

Thermal Degradation of Polymers. XVI. Thermal Analysis Studies on Poly(*p*-methoxystyrene) and Poly(*p*-hydroxystyrene) in Air and Nitrogen

R. H. STILL, *Department of Polymer and Fibre Science, UMIST, Manchester, England*, and A. WHITEHEAD,* *Department of Chemical Sciences, The Hatfield Polytechnic, Hatfield, Hertfordshire, England*

Synopsis

Comparative thermal degradation studies have been made in air and nitrogen on polystyrene (PS), poly(*p*-methoxystyrene) (PMS), poly(*p*-hydroxystyrene) (PHS) and *p*-hydroxystyrene/styrene copolymers (*p*-HS/S) by thermal analytical methods (TG and DSC). The degradation behavior shown by these polymers in an oxidizing or inert atmosphere is different. PMS and PS, however, degrade in a similar manner in the same test atmosphere, suggesting that similar degradation mechanisms are operative for these systems. Polymers containing *p*-HS behave differently to PMS and PS in both atmospheres. Their behavior in air is discussed in terms of the antioxidant effect of the phenolic hydroxyl grouping and the related crosslinking reactions. In nitrogen, the anomalous behavior is discussed in terms of the observed carbonization reaction.

INTRODUCTION

In a previous paper,¹ we reported the effect of pyrolysis temperature on the quantity and composition of the products obtained on vacuum pyrolysis of homopolymers of *p*-methoxystyrene (*p*-MS) and *p*-hydroxystyrene (*p*-HS). Quantitative studies were possible only with *p*-MS homopolymers since partial repolymerization of the *p*-HS monomer produced on degradation occurred. The quantity and the composition of pyrolysis products from poly(*p*-methoxystyrene) (PMS) were found to be independent of molecular weight in the range studied. Pyrolysis temperature was found to affect both the yield of monomer and the dimer/trimer fraction obtained in a manner similar to that reported previously for polystyrene (PS).^{2,3}

We now report thermal analytical studies on PMS and poly(*p*-hydroxystyrene) (PHS) in air and nitrogen by isothermal and dynamic thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Homopolymers of *p*-HS and *p*-MS and copolymers of *p*-HS with styrene (S) were prepared and characterized as previously reported.¹

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* Present address: Revertex Ltd., Harlow, Essex, England

Apparatus and Procedure

Thermogravimetric Analysis (TG). A Stanton thermobalance Model (HT-SM) fitted with a platinum-wound furnace was employed in these studies. Samples, 100 mg, were contained in preignited, recrystallized alumina crucibles (Royal Worcester WA2), and buoyancy corrections were made.

TABLE I
Dynamic and Isothermal TG Data

Polymer ^a	$[\eta]_0^b$	PDT, °C	50% DT, °C	W_{10}
PHS I	0.28	315	390	11
PHS II	0.30	280	425	15
<i>p</i> -HS/S VII	0.33	260	405	—
<i>p</i> -HS/S VIII	0.28	260	390	—
<i>p</i> -HS/S IX	0.28	260	380	—
PMS I	0.94	260	380	15
PMS II	c	260	380	15
PS I ^b	0.28	260	365	35
PS II ^b	1.23	260	365	35

^a Reference 1.

^b Reference 4.

^c \bar{M}_n 55,600.

Dynamic TG studies were made at a heating rate of 3°/min (nominal). Pure white spot nitrogen was introduced at the bottom of the furnace and was passed over the sample at a flow rate of 400 ml/min. The sample and the furnace were completely purged of air by passage of nitrogen over the sample for 1 hr prior to the commencement of the heating program.

Isothermal studies were made by preheating the furnace to the required temperature over the rise rod with nitrogen flowing through the furnace. The furnace was then quickly raised and the crucible containing the sample under test placed on the rise rod and the furnace lowered. During this operation, nitrogen was passed into the top of the furnace to minimize air entrainment by convection. The balance was switched on and weight loss recorded. Studies in air were made with static air replacing the flowing nitrogen atmosphere. All temperatures quoted are furnace wall temperatures. Both dynamic and isothermal studies were performed in triplicate.

Differential Scanning Calorimetry (DSC). A du pont 900 thermal analyzer equipped with a DSC cell capable of operation to 600°C was used. The sample (\approx 6 mg) was located in an open aluminium pan (7 mm in diameter), and an empty pan acted as the inert reference material. A heating rate of 20°C/min (nominal) was used in all experiments, and white spot nitrogen or air was used as purge gas at a flow rate of 400 ml/min.

Glass transition temperatures were determined from the average of six measurements in nitrogen. The transition temperature was obtained from the intersection of the initial baseline with the sloping portion of the curve produced as the baseline shifts during the transition.

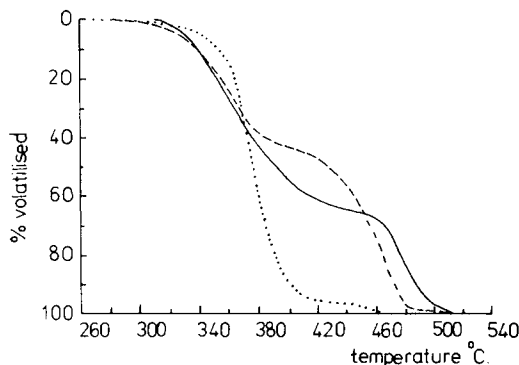


Fig. 1. Weight loss curves in static air for PHS and PMS: (····) PMS I or II; (- - -) PHS II; (—) PHS I.

DSC/Weight Loss Studies were made by removing the sample pan and weighing the sample on an analytical balance (± 0.0001 g).

Hot-Stage Microscope/DSC Studies. Polymer samples were removed from the DSC cell at various stages of degradation in air and visually examined. A Kofler hot-stage microscope was also used for continuous observation of samples subjected to a similar heating rate to that used in the DSC experiments ($20^\circ\text{C}/\text{min}$).

RESULTS AND DISCUSSION

Thermal Analysis Studies in Air

PHS homopolymers (I, II) and copolymers with styrene (PHS/S VII, VIII, and IX) of different composition were subjected to dynamic and isothermal thermogravimetric analysis (TG) studies in static air. The behavior of these systems and of PMS homopolymers (I and II) was compared with that of polystyrene (PS) in terms of the procedural decomposition temperature (*PDT*), the 50% decomposition temperature (50% *DT*) and the percentage weight lost in 10 min at 400°C (W_{10}). The data obtained are shown in Table I.

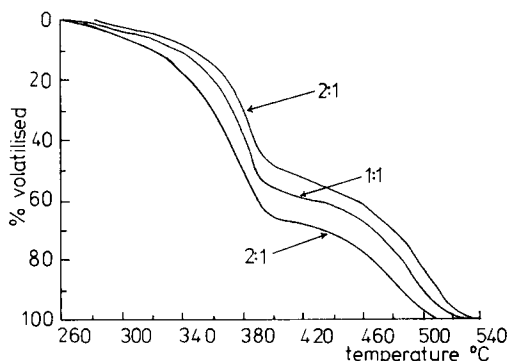


Fig. 2. Weight loss curves in static air for *p*-HS/S copolymers.

The *PDT* values of homopolymers from *p*-MS and S and copolymers from *p*-HS all have identical values. Thus, in the range studied, molecular weight of the homopolymers and copolymer composition have little effect on stability as assessed by this method. PHS, however, has a higher stability than PMS and PS even at the relatively low level of molecular weight that was available for study due to the anomalous preparative behavior previously described.¹ The behavior of PHS I and II in Figure 1 where PMS and PHS are compared suggests that effects similar to those observed for poly(*p*-*N,N*-dimethylaminostyrene) (PDAS),⁵ for poly(*m*-aminostyrene),⁶ and for the isomeric poly(*m*-hydroxystyrene)⁷ could be operative in this system.

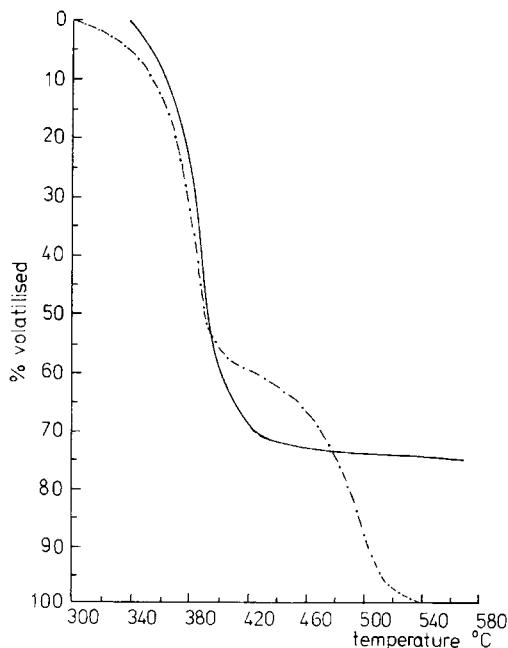


Fig. 3. Weight loss curves for PHS in static air and dynamic nitrogen: (—) nitrogen; (- · - ·) air.

With the *p*-HS/S copolymers, increasing the *p*-hydroxystyrene content displaces the weight loss traces away from the abscissa, Figure 2, and composition influences the rate of weight loss observed.

The effect of molecular weight on the thermogram shape for PDAS and the related amines poly(*m*-*N,N*-dimethylaminostyrene) and poly(*p*-*N,N*-diethylaminostyrene) was discussed in detail in previous papers.^{5,8,9} The behavior was ascribed to the inherent antioxidant action of the substituent grouping and the effects of molecular weight on chain mobility. That a similar effect is operative for PHS is shown by reference to the dynamic TG curves for PHS I in air and nitrogen shown in Figure 3. Further to this, the isothermal weight loss curves for PHS, PMS, and PS, Figure 4, indicate an apparent antioxidant action for PHS since PS and PMS are significantly less stable in air than in nitrogen. PHS, under isothermal conditions, is apparently highly efficient in resisting oxidative initiation of degradation, and the weight loss curves are identical. The differences in behavior between PHS I and II (Fig. 1) in air and the isothermal behavior of PHS in air and nitrogen (Fig. 4) and its dynamic TG behavior (Fig.

3) are similar to those observed previously for PDAS⁵ and ascribed to the effects of chain mobility on the antioxidant effect under the conditions of the experiment. Since PHS I and PHS II have T_g values of 164° and 171°C, respectively, similar effects to those observed for PDAS are to be expected on isothermal and dynamic TG.

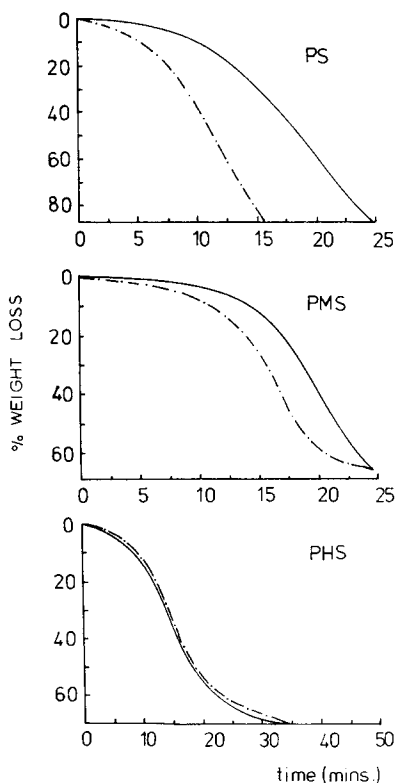


Fig. 4. Isothermal weight loss curves in air and nitrogen: (—) nitrogen; (- · - ·) air.

The behavior of PS on DSC in air was reported previously and contrasted with that observed for PDAS and other substituted aminostyrene systems.^{5,8,9}

The differences observed for PS and PDAS and related systems are again apparent for PHS compared with PS and PMS (Fig. 5) and for the *p*-HS/S systems (Fig. 6). The exothermic peak observed at 550°C (C exotherm)⁵ on these thermograms is the dominating feature of the degradation of systems containing *p*-HS. This behavior is similar to that observed previously and ascribed to the burning off of a carbonaceous residue.

Since the interpretation of DSC and DTA data is much more productive when related to the weight losses occurring, the percentage residue prior to the C exotherm and at other stages on the DSC trace were determined. In addition, the areas of the C exotherm obtained from comparable weights of polymer were obtained by the cutting and weighing procedure described previously for PDAS.⁵ The data are presented in Tables II and III.

In addition to the weight loss studies, the physical appearance of the samples during thermal degradation was monitored by heating a sample to a specific temperature and cooling rapidly in a nitrogen atmosphere. These studies yielded the data shown in Table IV.

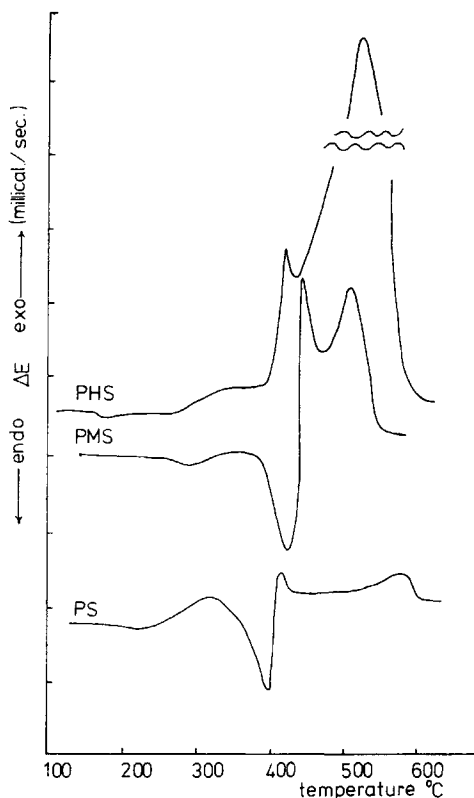


Fig. 5. DSC curves in dynamic air for PS PMS and PHS.

The higher values of the peak area:residue ratio observed for PMS and PHS as compared with that of PS and that reported earlier for PDAS⁵ suggest that a different reaction may obtain in these two systems. The behavior may in part arise from the combined oxygen in the molecules affecting the heat of combustion.

The appearance of the samples and the weight losses prior to the C exotherm suggest that this exotherm was due to the residue burning off during this period. The relatively small exotherm for PS is consistent with this explanation since it shows little tendency to form a carbonaceous residue. PMS gives a larger residue as evidenced by the crosslinking reaction observed on vacuum pyrolysis.¹ PHS similarly is observed to give a crosslinked residue on dynamic TG in nitrogen and on vacuum pyrolysis, even at low extents of degradation.¹

The discussion so far has centered around the C exotherm, but reference to Figures 5 and 6 indicates that the behavior recorded for the systems under study is much more complex.

PMS and PS (Fig. 5) are characterized by two exotherms separated by an endotherm prior to the C exotherm at $\approx 500^\circ\text{C}$. It is possible that the double exotherm results from the endothermic pyrolysis process being superimposed on a single exothermic process.

With systems containing *p*-HS, the anomalous behavior reported previously¹ is again evident (Figs. 5 and 6). The small exotherm (B exotherm) appearing as a shoulder (centered at approximately 420°C) on the major C exotherm is not readily explained.

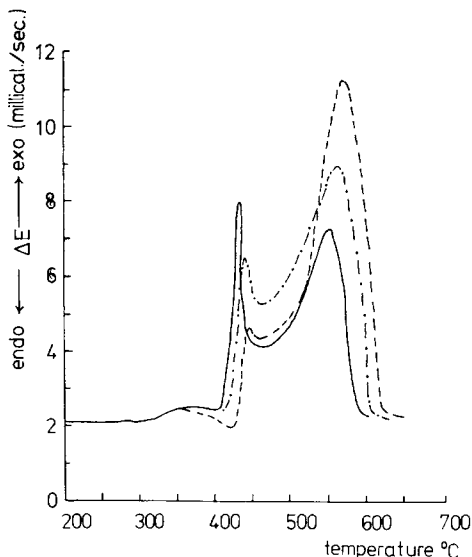


Fig. 6. DSC curves in dynamic air for *p*-HS/S copolymers: (—) *p*-HS:S = 1:2; (- - -) *p*-HS:S = 1:1; (- · - ·) *p*-HS:S = 2:1.

In the copolymers, the B exotherm decreases with increasing proportion of *p*-HS and is apparently unrelated to the carbonization process. Its behavior is similar to that reported previously for PDAS⁵ (exotherm A) and suggests the suppression of the secondary reactions by the inbuilt antioxidant action of the *p*-HS component.

With the *p*-HS/S copolymers (Fig. 6), the size of the C exotherm increases with increasing *p*-HS concentration, suggesting that the amount of carbonization is proportional to the concentration of *p*-HS present. Since PHS was found to give a high yield of carbonized residue in nitrogen and in vacuo, in contrast to the other systems studied, this behavior is not unexpected.

The overall degradation behavior of systems containing *p*-HS, therefore, results from a combination of the inherent antioxidant action of the hydroxyl substituent, the facility of the system to crosslink, and the inherent reactivity of the *p*-HS derived on degradation.

Thermal Analysis Studies in Nitrogen

Studies were also made on these systems in nitrogen by dynamic and isothermal TG, and the comparative thermal stability data obtained are presented in Table V. The PDT values observed for all the polymers were essentially similar and were independent of molecular weight in the range studied. As the molecular weight of the PMS and PS samples increased, there was, however, a slight increase in stability as measured by 50% *DT* and *W*₃₀. This may be attributed to the decreased rate of evolution of volatiles as a result of increased melt viscosity.

The shape of the weight loss curves in Figure 7 suggests that PMS and PS behave similarly losing weight in a single step. PHS, however, loses weight at an initially fast rate; but after approximately 70% volatilization, there is an abrupt decrease in weight loss.

Reference to Figure 8 shows that PMS and PS and PHS show distinct differences in the maximum rate of weight loss, with PMS > PS > PHS. The slight differences in rate between PMS and PS may be due to differences in the volatility of the degradation products. However, at the temperature of volatile production, the difference should be minimal, and it is more likely that the difference in rate is due to a basic difference in the rate constants for volatile production for the two polymers.

TABLE II
The C Exotherm^a

Polymer	Percentage residue in air at 480°C	Mass of C exotherm, mg	Peak mass/percentage residue
PHS I	25.8	417.0	16.2
PMS I	3.3	35.7	10.2
PS I	0.9	4.5	5.0

^a Reference 5.

TABLE III
Weight Losses During DSC Studies

Polymer	% Volatilized at specified temperatures		
	330°C	425°C	480°C
PHS I	1.3	74.2	79.7
PMS I	3.9	87.9	96.7
PS I	4.8	80.4	99.6

TABLE IV
Physical Appearance of Samples After Thermal Degradation Studies in Air After Cooling in Nitrogen

Polymer	Ambient temp.	330°C	430°C	480°C
PHS	white powder	yellow glass	deep red glass	black carbonaceous material
PMS	white powder or fiber	clear transparent glass	pale-green transparent glass with brown streaks	brown residue
PS	white powder or fiber	colorless transparent glass	yellow transparent glass with brown spots	brown residue

TABLE V
Comparative Thermal Stability of PS, PHS, and PMS

Mode of assessment	PS	PHS	PMS
PDT	340°C	350°C	340°C
50% DT	397°C	380°C	414°C
W ₃₀	94%	65%	88%

Examination of the residue obtained on heating PHS to 430°C reveals it to be a black, carbonaceous material.

Combustion analysis shows that the carbon content is increased from 79.9% for PHS to 84.7% for the residue, indicative of carbonization, this behavior being similar to that reported previously for PHS on vacuum pyrolysis.¹

The DSC curves shown in Figure 9 confirm the similarities and differences in degradation mechanism already suggested by dynamic TG. Heats of degradation were obtained from the areas of the endothermic peaks by comparison with the peak area produced by a known weight of zinc. The heat of fusion of

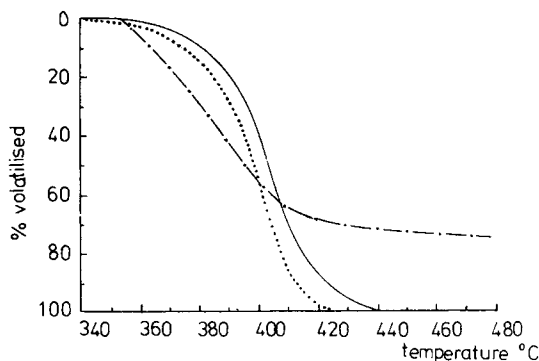


Fig. 7. Weight loss curves in dynamic nitrogen: (—) PMS; (---) PHS; (···) PS.

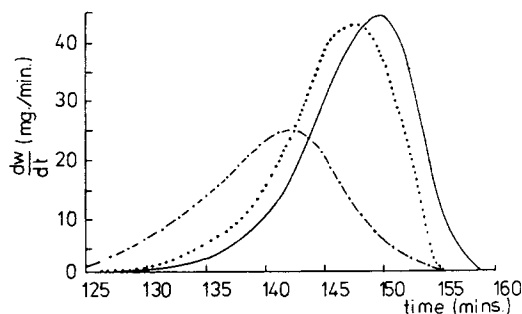


Fig. 8. Rate of weight loss curves in dynamic nitrogen: (—) PMS; (---) PHS; (···) PS.

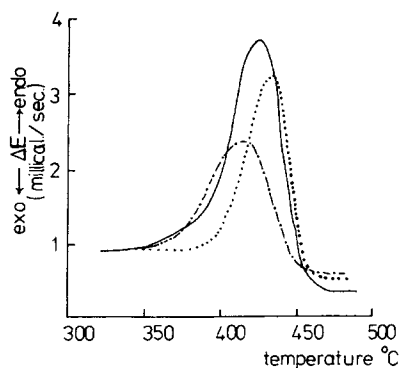


Fig. 9. DS6 curves in dynamic nitrogen: (—) PMS; (---) PHS; (···) PS.

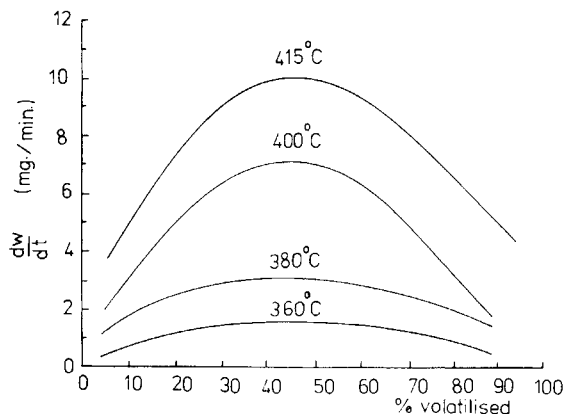


Fig. 10. Rate of weight loss curves for PS/PMS in nitrogen under isothermal conditions.

zinc was taken as 27 cal/g, and heats of degradation were calculated in terms of kcal/mole repeating unit of the original polymer. The value obtained was 19.6 kcal/mole for PS, 23.1 kcal/mole for PMS, and 11.9 kcal/mole for PHS.

To an approximation, the endothermicity of the degradation process will depend upon monomer yield and the heat of volatilization of the volatiles produced. On this basis, the degradation of PMS is more endothermic than PS since the products of degradation, although similar in quantity,¹ have much higher boiling points. PHS has a less endothermic degradation than PS because (a) the monomer repolymerizes,¹ (b) hydrogen transfer reactions will result in a reduced monomer yield, and (c) aromatization and carbonization occur during degradation.

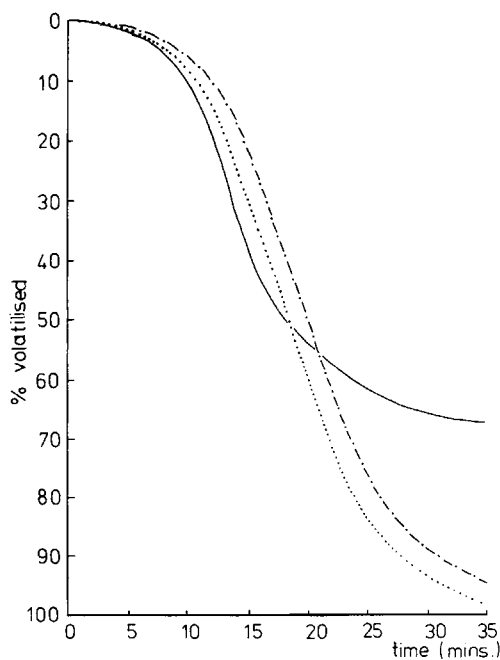


Fig. 11. Isothermal weight loss curves in dynamic nitrogen at 400°C: (---) PMS; (—) PHS; (····) PS.

Isothermal studies were made on PS, PMS, and PHS at a variety of temperatures. PMS and PS show similar rate of weight loss versus extent of degradation curves, with a maximum at 40% volatilization as shown in Figure 10 in accord with that found by Madorsky.¹¹ In Figure 11, % volatilized at 400°C is plotted against time for the three polymers. PHS loses weight at an initially fast rate, but at 70% volatilization there is a sudden decrease in the rate of weight loss due to carbonization. The authors' previous work on the vacuum pyrolysis of PHS and PMS¹ showed that the residues obtained from PHS were insoluble in solvents for normal PHS. The residue from PMS remained soluble at all extents of degradation. The crosslinked residues from PHS at degradation extents <70% gave the degradation behavior associated with the untreated polymer, suggesting the presence of thermolabile crosslinks formed during the cooling process.

The process is not, however, the same as for poly(*p*-N,N-dimethylaminostyrene) (PDAS) in nitrogen reported earlier,¹¹ since nonlabile crosslinks and carbonization occur in PHS, possibly because of reduced volatility of the degradation products as a result of H bonding.

Activation energies for the overall degradation process were determined by the method reported previously¹¹ and are: PS, 43 kcal/mole; PMS, 37 kcal/mole. PHS was not amenable to study because of the method used in the evaluation of kinetic data which is invalidated if a residue is formed.

The similarity in values for PS and PMS is in accord with the degradation behavior discussed in the previous paper¹ and contained within this paper, suggesting that a similar mechanism of degradation is operative in the two polymers. The behavior of PHS is again anomalous as a result of both structural features and the reactivity of the monomer.

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