

Thermal Degradation of Polymers. X. Thermal Analysis Studies on Poly(*p*-N,N-dimethylaminostyrene) Homopolymers and Copolymers with Styrene in Nitrogen

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Synopsis

Studies have been made on the effect of the molecular weight of *p*-N,N-dimethylaminostyrene homopolymers and the composition of its copolymers with styrene on the glass transition temperature. Comparative thermal degradation studies have been made on polystyrene and *p*-N,N-dimethylaminostyrene polymers by thermal analytical methods (TG, DTA, and DSC). The differences in thermal stability and overall thermal degradation behavior of the two systems are discussed in terms of the differences in their degradation mechanisms.

INTRODUCTION

In previous papers,^{1,2} we reported the effect of pyrolysis temperature on the quantity and composition of the products obtained on vacuum pyrolysis of homopolymers of *p*-N,N-dimethylaminostyrene (*p*-DAS) and its copolymers with styrene (S). The nature and composition of the pyrolysis products 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. The monomer yield was significantly less than that for polystyrene under identical conditions. The greater complexity of the fractions containing monomer and dimer/trimer, respectively, was ascribed to reactions involving methyl group migration after thermal cleavage of the nitrogen-methyl group bond of the substituent in the benzene ring. We now report thermal analytical studies on these polymers by isothermal and dynamic thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Homopolymers of *p*-N,N-dimethylaminostyrene (*p*-DAS) and copolymers with styrene (S) were prepared and characterized as previously described.¹

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Apparatus and Procedure

Thermogravimetric Analysis (TG). A Stanton thermobalance Model (HT-SM) fitted with a platinum-wound furnace capable of operation from room temperature to 1500°C was employed in these studies. Samples, 100 mg each, were contained in preignited recrystallized alumina crucibles (Royal Worcester WA2), and buoyancy corrections were made for the effect of the crucible.

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 programme.

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. 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 (≈ 6 mg) was located in an open aluminum 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 was used as purge gas at a flow rate of 400 ml/min.

Differential Thermal Analysis (DTA). The du Pont 900 thermal analyzer equipped with the intermediate DTA cell was used for these studies. The sample was located in a silica macrotube, and an identical tube containing preignited alumina acted as the inert reference. In all experiments, a heating rate of 20°C/min (nominal) was used together with a flow rate of 400 ml/min of white spot nitrogen. Glass transition temperatures were determined using this apparatus from the average of six determinations. 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.

RESULTS AND DISCUSSION

Glass Transition Temperatures

The effect of homopolymer molecular weight on the glass transition temperature as measured by dynamic DTA is shown in Table I. The results for the homopolymers are similar to those reported by Wunderlich and Bodily³ and Jenckel and Uebereiter⁴ for the effect of molecular weight on the glass transition of polystyrene (PS). PS shows a similar rapid rise in T_g with increasing molecular weight with effective stabilization in range $\bar{M}_n = 100,000$. For PS in the molecular weight range studied for the *p*-DAS homopolymers, the T_g varies from 85°C at $\bar{M}_n = 12,000$ to $T_{g\infty} = 100^\circ\text{C}$.⁶ Thus, it would appear that the effect of molecular weight on T_g is more pronounced in the case

TABLE I
Glass Transition Temperatures for PDAS Homopolymers

Sample no.	$[\eta]_0$	\bar{M}_n (a)	T_g ,	$\frac{10^3}{T_g} \text{ } ^\circ\text{K}^{-1}$	$\frac{10^4}{\bar{M}_n}$
1	0.98	520,000(b)	143	2.404	0.01923
2	0.42	102,000	142	2.410	0.09804
3	0.33	71,990	140	2.421	0.1389
4	0.28	45,700	136	2.445	0.2188
5	0.24	34,300	133	2.463	0.2915
6	0.18	24,200	125	2.513	0.4132
7	0.12	12,200(b)	109	2.618	0.8197

^a Determined by osmometry.¹

^b Calculated using $[\eta]_0 = KM^\alpha$, where $K = 6.17 \times 10^{-4}$, $\alpha = 0.56$.⁽¹⁾

of PDAS. The effect of molecular weight upon T_g has been ascribed to the effect of chain ends on the polymer free volume. As the number of chain ends in the system increases, the free volume increases, with a consequent decrease in T_g .⁵ Fox and Flory⁶ and Uebereiter and Kanig⁷ have derived equations which relate T_g at a given molecular weight M to that at infinite molecular weight $T_{g\infty}$:

$$T_g = T_{g\infty} - \frac{A}{M} \quad (1)$$

and

$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{B}{M} \quad (2)$$

where A and B are empirical constants which involve contributions from the polymer free volume. The experimental data plotted according to eqs. (1) and (2) are shown in Figure 1. Bearing in mind the polydispersity of the samples and the range of molecular weights involved the behavior is fairly adequately described by these equations with $T_{g\infty} = 146^\circ\text{C}$ and the constants $A = 4.55 \times 10^{5^\circ}\text{C}$ and $B = 2.857^\circ\text{K}$.

Bueche⁵ has shown how the value of A in eq. (1) may be used to calculate the additional free volume associated with a chain end from the relationship

$$A = \frac{2\rho N\theta}{\Delta\alpha} \quad (3)$$

where ρ is the polymer density, N is Avogadro's number, θ is the free volume contribution of each chain end, and α is the difference in expansion coefficient in the liquid and glass states. Inserting the experimental value of A in the equation and assuming ρ and $\Delta\alpha$ to have similar value to those for poly(α -methylstyrene),^{8,9} θ may be calculated to be 108 \AA^3 , which is reasonable when compared with reported values for PS⁵ of 80 \AA^3 and for poly(α -methylstyrene)⁸ of 85 \AA^3 .

The overall increase in T_g of PDAS when compared with PS probably arises as a result of a combination of (a) dipolar interaction between the substituted phenyl groups on the same and adjacent chains resulting in an overall increase in chain stiffness; (b) increased interchain steric hindrance as described by Barb¹⁰ for alkyl- and halogen-substituted polystyrenes. The dipole-

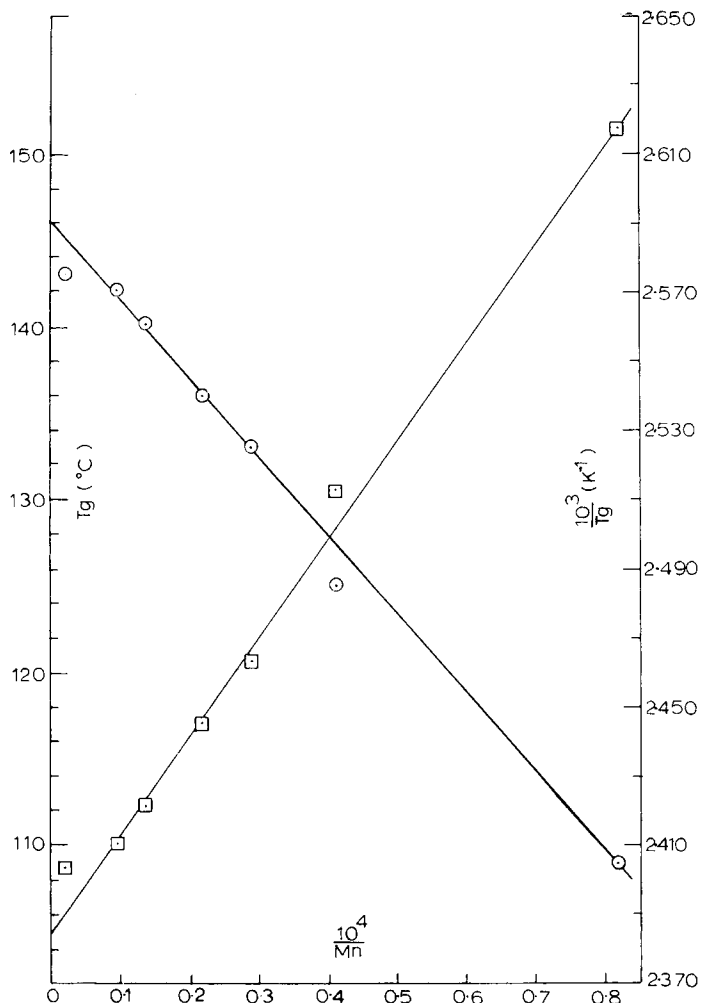


Fig. 1. Glass transition temperature and molecular weight plotted according to eq. (1) (○) and eq. (2) (◻).

lar interaction arises as a result of the electronic effects of the *N,N*-dimethylamino grouping ($-I$ effect counterbalanced by $+M$ effect). The repeating unit of the homopolymer may thus be expressed as a resonance hybrid with the following contributing canonical forms:

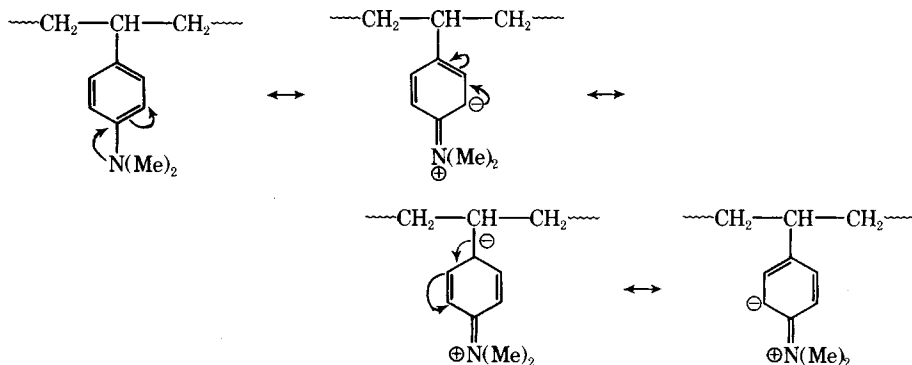


TABLE II
Glass Transition Temperatures for Styrene-*p*-N,N-Dimethylaminostyrene Copolymers

Sample no. ^a	$[\eta]_0$	\bar{M}_n	$T_g, ^\circ\text{C}$	Approx. molar ratio <i>p</i> -DAS:S
8	0.24	37,000	107	1:2
9	0.23	36,000	111	1:1
10	0.23	36,000	119	2:1
11	0.79	324,000	126	1:1

^a Reported previously.¹

TABLE III
Comparative Thermal Stability of PS and PDAS

Mode of assessment	PS	PDAS
PDT, $^\circ\text{C}$	340	350
50% DT, $^\circ\text{C}$	397	414
$W_{30}, \%$	94	47.5

The effect of spacing out these groupings with styrene units is shown in Table II, which shows the effect of copolymer composition on T_g . It can be seen that as the percentage *p*-DAS in the copolymer increases, the T_g increases, suggesting an increase in dipolar interaction and interchain steric hindrance in these systems as the random spacer groups (styrene units) are progressively diluted. Molecular weight also has an effect in these systems, as can be seen from a consideration of samples 9 and 11 which have similar compositions but markedly different molecular weights.

The copolymers cannot, therefore, be adequately described by the equations described by Di Marzio and Gibbs¹¹ and Wood¹² for random copolymers derived from comonomers of similar composition:

$$A_1C_1(T_g - T_{g1}) + A_2C_2(T_g - T_{g2}) = 0 \quad (3)$$

where A_1 and A_2 are constants, C_1 and C_2 are the weight fractions of the two comonomers, and T_{g1} and T_{g2} are glass transition temperatures of the two homopolymers.

That these copolymers were random was shown from the observation that they exhibited only a single baseline shift, in contrast to that observed by Noel¹³ for block copolymer systems of S and *p*-DAS, which gave a double baseline shift corresponding to the two glass transition temperatures of the homopolymer blocks.

Thermal Stability Studies

The thermal stability of PDAS and PS in a nitrogen atmosphere has been compared by dynamic TG in terms of (a) the procedural decomposition temperature (PDT), the temperature at which weight loss becomes observable; (b) the temperature at which 50% decomposition occurred (50% DT).

Isothermal TG studies also yielded the percentage weight loss which occurred in 30 min at 400 $^\circ\text{C}$ (W_{30}). The results obtained for these parameters are summarized in Table III. It can be seen that each of the methods of ther-

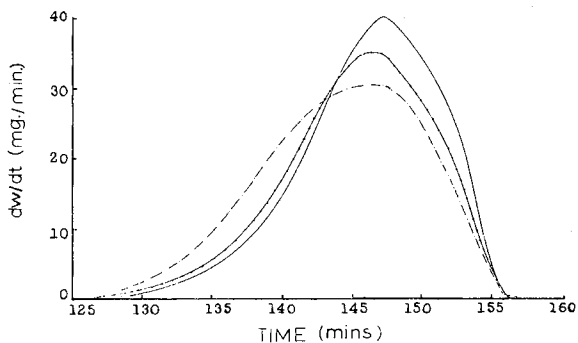


Fig. 2. Effect of $[-N(Me)_2]$ on the rate of weight loss: (—) PS; (---) PDAS; (-·-·-) *p*-DAS/S 1:1 copolymer.

mal stability assessment used indicates PDAS to be more stable than PS. The slightly increased PDT of PDAS may be explained on the basis of the methyl group migration observed in the pyrolysis of PDAS.¹ In the early stages of weight loss (<1.0%), the concentration of active polymer chain radicals is small. Thus, a small amount of methyl migration to the active polymer chain radical will effectively postpone weight loss until a higher temperature is reached and the rate of production of polymer chain radicals will be greater. Molecular weight in range studied was found not to affect the observed PDT of PDAS samples in nitrogen. As the molecular weight of the PDAS sample increased, there was, however, a slight increase in stability as measured by 50% DT and W_{30} which is probably due to the decreased rate of evolution of volatiles as a result of increased melt viscosity.

Reference to Figure 2 shows that PS and PDAS show distinct differences in the maximum rate of loss with $PS > PDAS$. The decreased rate of weight loss for PDAS is expected on the basis of methyl migration, since this competes with the depropagation process and hydrogen transfer reactions leading to volatile formation. The effect and importance of the $-N(Me)_2$ group on the rate of volatilization is seen in Figure 2 where PDAS, PS, and the *p*-DAS:S 1:1 copolymer are compared. It can be seen that as the concentration of $-N(Me)_2$ -containing units in the polymer increases, there is a decrease in the maximum rate of weight loss as a result of the increased potential for methyl group migration.

The DSC curves shown in Figure 3 confirm the differences in the 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 zinc was taken as 27 cal/g, and the heats of degradation were calculated in terms of kcal/mole repeating unit of the original polymer. The value obtained for PS was 19.6 kcal/mole repeating unit and PDAS 15.8 kcal/mole repeating unit. In the case of PS, it has been shown by Madorsky¹⁴ that degradation in inert atmospheres at atmospheric pressure yields larger quantities of monomer than the yield from vacuum pyrolysis. Hence, the major contributor to the amount of heat involved in the degradation process will be the endothermic unzipping reaction. In addition, the vaporization of the products of degradation including dimer and trimer will be endothermic and dependent on

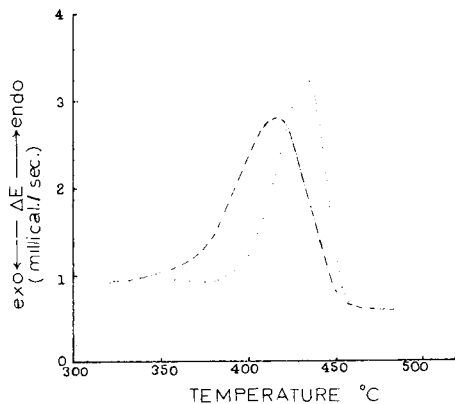
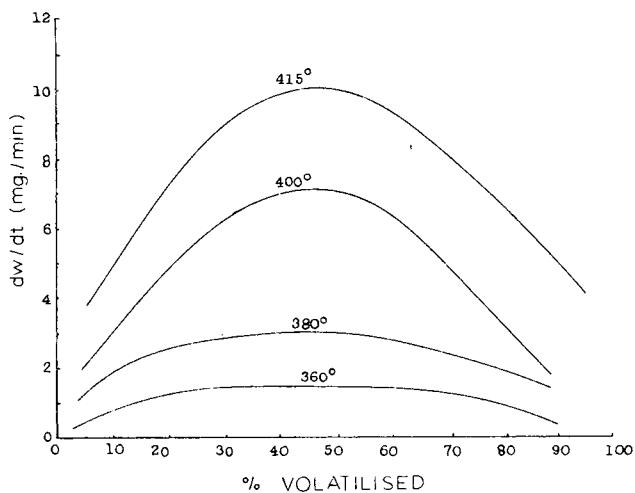
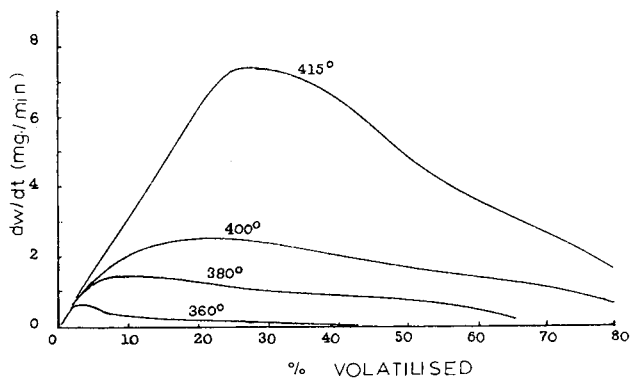


Fig. 3. DSC curves for PS and PDAS in dynamic nitrogen: (.....) PS; (- · - · - ·) PDAS.



(a)



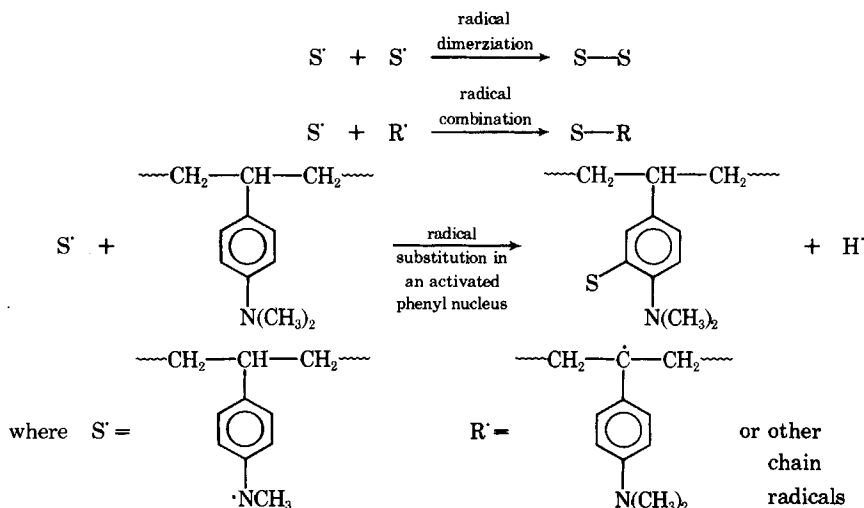
(b)

Fig. 4. (a) Rate of weight loss vs. % volatilization for PS in dynamic nitrogen. (b) Rate of weight loss vs. % volatilization for PDAS in dynamic nitrogen.

their respective heat of vaporization. This in its turn is to an approximation dependent only on the boiling point of the compounds as described by Trouton's law ($\lambda/T_b = 21 \text{ kcal mole}^{-1} \text{ deg}^{-1}$, where λ is the latent heat of vaporization and T_b is the boiling point). The application of Trouton's law, however, assumes that the volatiles are produced at their boiling point. Thus, to an approximation the endothermicity of the degradation process will depend upon the monomer yield and the heat of volatilization of the volatiles produced. In addition, the faster the rate of weight loss, the lower the temperature of weight loss; and the higher the boiling points of the products, the greater the endothermic nature of the degradation. On this basis, the degradation of PDAS is less endothermic than that of PS because there is a significantly reduced monomer yield¹ even though the products have higher boiling points.

Isothermal weight loss studies were made on PS and PDAS at a variety of temperatures. In Figures 4a and 4b, rate of weight loss is plotted against extent of degradation and in Figure 5, % volatilized at 400°C is plotted against time for the two polymers. From Figure 4a, it can be seen that PS displayed a maximum at 40% volatilization in accord with previously reported work^{15,16,17} and at variance with zero- or first-order behavior. PDAS (Fig. 4b) shows behavior similar to that observed by Madorsky and Straus¹⁷ for PS crosslinked with low percentages of divinylbenzene. This suggests that a crosslinking process might be responsible for the behavior of PDAS. The authors' previous work^{1,2} on the vacuum pyrolysis of PDAS showed that the residues obtained on pyrolysis at temperatures in excess of 275°C were crosslinked. In addition, these crosslinked materials were shown to contain thermolabile bonds which could be disrupted to yield monomer in similar quantity to that obtained from the untreated polymer. DSC studies also showed the crosslinked and the nonheat-treated material to behave in an identical manner.

These thermolabile crosslinked structures can arise as a result of intermolecular reactions of the stabilized radical (S·) produced on N-Me bond cleavage, reacting by the following routes:



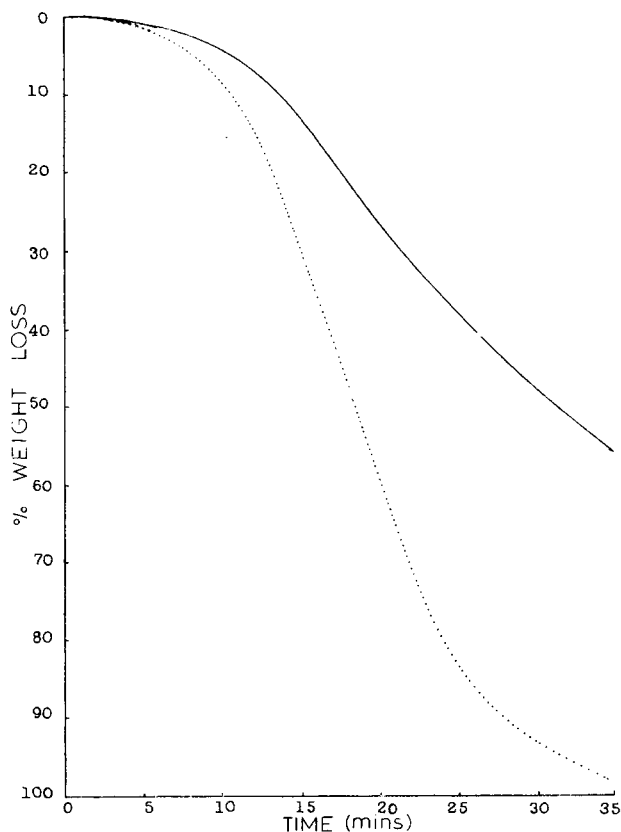


Fig. 5. Isothermal weight loss curves for PS and PDAS in dynamic nitrogen at 400°C: (.....) PS; (—) PDAS.

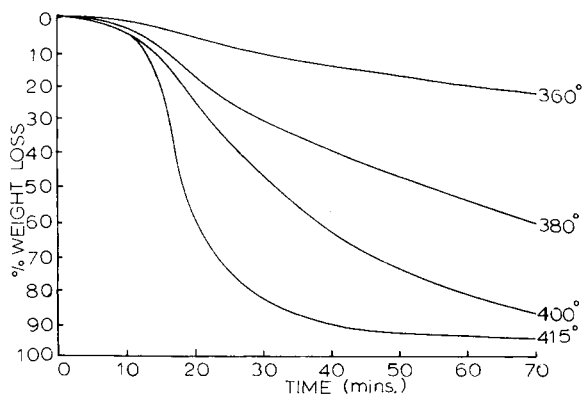


Fig. 6. Isothermal weight loss curves for PDAS in dynamic nitrogen.

Radical dimerization would yield the weak N-N bond, whereas the other processes would yield the more stable C-N bond. Only a small concentration of crosslinks would be in equilibrium with the stabilized radicals ($S \cdot \rightleftharpoons$ crosslinks).

As degradation proceeds, the concentration of stabilized radicals (S \cdot) arising as result of methyl migration will increase. As a consequence, the number of crosslinks will increase and the rate of weight loss will decrease. The loss of radicals by unzipping and intramolecular transfer followed by volatilization will move the position of equilibrium to the left and destroy a proportion of the crosslinks already formed. In this way, volatilization will go to completion at a much reduced rate.

Alternatively, the observations made from Figures 4b and 5 may be due to a complex interaction of the unzipping process and the methyl migration process without crosslinking, possibly also involving H \cdot transfer from the backbone. The effect of an increase in temperature on the isothermal weight loss curves (Fig. 6) of PDAS is to increase the extent of volatilization prior to crosslinking. This suggests that the rate of unzipping increases more with increase in temperature than the rate of methyl transfer.

The crosslinking phenomena is not clearly defined on dynamic TG; and this probably arises because, at the temperature at which there is a sufficient concentration of stabilized radicals, the existence of thermolabile bonds is even more unfavored.

Activation energies for the overall degradation process were determined from isothermal thermogravimetry from the slope of the plot of $\log K$ (the reaction rate constant) versus the reciprocal of the absolute temperature and are for PDAS 52 and PS 43 kcal/mole, respectively. The value for PS contrasts with the values found by Madorsky¹⁶ for PS in vacuo (55 kcal/mole) and by Anderson and Freeman¹⁸ (53 kcal/mole). However, the value obtained in this work is in accord with those recently reported for PS in nitrogen by Kokta and co-workers¹⁹ and by Malhotra and co-workers²⁰ who investigated the variation of activation energy with molecular weight for PS samples in the range of M_n 900– 1.8×10^6 .

If the activation energy is taken as a measure of the ease of volatile production, the higher value of PDAS compared with that of PS supports the methyl migration mechanism to an active polymer radical.

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