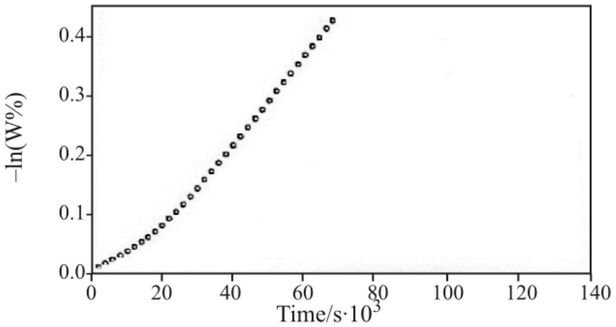


Fig. 7 Kinetic plot for the thermal degradation at 280°C of poly(styrene) produced by conventional radical techniques

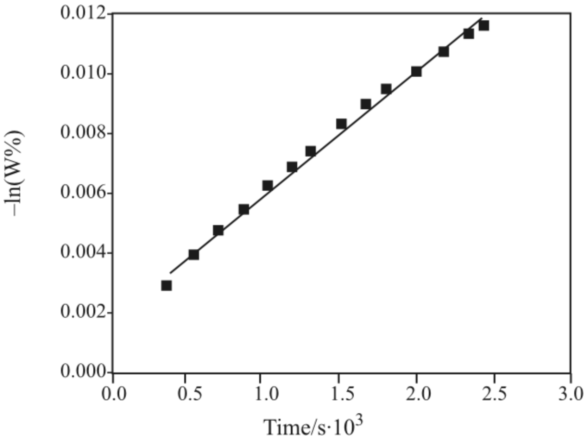


Fig. 8 Early portion of the kinetic plot for the thermal degradation at 280°C of poly(styrene) produced by conventional radical polymerization

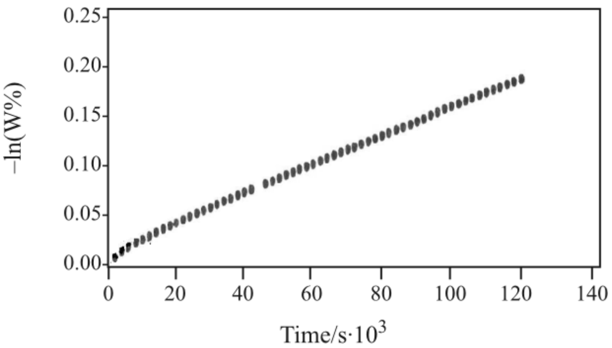


Fig. 9 Kinetic plot for the thermal degradation at 280°C of fully head-to-head poly(styrene)

The rate constant determined from the slope of this plot is $4.15\cdot10^{-6}$ s^{-1}. This is almost identical to the rate constant ($3.49\cdot10^{-6}$ s^{-1}) for the thermal degradation of the fully head-to-head polymer which is linear over the entire range of degradation (Fig. 9). This suggests that the same process is occurring during initial degradation of both polymers, i.e., the initial degradation of general purpose poly(styrene) containing a single head-to-head unit as a consequence of polymerization termination by radical coupling is identical to that of the fully head-to-head polymer.

This is likely mainchain scission at head-to-head units. The material produced by conventional radical polymerizations contains one head-to-head unit per chain as a consequence of termination by radical coupling [14]. The fully head-to-head polymer, of course, contains multiple head-to-head linkages. Degradation over the full range of decomposition corresponds to the cleavage of head-to-head units with little formation of volatile products. That this is indeed the case is apparent from 1. the observation that the molecular mass of the heat-to-head polymer continues to decrease as degradation occurs and 2. analysis of the effluent from degradation of the two polymers by GC/MS.

Evolved gas analysis for the degrading polymers was conducted by thermogravimetry/mass spectrometry (TG/MS) and thermogravimetry/gas chromatography/mass spectrometry (TG/GC/MS). In the first case, samples were held at 280°C for 80 min with any volatile fragments formed being carried by the helium purge gas to a mass selective detector tuned to *m*/*e* 104 (styrene monomer). For the head-to-head polymer no signal was detected nor was any measurable mass loss noted, i.e., the polymer was relatively mass stable at 280°C over the course of the experiment (it should be noted that the time at 280°C for this experiment was much shorter than that previously utilized for thermogravimetry at 280°C). In contrast, the conventional polymer lost 7.7% of its initial mass.

The TG/GC/MS experiments were even more revealing. The experiments were identical to those described above except that the volatiles formed from degradation of the polymer were carried onto the GC column prior to the mass selective detector. Again, the head-to-head sample lost very little mass at 280°C for 80 min. The behavior of the conventional polymer stands in sharp contrast to that of the head-to-head polymer. The TG/GC/MS chromatogram is shown below in Fig. 10. The only volatile compound formed from initial degradation of conventional poly(styrene) at 280°C is styrene monomer.

For comparison, both chromatograms are shown in Fig. 11.

It is clear in this comparison that while degradation of conventional poly(styrene) occurs when the polymer is subjected to 280°C for even a short time and that styrene monomer is evolved, the head-to-head polymer is relatively mass stable at this temperature and no styrene monomer is evolved.

The results of the evolved gas analysis are fully consistent with those generated by thermogravimetry. They suggest that the thermal degradation of conventional poly(styrene), particularly at low temperature (<300°C), is initiated at head-to-head linkages present in the polymer as a consequence of polymerization termination by radical coupling. The macroradicals formed then undergo sequential unzipping to evolve styrene monomer.

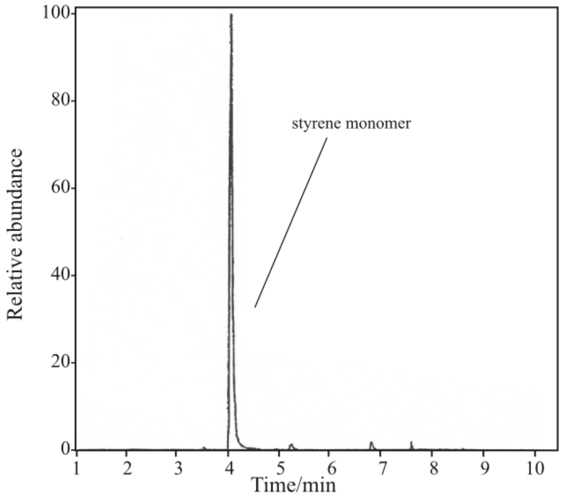


Fig. 10 Evolved-gas chromatogram (TG/GC/MS) for initial degradation of conventional atactic poly(styrene) at 280°C

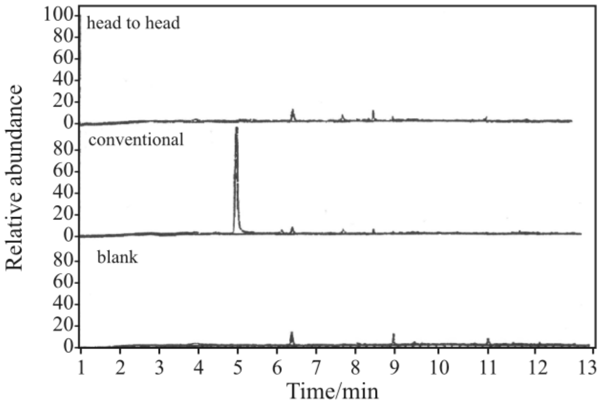


Fig. 11 Evolved-gas chromatograms (TG/GC/MS) for initial degradation of poly(styrene)s at 280°C

If the head-to-head linkage were not present the polymer should be much more thermally stable, i.e., the rapid evolution of styrene monomer at 280°C should not be observed. A fully head-to-tail polymer, i.e., a polymer containing no head-to-head units, was produced by nitroxyl mediated radical polymerization of styrene followed by reductive removal of the nitroxyl end groups [3]. A comparison of the degradation behavior of this polymer with that of conventional poly(styrene) is shown in Fig. 12.

The fully head-to-tail polymer (no head-to-head units) is much more stable at 280°C, than the conventional polymer. As noted above, two different processes are involved in the decomposition of the conventional polymer. The initial reaction involves mainchain cleavage at head-to-head units to produce macroradicals which then evolve monomer at a rate much greater than that for the initial chain cleavage. On the other hand, degradation of the fully head-to-tail (no head-to-head units) polymer results from random

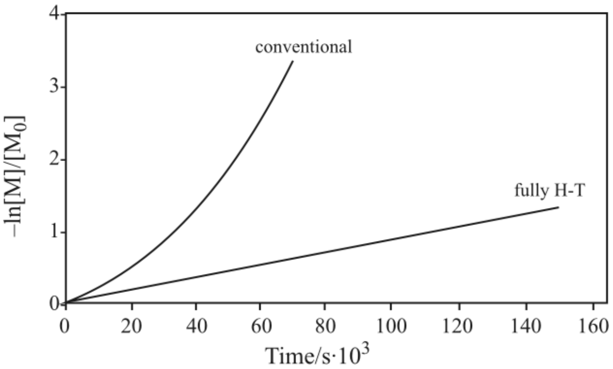


Fig. 12 Thermal degradation at 280°C of poly(styrene) containing no head-to-head units and poly(styrene) produced by conventional radical techniques

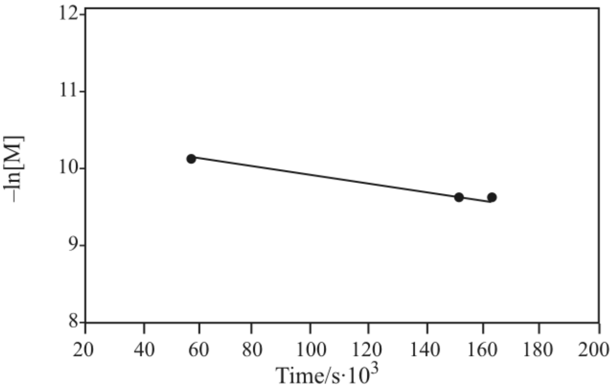


Fig. 13 Change in molar mass of fully head-to-tail poly(styrene) as function of time at 280°C

mainchain cleavage with a rate constant of $8.70\cdot10^{-6}$ s^{-1}. Random chain scission is confirmed by a decrease in polymer molecular mass as a function of time (Fig. 13). At higher temperatures the decomposition behavior of both polymers is more complex.

Plots for degradation at 320°C are displayed in Fig. 14.

When the decomposition temperature was raised to 350°C, the degradation characteristics of both polymers were very similar to those at 320°C. However, the degradation of conventional poly(styrene) was still much more rapid than that for the polymer containing no head-to-head units. At this temperature it is likely that several processes are occurring simultaneously, i.e., sufficient energy is available to bring about random chain scission in both polymers and structural differences are not as apparent as for degradation at lower temperatures.

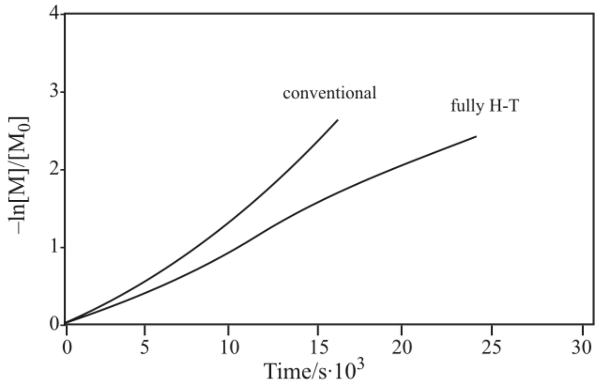


Fig. 14 Kinetic plots for thermal degradation of poly(styrene) containing no head-to-head units and general purpose poly(styrene) at 320°C

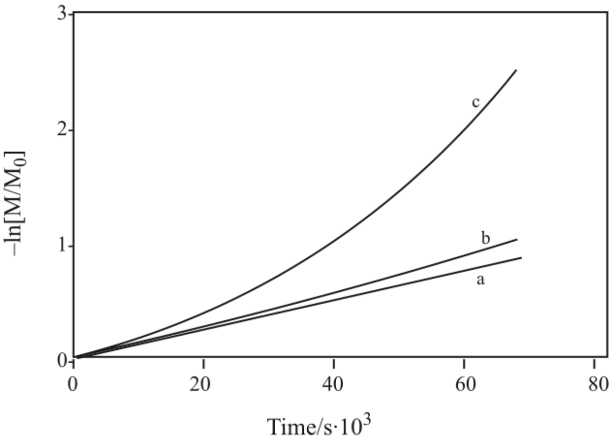


Fig. 15 Comparison of the thermal degradation of a – fully head-to-tail poly(styrene) produced by mediated radical polymerization, b – head-to-tail poly(styrene) generated by anionic techniques and c – general purpose poly(styrene) produced by conventional radical polymerization

Poly(styrene) produced by anionic polymerization contains no head-to-head units and should display stability greater than that observed for poly(styrene) generated by conventional radical techniques. A commercial polymer produced by anionic techniques was examined by thermogravimetry. The degradation characteristics for this material are very similar to those of poly(styrene) generated by nitroxyl mediated radical polymerization. For comparison kinetic plots are displayed in Fig. 15.

Both polymers generated by methods that preclude the inclusion of a head-to-head unit in the mainchain are much more thermally stable than material produced by conventional radical techniques and containing one head-to-head unit per chain as a consequence of polymerization termination by radical coupling.

Conclusions

The establishment of a detailed understanding of the degradation of two types of polymers, vinylidene chloride/acrylate barrier resins and poly(styrene)s, has been facilitated by the use of thermogravimetry. In both cases, at the temperatures of interest, the degradation corresponds to a single, well-defined process such that meaningful kinetic data may be obtained from thermogravimetry. These may be coupled with evolved gas analysis, spectroscopic characterization, and chromatographic analysis to provide a thorough description of the degradation reaction. The degradation of vinylidene chloride copolymers at temperatures below 250°C corresponds to sequential dehydrochlorination in the vinylidene chloride sequences initiated at an allylic dichloromethylene unit. The degradation, at temperatures below 300°C, of atactic poly(styrene) produced by conventional radical techniques is initiated by homolytic cleavage of a head-to-head unit present in the mainchain as a consequence of polymerization termination by radical coupling. The macroradicals thus formed then rapidly expel styrene monomer.

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