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Thermal Degradation of Polymers. XI. Synthesis, Polymerization, and Thermal Characterization of Polymers of *p*-N,N-Diethylaminostyrene in Nitrogen

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Synopsis

The monomer *p*-N,N-diethylaminostyrene has been synthesized from *p*-N,N-diethylaniline and homopolymerized and copolymerized with styrene using 2,2′-azobisisobutyronitrile as free-radical initiator. The polymers have been characterized by thermal analysis (DTA, DSC, and TG). Glass transition temperatures have been measured and activation energies for degradation in nitrogen have been established by a variety of methods for comparative purposes.

INTRODUCTION

In previous papers,[1-6] we have reported the effects of various substituents on the products of degradation and the mechanisms of degradation of substituted polystyrenes as studied by vacuum pyrolysis and the thermal analysis techniques (differential thermal analysis, DTA; differential scanning calorimetry, DSC; thermogravimetry, TG). We now report (a) the synthesis of *p*-N,N-diethylaminostyrene (*p*-DEAS), its polymerization, copolymerization, and the characterization of the resulting polymers; (b) the effect of homopolymer molecular weight and copolymer composition on the glass transition temperature; (c) the effect of the *p*-N,N-diethylamino substituent on the degradation of these polymers as evaluated by dynamic and isothermal TG and by DSC.

EXPERIMENTAL

Materials

The monomer was synthesized from N,N-diethylaniline by the following route:

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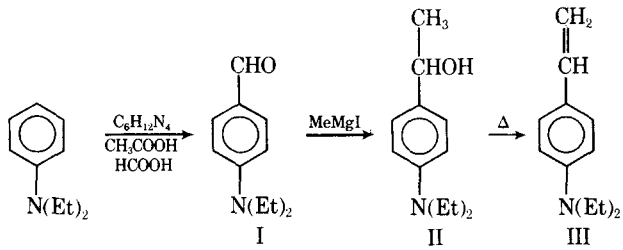

N,N-Diethylaniline was converted to *p*-N,N-diethylaminobenzaldehyde (I) by a modification of Duff's method[7] for the preparation of substituted aminobenzaldehydes. N,N-Diethylaniline (60 g), ethanol (40 ml), and hexamine (80 g) were placed in a 1-liter, three-necked flask equipped with a dropping funnel, reflux condenser, and thermometer. The reaction mixture was heated on a water bath and boiled under reflux for 3 hr while a mixture of glacial acetic acid (90 ml) and 90% formic acid (90 ml) was added dropwise. The reaction mixture was boiled under reflux for a further 2 hr and then cooled and added to vigorously stirred ice-cold 0.5*N* hydrochloric acid (1.2 liter). The resulting yellow precipitate was filtered, dried, and recrystallized from petroleum ether (bp 40–60°C). The product so obtained in 37% yield had mp 40–41°C (lit.[8] mp 41°C).

The conversion of *p*-N,N-diethylaminobenzaldehyde (I) into α-methyl-*p*-N,N-diethylaminobenzyl alcohol (II) was effected in similar manner to that for the conversion of *p*-N,N-dimethylaminobenzaldehyde into α-methyl-*p*-N,N-dimethylaminobenzyl alcohol.[9,10] Magnesium turnings (10 g) and anhydrous ether (30 ml) were placed in a 2-liter, three-necked flask equipped with a magnetic stirrer and a reflux condenser and a dropping funnel protected by calcium chloride drying tubes. Methyl iodide (60 g) in anhydrous ether (500 ml) was added dropwise over 2 hr and the reaction mixture stirred for a further 30 min to complete the reaction. N,N-Diethylaminobenzaldehyde (50 g) dissolved in ether (250 ml) was then added over a period of 2 hr. The resultant solid complex in ether was decomposed by shaking the ethereal solution with a saturated solution of ammonium chloride (60 g), ice (100 g), and ammonia (30 ml, d. 0.88) and then extracted with ether (3 × 75 ml). The extract was washed with ammonical ferrous hydroxide (to remove peroxides) and dried over anhydrous sodium sulfate. The ether was removed at room temperature by the application of slightly reduced pressure, yielding a yellow-green oily liquid in 91% yield. The infrared spectrum indicated hydroxyl absorption and absence of the aldehydic groups absorption (C—H and $-\overset{\overset{\displaystyle H}{|}}{C}{=}O$) present in the reactant. This compound could not be further purified since spontaneous dehydration occurred on distillation. It had N_D^{22} = 1.5743 and bp 100°C/0.35 mm Hg (with decomposition by dehydration).

The conversion of compound II into *p*-N,N-diethylaminostyrene (III) was achieved by distillation of small portions (5 g) plus 1% diphenyl picrylhydrazyl at 0.5–0.2 mm Hg under nitrogen from a silicone oil bath maintained at 150–180°C. A pale-yellow liquid was collected in the receiver maintained in an ice–salt bath. The distillate was dried over anhydrous sodium sulfate and redistilled yielding as main fraction a yellow liquid, bp 90–93°C/0.3 mm Hg,

N_D^{22} 1.5845, in 51% yield. Combustion analysis yielded the following figures:

ANAL. Calcd for $C_{12}H_{17}N$: C, 82.28%; H, 9.71%; N, 8.01%; Found: C, 81.50%; H, 9.80%; N, 8.10%.

The monomer was homopolymerized in bulk under nitrogen at 70°C in sealed soda-glass test tubes using α,α'-azobisisobutyronitrile (AZBN) as initiator at concentrations between 0.1% and 4.0% on monomer weight. This yielded poly(*p*-N,N-diethylaminostyrenes) (PDEAS) 1–5 of atactic stereochemical configuration and different molecular weights.

Purification prior to characterization was effected in the following manner: The solid rods of polymer were dissolved in AnalaR toluene to give 5% w/v solutions which were added dropwise to excess mechanically stirred isopropanol. The resulting fibrous polymer was filtered at the pump through sintered glass crucibles and washed with isopropanol and dried at 20°C/0.1 mm Hg to constant weight. Three representative samples, PDEAS 3, 4, and 5, were subjected to combustion analysis.

ANAL. Calcd for $C_{12}H_{17}N$: C, 82.28%; H, 9.71%; N, 8.01%; Found for PDEAS 3: C, 82.10%; H, 9.80%; N, 8.20%; for PDEAS 4: C, 82.20%; H, 10.00%; N, 8.00%; for PDEAS 5: C, 82.10%; H, 10.00%; N, 8.10%.

PDEAS samples were characterized by intrinsic viscosity determination in toluene at 25°C using an Ubbelohde No. 1 dilution viscometer. The data presented in Table I show the polymers to have sensibly different molecular weights. Copolymerization of styrene (S) and *p*-N,N-diethylaminostyrene (*p*-DEAS) in various molar ratios under similar conditions with an initator concentration of ≃ 1.0% on total monomer weight yielded copolymers 6, 7, 8, and 9 after 4 hr as solid glasses. Purification and characterization by viscometry and combustion analysis were effected as previously described for the homopolymers.

TABLE I
Intrinsic Viscosities of PDEAS Homopolymers

Sample no.	% AZBN	Intrinsic viscosity $[\eta]_0$
1	0.11	0.55
2	0.84	0.39
3	1.07	0.31
4	2.73	0.22
5	3.90	0.18

TABLE II
Composition and Intrinsic Viscosities of S:*p*-DEAS Copolymers

Sample no.	% AZBN	Approx. molar ratio S:*p*-DEAS	Molar ratio from combustion analysis	Intrinsic viscosity $[\eta]_0$
6	0.87	2:1	2.20:1	0.52
7	1.11	1:1	1.11:1	0.45
8	0.89	0.5:1	0.62:1	0.43
9	0.09*	2:1	1.79:1	0.93

[a] Solid after 24 hr at 70° C.

ANAL. Found for copolymer 6: C, 88.00%; H, 8.50%; N, 3.70%. Calcd for C_8H_8:$C_{12}H_{17}N$ = 2.20:1: C, 88.09%; H, 8.53%; N, 3.36%. Found for copolymer 7: C, 86.30%; H, 8.80%; N, 4.80%. Calcd for C_8H_8: $C_{12}H_{17}N$ = 1.11:1: C, 86.28%; H, 8.90%; N, 4.81%. Found for copolymer 8: C, 85.40%; H, 9.60%; N, 5.70%. Calcd for C_8H_8: $C_{12}H_{17}N$ = 0.62:1: C, 84.99; H, 9.16; N, 5.83%. Found for copolymer 9: C, 87.50%; H, 8.50%; N, 3.70%. Calcd for C_8H_8: $C_{12}H_{17}N$ = 1.79:1: C, 87.48%; H, 8.65%; N, 3.85%.

The data presented in Table II show copolymers 6–8 to have similar molecular weights. Styrene was similarly polymerized using AZBN at two different concentrations (0.24% and 0.99% on monomer weight) yielding polystyrenes PS10 and 11 of molecular weight 3.89×10^5 and 4.98×10^4, respectively, as derived from the Mark-Houwink equation where $[\eta]_0$ was determined in toluene at 25°C and K and α are those reported by Green,[11] viz., $K = 1.16 \times 10^{-4}$ and $\alpha = 0.72$.

Apparatus and Procedure

Differential Thermal Analysis (DTA). A du Pont 900 thermal analyzer equipped with a cell capable of operation from −100° to +550°C was employed. The sample was located in a glass macrotube, and an identical tube containing glass beads acted as the inert reference material. In all experiments, a heating rate of 20°C/min (nominal) and a flow rate of 400 ml/min of nitrogen was employed. The glass transition temperature (T_g) was determined as previously described[12] for all the polymers. Five determinations were made for each polymer and the average T_g calculated.

Differential Scanning Calorimetry (DSC). A du Pont 900 thermal analyzer equipped with a DSC cell capable of operation from ambient to 600°C was used. The sample (≃6 mg) was located in an uncrimped aluminum pan (7 mm in diameter), and an empty pan acted as the inert reference. A heating rate of 20°C/min (nominal) was used together with a flow rate of 400 ml/min of nitrogen.

Thermogravimetry (TG). Dynamic TG studies were made using a du Pont 900 thermal analyzer equipped with a 950 thermogravimetric analysis attachment. Samples of polymer (≃10 mg) contained in an aluminum bucket were subjected to a linear heating rate of 8°C/min (nominal) in dynamic nitrogen flowing over the sample at 250 ml/min.

Isothermal TG studies were made using the above apparatus in its isothermal mode by the following method. The furnace was heated to the required temperature in the operational position and the apparatus was allowed to come to thermal equilibrium with nitrogen passing through the quartz tube. The furnace was then rolled away from the tube and the sample/crucible added to the rise rod. The furnace was then placed over the sample and the weight loss recorded for periods of up to 90 min. The nitrogen flow rate was 250 ml/min, and sample sizes of approximately 10 mg were used.

Infrared Spectroscopy (IR). Spectra were recorded on a Unicam spectrophotometer Model SP200. Liquid samples were run as thin films between sodium chloride plates. Polymer samples were run as 1% suspensions in potassium bromide discs.

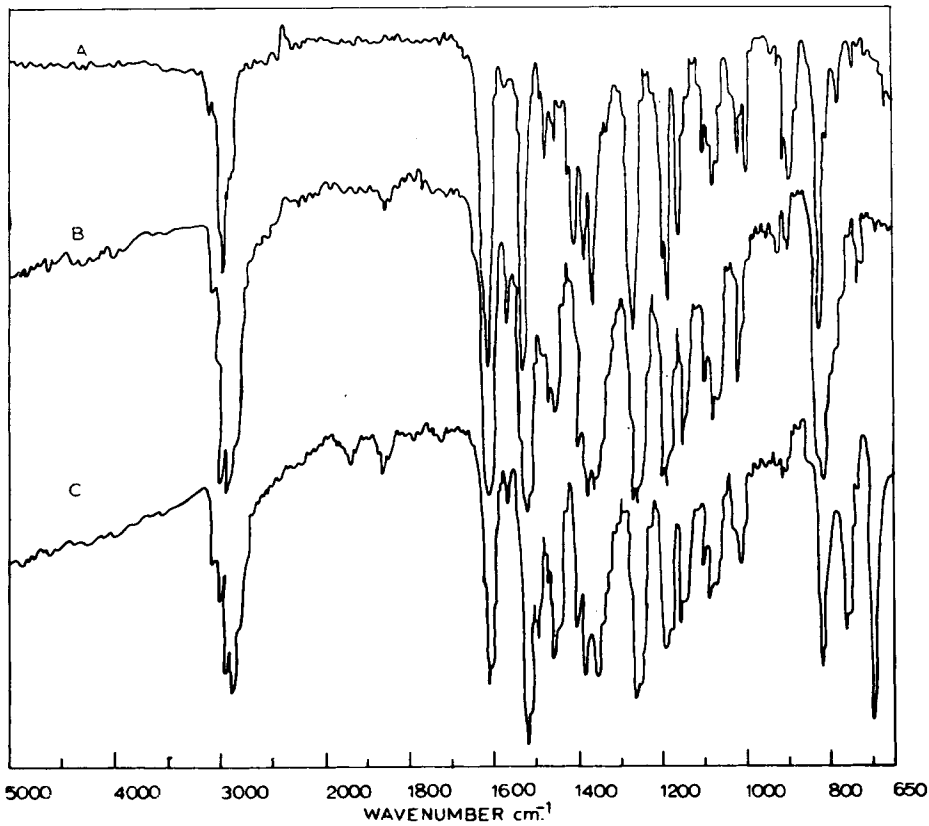

Fig. 1. Infrared spectra of (a) *p*-N,N-diethylaminostyrene; (b) poly(*p*-N,N-diethylaminostyrene); (c) styrene/*p*-N,N-diethylaminostyrene copolymer.

DISCUSSION

The monomer *p*-N,N-diethylaminostyrene (*p*-DEAS) has been synthesized from N,N-diethylaniline and its conversion to poly(*p*-N,N-diethylaminostyrene) (PDEAS) has been achieved using azobisisobutyronitrile as free-radical initiator. The synthesis was effected by methods which have been utilized previously for the synthesis of *p*-N,N-dimethylaminostyrene.[5,10] Both the monomer and its precursor α-methyl-*p*-N,N-diethylaminobenzyl alcohol are new compounds. Combustion analysis figures and the IR spectrum of the monomer shown in Figure 1a are consistent with the formula $C_{12}H_{17}N$. Polymerization with a nonoxidizing radical source proceeded smoothly in bulk, and reference to Table I shows that the normal initiator concentration, intrinsic viscosity, and hence molecular weight relationship is obeyed. Molecular weights were calculated on the basis of the Mark-Houwink equation, where K and α were taken as 6.17×10^{-4} and 0.56, respectively. These values are those which were obtained experimentally for the related *p*-N,N-dimethylamino-substituted polymer.[5] Inspection of the IR spectrum of a representative homopolymer sample (Fig. 1b) shows the disappearance of bands associated with the vinylic grouping.

Copolymerization of p-N,N-diethylaminostyrene with styrene using an approximately constant concentration of AZBN was effected to completion and resulted in the case of copolymers 6, 7, and 8 in similar molecular weights (see Table II) and polymers richer in the styrene component than the original feed stock. Copolymer 9 is apparently anomalous in this respect; but it is not directly comparable with the other copolymers, since it was polymerized with a lower AZBN concentration over a much longer period of time where the purely thermal mode of polymerization may have played the dominant role in polymerization.

Inspection of the IR spectrum of a representative copolymer[7] (Fig. 1c) shows the normal features of the homopolymer spectrum together with those of the monosubstituted benzenoid nucleus associated with the styrene units within the chain. Combustion analysis has been used to assess the average repeating unit within the copolymers.

The effect of molecular weight on the glass transition temperature of the PDEAS homopolymers in shown in Table III together with those for the PS samples. The results for PS are in accord with previous data[13,14] which showed the glass transition temperature of PS to increase with increasing molecular weight, reaching a maximum value at molecular weights of the order of 50–100,000 where the relative effects of decreasing the number of chain ends in the system becomes negligible.

It would appear that a similar but much less pronounced effect occurs with PDEAS which has a $T_{g\infty}$ value only slightly higher than that of PS. This behavior contrasts markedly with that described earlier for poly(p-N,N-dimethylaminostyrene) (PDAS).[12] The T_g for PDAS shows a marked molecular weight dependence with T_g 109°C at $\bar{M}_n$ 12,000, rising to a $T_{g\infty}$ value of 146°C. The increase in $T_{g\infty}$ when compared with PS was ascribed to a combination of (a) dipolar interaction between adjacent substituted phenyl ring systems in the same or neighboring chains as a result of the electronic effects of the p-N,N-dimethylamino substituent, and (b) increased interchain steric hindrance. These effects increase the overall chain stiffness resulting in the elevation of $T_{g\infty}$ as compared with PS in a similar manner to that described by Barb[15] for alkyl- and halogen-substituted polystyrenes.

It is apparent, however, that with PDEAS, increasing the bulkiness and flexibility of the N,N-dialkyl substituent on the ring affects these chain stiffening effects. Reduction of interchain steric hindrance occurs together with

TABLE III
Glass Transition Temperatures for PDEAS Homopolymers

Polymer	Sample no.	$[\eta]_0$	$\bar{M}_n \times 10^{-4}$ [a]	T_g, °C	$10^4/\bar{M}_n$
PDEAS	1	0.55	18.54	105	0.0539
PDEAS	2	0.39	10.03	102	0.0997
PDEAS	3	0.31	6.66	101	0.1502
PDEAS	4	0.22	3.61	101	0.2771
PDEAS	5	0.18	2.52	100	0.3965
PS	10	0.28	4.98 [b]	96	—
PS	11	1.23	38.9 [b]	100	—

[a] Calculated using $[\eta]_0 = KM^{\alpha}$, where $K = 6.17 \times 10^{-4}$, $\alpha = 0.56$.
[b] Calculated using $[\eta]_0 = KM^{\alpha}$, where $K = 1.16 \times 10^{-4}$, $\alpha = 0.72$.

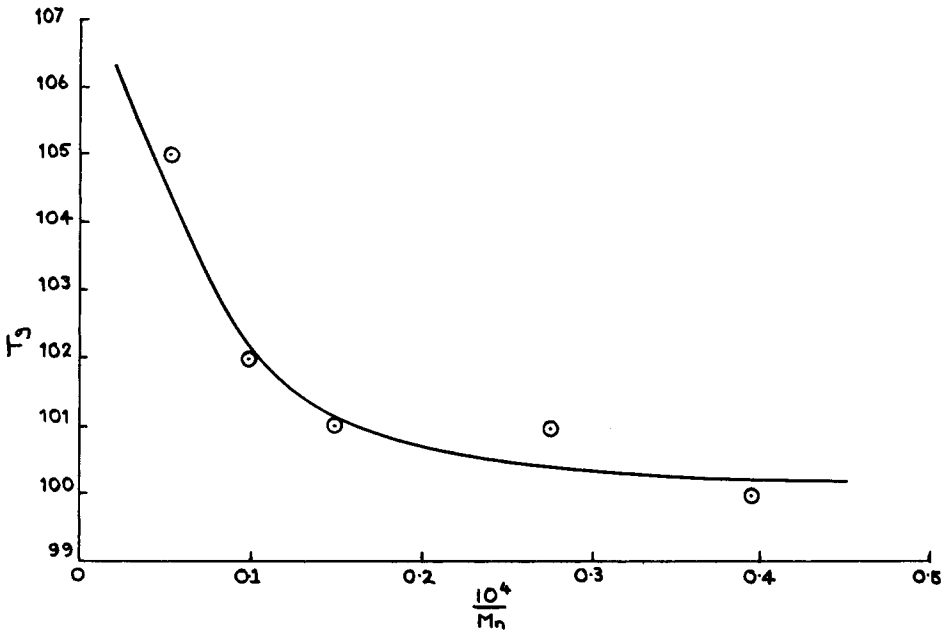

Fig. 2. Glass transition temperature and molecular weight plotted according to the Flory-Fox equation.

the effect of the bulky group on the close packing of the chains, which results in lower dipolar interaction and an overall reduction in the $T_{g\infty}$ of PDEAS compared with PDAS.

In addition, it would appear that the effects of the change in "free volume" of the polymer chain ends as the molecular weight of PDEAS increases is small in comparison with the "swept free volume" associated with the *p*-N,N-diethylamino substituent and the effect of the bulk of that substituent on chain packing.

If the data is plotted according to the Flory and Fox equation[16] as shown in Figure 2. It can be seen that this relationship only appears to hold for the higher molecular weight samples. This is, of course, subject to a degree of uncertainty since the molecular weights were derived using the Mark-Houwink equation assuming that the constants were similar to those obtained experimentally for PDAS and that they applied over the whole molecular weight range studied. Computation of the free volume of the chain end from the initial slope of the curve (Fig. 2) by the method described previously for PDAS[12] leads to a value of 134 Å^3.

The glass transition temperatures for the copolymers are shown in Table IV. In the range studied, it is clear that as the molar percentage of *p*-DEAS is increased, the T_g increases. The results, however, cannot be assessed using the Gibbs-Di Marzio and Wood[17,18] relationship since both compositional and molecular weight effects are present in these systems. In all cases, one T_g was observed confirming the random nature of these copolymers.

In addition to the studies discussed above, the polymers were subjected to thermal degradation in nitrogen to assess the effect of the *p*-N,N-diethylamino substituent on the degradation behavior and thermal stability as compared with polystyrene. The behavior of PDEAS homopolymers as com-

pared with the two PS samples is compared in Table V. The data presented in Table V show that, within experimental error, molecular weight had no effect upon the PDT, the 50% DT, or the thermogram shape for PDEAS homopolymer samples. Isothermal weight loss studies similarly revealed no significant differences between PDEAS samples 1–5 with W_{30} at 400°C (% weight loss in 30 min) being 95%, comparable with PS at 94%.

PS showed a molecular weight effect upon PDT, with the lower molecular weight sample giving a reduced PDT. This behavior is similar to that recently reported by Malhotra and co-workers[17] who found that decomposition of PS in nitrogen for the molecular weight range of 900–1.6 × 10^5 begins between 200° and 350°C, dependent on molecular weight. In addition, they found that 100% decomposition occurred at higher temperatures for the lower molecular weight samples, as was observed in this work for both PS and PDEAS.

Thus, it would appear that PDEAS and PS show similar stability when assessed by these methods.

Further to this, the DSC traces (Fig. 3) show marked similarity with corrected peak minima at 422°C for PS and 414°C for PDEAS. PDEAS would thus appear to be slightly less stable than PS under these conditions. Heats of degradation for PS and PDEAS are also similar, with PS 19.7 kcal/mole repeating unit and PDEAS 20.85 kcal/mole repeating unit. This overall behavior of PDEAS contrasts sharply with that of PDAS reported previously[12] (PDT, 350°C; 50% DT, 414°C; W_{30}, 47.5%; heat of degradation, 15.8 kcal/mole repeating unit), suggesting that a different mechanism of degradation is

TABLE IV
Glass Transition Temperatures for S:*p*-DEAS Copolymers

Copolymer sample no.	Molar ratio S:*p*-DEAS	$[\eta]_0$	T_g, °C
6	2.20:1	0.52	95
7	1.11:1	0.45	100
8	0.62:1	0.43	102
9	1.79:1	0.93	95

TABLE V
Comparative Thermal Stabilities of PDEAS and PS as Assessed by TG in Dynamic Nitrogen

Polymer sample	Temperature, °C, for specified % weight loss			
	0[a]	10	50[b]	75
PDEAS 1	353	397	417	428
PDEAS 2	350	393	416	427
PDEAS 3	345	390	415	429
PDEAS 4	353	394	419	431
PDEAS 5	353	398	423	434
PS 10	314	394	421	431
PS 11	357	402	422	430

[a] PDT procedural decomposition temperature.
[b] 50% DT (50% decomposition temperature).

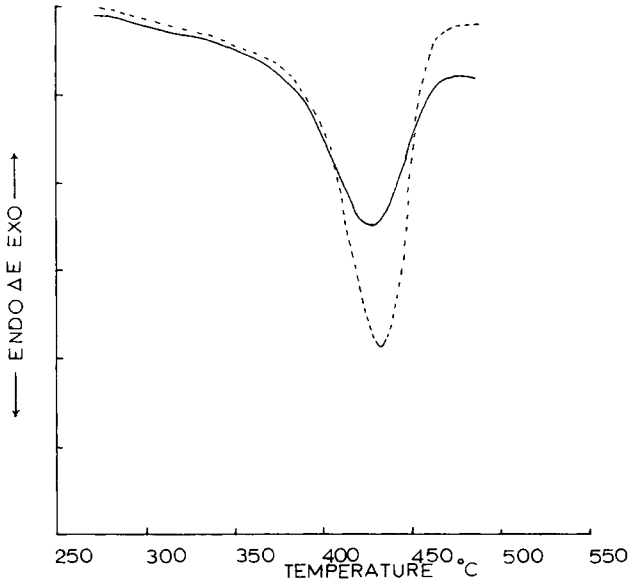

Fig. 3. DSC curves for PS and PDEAS in dynamic nitrogen: (- - - - - -) PS, 4.05 mg; (—) PDEAS, 4.60 mg.

operative in the two systems. Studies are currently in progress on the vacuum pyrolysis of this system and will be the subject of a future publication.

Comparative studies on the S/*p*-DEAS systems were also made and the results obtained are shown in Table VI. The data presented in Table VI indicate that the stability is independent of copolymer composition.

Heat of reaction data from DSC studies are shown in Table VII, which show an increase in ΔH as the styrene content of the system increases.

Kinetic Studies

Comparative studies were made using TG and DSC. Activation energies were derived from dynamic TG data by the MaCallum and Tanner[20] method (method I) and from isothermal data (method II), and the results are shown in Table VIII. Similar studies were made using DSC by the methods of

TABLE VI
Comparative Thermal Stabilities of
S:*p*-DEAS Copolymers Assessed by TG in Dynamic Nitrogen

Copolymer sample no.	S:*p*-DEAS ratio[a]	Temperature, °C, for specified % weight loss			
		0[b]	10	50[c]	75
6	2.20:1	355	396	421	433
7	1.11:1	353	398	423	435
8	0.62:1	353	398	423	434
9	1.79:1	359	404	425	434

[a] Evaluated by combustion analysis.
[b] PDT.
[c] 50% DT.

Friedman[21] and Reich.[22] The results obtained are shown in Table IX.

The results presented in Tables VIII and IX indicate the difficulties associated with the derivation of kinetic parameters from a process as complex as PS degradation. The order of reaction for PS degradation has been shown to vary with the percentage degradation,[19] and the activation energy has been shown to vary with the molecular weight and the % degradation of the sample.[18,22] Thus, it is not surprising that the different methods show different values for the activation energies and orders of reaction which are dependent on the mode of assessment. Each method, while not representative of one particular degradation reaction, should yield results which are comparable from system to system provided similar polymers degrading by similar mechanisms are being studied.

The results shown in Tables VIII and IX can, therefore, be regarded only as qualitative and as such generally indicate a similar order of stability for all systems, with PS being slightly less stable than PDEAS by this method of assessment.

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TABLE VII
Heats of Degradation in Dynamic Nitrogen

Polymer	ΔH, kcal/kg
PDEAS	119.1
PS	189.1
Copolymer 6	153.3
Copolymer 7	140.8
Copolymer 8	134.8

TABLE VIII
Kinetic Parameters Evaluated by Thermogravimetry

Polymer	Activation Energy, kcal/mole	
	Method I[a]	Method II[b]
PDEAS 1	49.9	48.5
S:*p*-DEAS 7	47.6	50.4
PS	46.6	48.7

[a] At 0.4 fraction conversion.
[b] Assuming a first order reaction.

TABLE IX
Kinetic Parameters Evaluated by DSC

Polymer	Reich method			Friedman method	
	E, kcal/mole	*n*	Temp, °C	E, kcal/mole	*n*
PDEAS 1	60.9	1.44	386—414	55.8	0.68
S:*p*-DEAS 7	59.8	1.39	381—419	55.1	1.08
PS	51.8	0.97	381—450	57.8	1.34

References

1. R. H. Still and C. J. Keattch, *J. Appl. Polym. Sci.*, **10,** 193 (1966).
2. R. H. Still, P. B. Jones, and A. L. Mansell, *J. Appl. Polym. Sci.*, **13,** 401 (1969).
3. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13,** 1555 (1969).
4. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13,** 2033 (1969).
5. R. H. Still, M. B. Evans, and A. Whitehead, *J. Appl. Polym. Sci.*, **16,** 3207 (1972).
6. R. H. Still and A. Whitehead, *J. Appl. Polym. Sci.*, **16,** 3223 (1972).
7. J. C. Duff, *J. Chem. Soc.*, 276 (1945).
8. J. P. Dippy, L. T. Hogarth, H. B. Watson, and F. R. William, *J. Soc. Chem. Ind.* **56,** 346T (1937).
9. C. S. Marvel, C. O. Overberger, R. E. Allen, and J. H. Saunders, *J. Amer. Chem. Soc.*, **68,** 737 (1946).
10. C. L. Arcus and W. A. Hall, *J. Chem. Soc.*, 4199 (1963).
11. J. H. S. Green, *J. Polym. Sci.*, **34,** 514 (1959).
12. R. H. Still and A. Whitehead, *J. Appl. Polym. Sci.*, **20,** 627 (1976).
13. B. Wunderlich and D. W. Bodily, *J. Appl. Phys.*, **35,** 103 (1964).
14. E. Jenckel and K. Ueberreiter, *Z. Phys. Chem.*, **A182,** 361 (1938).
15. W. G. Barb, *J. Polym. Sci.*, **37,** 515 (1959).
16. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21,** 587 (1950).
17. E. A. Di Marzio and J. H. Gibbs, *J. Polym. Sci.*, **40,** 121 (1959).
18. L. A. Wood, *J. Polym. Sci.*, **28,** 319 (1958).
19. S. L. Malhotra, J. Hesse, and L. P. Blanchard, *Polymer*, **16**(2), 81 (1975).
20. J. R. MacCallum and J. Tanner, *Eur. Polym. J.*, **6,** 907 (1970).
21. H. L. Friedman, *J. Polym. Sci., B* **7,** 41 (1969).
22. L. Reich, *Makromol. Chem.*, **123,** 42 (1969).
23. B. V. Kokta, J. L. Valade, and W. N. Martin, *J. Appl. Polym. Sci.*, **17,** 1 (1973).

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