

Thermal Degradation of Polymers. XII. Synthesis, Polymerization and Thermal Characterization of Polymers of *m*-N,N-Dimethylaminostyrene in Nitrogen

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Synopsis

The monomer *m*-N,N-dimethylaminostyrene has been synthesized from acetophenone 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 parts X and XI of this series,^{1,2} we discussed the effect of molecular weight and copolymer composition on the thermal behavior of poly(*p*-N,N-dimethylaminostyrene) (PDAS) homopolymers and copolymers¹ and poly(*p*-N,N-diethylaminostyrene) (PDEAS) homopolymers and copolymers² in nitrogen.

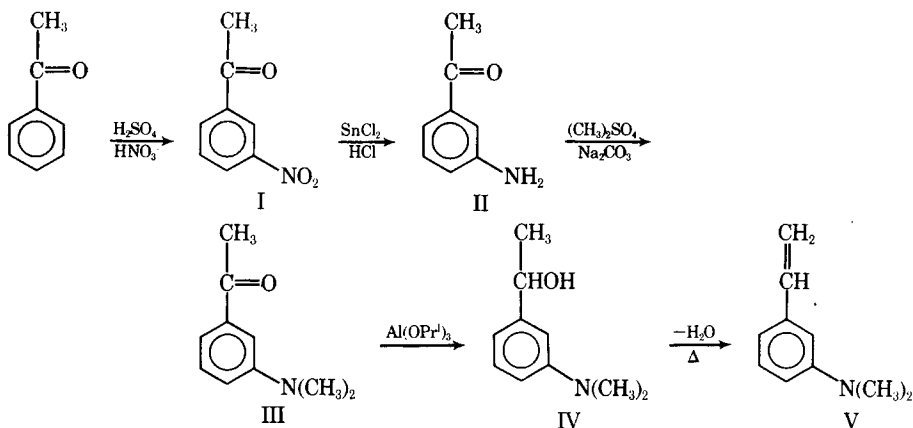
We now report studies on the synthesis, polymerization, and copolymerization of *m*-N,N-dimethylaminostyrene polymers (*Pm*DAS), and their characterization by thermal analytical techniques [thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC)].

EXPERIMENTAL

Materials

The monomer was synthesized from acetophenone by the following route:

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Acetophenone was converted to *m*-nitroacetophenone (I) by a method previously reported.³ Compound (I) was converted to *m*-aminoacetophenone by modification of a previously reported method for the reduction of *m*-nitrostyrene.³ Stannous chloride dihydrate (206 g) and concentrated hydrochloric acid (133 ml) were stirred together for 30 min in a 1-liter, three-necked flask equipped with a reflux condenser, a dropping funnel, and a thermometer. The reaction vessel was maintained at 70–80°C, and a green-yellow solution was obtained to which was added over a period of 30 min a solution of *m*-nitroacetophenone mp 77–78°C (33 g) in ethanol (50 ml). After addition was complete, the solution was boiled under reflux for 1 hr. The reaction mixture was then cooled and added dropwise to a vigorously stirred ice-cold solution of sodium hydroxide (266 g) in water (700 ml). The precipitated product was filtered and extracted with chloroform (4 × 75 ml). The chloroform extract was dried over anhydrous sodium sulfate and the chloroform removed by distillation. It gave on recrystallization from industrial methylated spirit *m*-aminoacetophenone mp 94–95°C in 85% yield.

The conversion of *m*-aminoacetophenone to *m*-dimethylaminoacetophenone was effected by a modification of Komogawas procedure.⁵ *m*-Aminoacetophenone (13.6 g) and a 7% solution of sodium carbonate (500 ml) were stirred together in a 1-liter, three-necked flask equipped with a reflux condenser, a dropping funnel, a thermometer, and a magnetic stirrer. Dimethyl sulfate (32 ml) was added dropwise to the stirred solution over a period of 1 hr. The temperature of the reaction media was then raised to 60°C and maintained at this temperature for 1 hr. The unreacted dimethyl sulfate was then decomposed by the addition of solid sodium hydroxide (20 g). *m*-*N,N*-Dimethylaminoacetophenone was then extracted from the reaction medium with ether (4 × 75 ml). The combined ethereal extract was dried over anhydrous sodium sulfate and the ether removed by rotary film evaporation. The resultant product was boiled under reflux for 3 hr with a threefold excess of acetic anhydride to remove the monomethyl derivative. The cooled solution was dissolved in ether and extracted with 2*N* hydrochloric acid. The acid extract was neutralized with 2*N* sodium hydroxide and *m*-*N,N*-dimethylaminoacetophenone extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate and the ether removed by rotary film evaporation.

m-N,N-Dimethylaminoacetophenone was obtained by distillation at reduced pressure. It had bp 110–112°C/0.5 mm Hg (lit.⁵ 98°/4 mm); yield 63%.

m-N,N-Dimethylaminoacetophenone (III) was converted into α -methyl-*m*-N,N-dimethylaminobenzyl alcohol (IV) by reduction with aluminum isopropoxide by the following method:

Aluminum foil (4.72 g), mercuric chloride (0.055 g), and dry isopropanol (194 ml) were placed in a 500-ml flask equipped with a reflux condenser, a dropping funnel, and a thermometer. The isopropanol was boiled under reflux until the aluminum had dissolved (6 hr). *m*-N,N-Dimethylaminoacetophenone (55 g) was then added to the solution and the reaction mixture was boiled under reflux for a further 2 hr. The excess of isopropanol and the acetone formed in the reaction were then removed by distillation at slightly reduced pressure. The residue was then treated with 2*N* sodium hydroxide and then extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate and the ether removed and the product obtained by fractional distillation at 101–103°C/0.09 mm Hg, N_D^{25} 1.5555 in 64% yield (lit.⁶ bp 126–128°C/2 mm Hg, N_D^{22} 1.5620).

The dehydration of α -methyl-*m*-N,N-dimethylaminobenzyl alcohol was effected in a similar manner to that of Mannecke and Kossmehl.⁶ Compound IV (5 g) was added dropwise to activated alumina (16 g) maintained at 280–300°C in a pear-shaped distillation flask, and the products of reaction allowed to distil out of the reaction vessel under nitrogen at a pressure of 0.1–0.2 mm Hg. The distillate was condensed in a receiver cooled in an ice-salt bath. The colorless liquid so obtained was dried over anhydrous sodium sulfate and redistilled in nitrogen under vacuum in the presence of diphenyl picryl hydrazyl. The main fraction obtained in 74% yield had bp 57–59°C/0.025 mm Hg, N_D^{22} 1.5872 (lit.⁵ bp 105°C/2 mm; lit.⁷ N_D^{22} 1.5863).

ANAL. Found: C, 81.30%; H, 8.70%; N, 9.40%. Calcd for C₁₂H₁₃N: C, 81.63%; H, 8.84%; N, 9.52%.

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 0.2% and 3.2% on monomer weight. This yielded poly(*m*-N,N-dimethylaminostyrenes) (*PmDAS*) 1–4 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 to constant weight at 2 mm Hg (three to four days). Three representative samples, *PmDAS* 1–3, were subjected to combustion analysis.

ANAL. Found for *PmDAS* 1: C, 81.50%; H, 9.10%; N, 9.30%; *PmDAS* 2: C, 81.80%; H, 8.90%; N, 9.40%; *PmDAS* 3: C, 81.70%; H, 9.00%; N, 9.50%. Calcd for C₁₀H₁₃N: C, 81.63%; H, 8.84%; N, 9.52%.

PmDAS samples were characterized by intrinsic viscosity determination in toluene at 25° using a Ubbelohde No. 1 dilution viscometer. The data presented in Table I show the polymers to have sensibly different molecular weights.

TABLE I
Intrinsic Viscosities for *PmDAS* Homopolymer

<i>PmDAS</i> sample no.	AZBN, %	Intrinsic viscosity $[\eta]_0$
1	0.18	0.83
2	1.11	0.35
3	1.77	0.32
4	3.26	0.15

TABLE II
S:m-DAS Copolymer Characterization Data

Sample no.	AZBN, %	Approx. molar ratio <i>S:mDAS</i>	Molar ratio from combustion <i>S:mDAS</i> analysis	Intrinsic viscosity $[\eta]_0$
5	1.16	2.5:1	2.43:1	0.42
6	0.99	1.5:1	1.56:1	0.48
7	1.09	0.5:1	0.56:1	0.55

Copolymerization of styrene (*S*) and *m*-*N,N*-dimethylaminostyrene (*m-DAS*) in various molar ratios under similar conditions with an initiator concentration of $\approx 1.0\%$ on total monomer weight yielded copolymers 5, 6, and 7 after 6 hr as solid glasses. Purification and characterization by viscometry was effected as previously described for the homopolymers. Combustion analysis was performed on all copolymer samples.

ANAL. Found for copolymer 5: C, 88.60%; H, 8.30%; N, 3.40%. Calcd for $C_8H_8:C_{10}H_{13}N = 2.43:1$: C, 88.39%; H, 8.11%; N, 3.49%. Found for copolymer 6: C, 87.00%; H, 8.10%; N, 3.49%. Calcd for $C_8H_8:C_{10}H_{13}N = 1.56:1$: C, 87.23%; H, 8.23%; N, 4.52%. Found for copolymer 7: C, 84.70%; H, 8.70%; N, 6.80%. Calcd for $C_8H_8:C_{10}H_{13}N = 0.56:1$: C, 84.71%; H, 8.50%; N, 6.77%.

The data presented in Table II show the copolymers to have similar molecular weights.

Polystyrene samples 8 and 9 were prepared and characterized as previously reported² (part XI of this series) for samples PS10 and 11.

Apparatus and Procedure

Thermal analysis studies using differential thermal analysis (DTA), differential scanning calorimetry (DSC), and dynamic and isothermal thermogravimetry (TG) were made as previously reported in part XI.²

RESULTS AND DISCUSSION

The monomer *m-DAS* has been synthesized from acetophenone by modification of the known route, and polymerized using a nonoxidizing radical source (AZBN) to yield homopolymers 1–4 of different molecular weights and copolymers with styrene (5–7) having different compositions.

Reference to Tables I and III shows the normal initiator concentration/molecular weight relationship to be obeyed for the homopolymer systems.

The effect of molecular weight on the glass transition temperature of the

TABLE III
 Glass Transition Temperatures for *PmDAS* homopolymers

Polymer	sample no.	$[\eta]_0$	$\bar{M}_n \times 10^{-4}$	$T_g, ^\circ\text{C}$
<i>PmDAS</i>	1	0.83	38.65	86
<i>PmDAS</i>	2	0.35	8.269	83
<i>PmDAS</i>	3	0.32	7.047	82
<i>PmDAS</i>	4	0.15	1.821	80
PS	10	0.28	4.980 ^a	96
PS	11	1.23	38.900 ^a	100

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

 TABLE IV
 T_g Values for Various Substituted Polystyrenes^b

Polymer	Position of substitution	
	meta	para
Poly(methylstyrene)	82	105
Poly(chlorostyrene)	90	128
Poly(<i>N,N</i> -dimethylaminostyrene) ^a	87	146

^a Reference 1 and this paper.

PmDAS homopolymers is shown in Table III, together with those for representative PS samples. The results for PS have been discussed in a previous paper.²

The molecular weight data reported for *PmDAS* was calculated using the constants obtained experimentally for the related poly(*p*-*N,N*-dimethylaminostyrene) homopolymers (PDAS) in toluene, namely, $\alpha = 0.56$ and $K = 6.17 \times 10^{-4}$.

It is apparent that the effect of molecular weight on T_g for *PmDAS* is of a similar order to that observed for poly(*p*-*N,N*-diethylaminostyrene) (PDEAS) reported previously,² viz., 100°C at \bar{M}_n 24,900, 105°C at \bar{M}_n 183,600. The magnitude of the T_g and molecular weight effects observed for the present polymers contrasts markedly with that shown by *p*-*N,N*-dimethylaminostyrene (*p*-DAS) homopolymers reported in an earlier paper.¹ The T_g of PDAS ranges from 109°C at \bar{M}_n 12,200, rising to a $T_{g\infty}$ value of 146°C.

The overall reduction in the value of the T_g of *PmDAS* compared with PDAS is similar to that observed by Barb⁸ for methyl- and chloro-substituted polystyrenes, as shown in Table IV.

Barb ascribed the reduction of the T_g in the case of meta substituents by reference to atomic models, to "loosening" of the structure without offering the opportunity of steric interference of the substituent with segments of other chains, which he showed to occur with the corresponding para substituents resulting in chain stiffening.

The increase in T_g for chloro-substituted styrenes over that observed for the similarly sized methyl-substituted styrene and for PS was ascribed to the additional dipolar effect in the chlorostyrene system due to the electronic effects ($-I + M$) of the substituent chlorine atom.

Similar effects to those suggested by Barb may account for the increase in

TABLE V
 T_g for S:m-DAS Copolymers

Copolymer sample no.	Molar ratio ^a S:m-DAS	$[\eta]_0$	$T_g, ^\circ\text{C}$
5	2.43:1	0.42	94
6	1.56:1	0.48	92
7	0.56:1	0.55	84

^a From combustion analysis.

the T_g of PDAS¹ compared with PS and PmDAS. The reduction in T_g for PmDAS compared with PS and PDAS arises as a result of the effects of the nonsymmetrical, pendent, substituted phenyl nucleus on chain "loosening" interchain steric hindrance and dipolar interaction.

The smaller effect of molecular weight on T_g in the PmDAS system compared with PDAS may be ascribed to the effect of the nonsymmetrical substituted phenyl group on the overall "free volume" of the polymer, which is relatively unaffected by increasing the number of chain ends in the system. If the data presented in Table III are plotted according to the Flory-Fox equation,⁹ the curve shown in Figure 1 is obtained. This shows the equation to hold for this system only at high molecular weights if the assumptions made in deriving the molecular weight data are tenable.² Computation of the free volume of the chain end from the initial slope of the curve by the method previously described for PDAS¹ leads to a value of 79 \AA^3 .

Table V shows the glass transition temperatures for the copolymer systems. In the range studied, it is clear that as the molar percentage of S is in-

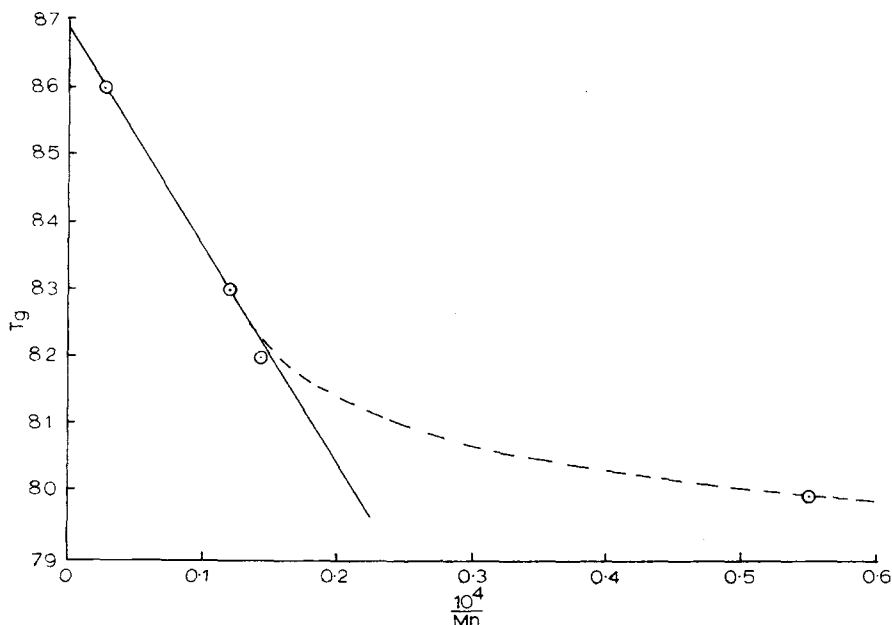


Fig. 1. Flory-Fox plot for PmDAS homopolymers.

TABLE VI
Comparative Thermal Stabilities of *Pm*DAS and PS as Assessed
by TG in Dynamic Nitrogen

Polymer sample	Temperature, °C, for specified % weight loss			
	0 ^a	10	50 ^b	75
<i>Pm</i> DAS 1	338	393	426	439
<i>Pm</i> DAS 2	343	402	430	446
<i>Pm</i> DAS 3	348	402	431	447
<i>Pm</i> DAS 4	340	402	434	447
PS 10	314	394	421	431
PS 11	357	402	422	430

^a PDT (procedural decomposition temperature).

^b 50% DT (50% decomposition temperature).

creased, the T_g increases. This behavior is again different from that reported previously for styrene/*p*-DAS copolymers¹ and suggests a reduction in the chain "loosening" effect of the *m*-N,N-dimethylamino substituent and an increase in van der Waals interaction as the system is progressively diluted with substituted phenyl units. In no case was more than one T_g observed, confirming the random nature of these copolymer systems.

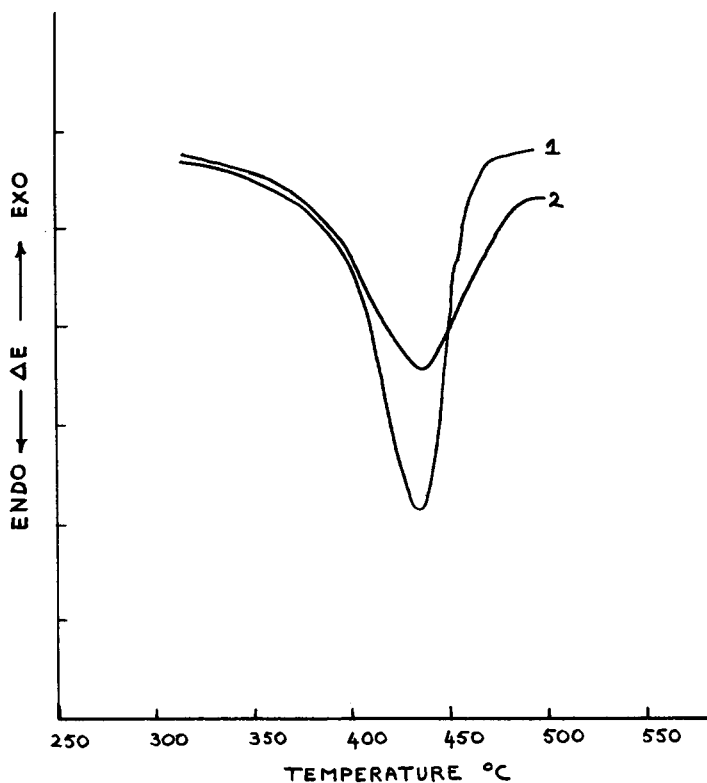


Fig. 2. DSC curves in nitrogen for *Pm*DAS and PS: (1) PS sample weight 4.05 mg; (2) *Pm*DAS 1, sample weight 4.50 mg.

TABLE VII
Comparative Thermal Stabilities of S:*m*-DAS Copolymers Assessed
by TG in Dynamic Nitrogen

Copolymer sample no.	S: <i>m</i> -DAS ratio ^a	Temperature, °C, for specified % weight loss			
		0 ^b	10	50 ^c	75
5	2.43:1	338	389	421	435
6	1.56:1	338	393	424	438
7	0.56:1	330	385	422	438

^a Evaluated by combustion analysis.

^b PDT.

^c 50% DT.

TABLE VIII
Heats of Degradation in Dynamic Nitrogen

Polymer	ΔH, kcal/kg
<i>Pm</i> DAS 1	117.6
<i>Pm</i> DAS 2	118.6
<i>Pm</i> DAS 3	119.7
Copolymer 5	159.0
Copolymer 6	152.4
Copolymer 7	135.3
PS	189.1

Thermal Stability Studies

The polymers were subjected to thermal degradation in nitrogen to assess the effect of the *m*-N,N-dimethylamino substituent on the degradation behavior and the thermal stability as compared to PS. The behavior of *Pm*DAS homopolymers and the two PS samples is compared in Table VI. The data show that within experimental error for *Pm*DAS samples, molecular weight had no effect on thermogram shape or the derived parameters such as PDT or 50% DT values. Isothermal studies similarly revealed no significant differences between *Pm*DAS 1–4 with W_{30} at 400°C being 93%, compared with a W_{30} value for PS of 94%. The data for PS were discussed in the previous paper.²

The values obtained for PS and *Pm*DAS and PDEAS² indicate that these systems have similar stabilities as assessed by dynamic and isothermal methods. Further to this, the DSC traces (Fig. 2) show marked similarity with a corrected peak minimum of 422°C for PS and 425°C for *Pm*DAS compared with PDEAS² 414°C.

The behavior of *Pm*DAS contrasts with that reported for PDAS¹ (PDT, 350°C; 50% DT, 414°C; W_{30} , 47.5%), suggesting that a different mechanism of degradation operates in the two systems. Vacuum pyrolysis of *Pm*DAS and product analysis studies are currently in progress and will be the subject of a future publication.

Comparative studies on the S:*m*-DAS copolymers are shown in Table VII. The data indicate that the stability is independent of copolymer composition in the range studied.

TABLE IX
Kinetic Parameters Evaluated by Thermogravimetry

Polymer	Activation energy, kcal/mole	
	Method I ^a	Method II ^b
<i>Pm</i> DAS 1	51.4	52.6
<i>S:m</i> -DAS 6	50.9	49.8
PS	46.6	48.7

^a At 0.4 fractional conversion.

^b Assuming a first order reaction.

TABLE X
Kinetic Parameters Evaluated by DSC

Compound	Reich method			Friedman method	
	<i>E</i> , kcal/mole	<i>n</i>	Temp, °C	<i>E</i> , kcal/mole	<i>n</i>
<i>Pm</i> DAS 1	54.5	1.33	381–461	47.0	0.91
<i>S:m</i> DAS 6	53.1	1.19	381–454	50.8	1.30
PS	51.8	0.97	381–450	57.8	1.34

Heats of reaction data from DSC studies are shown in Table VIII which show an increase in ΔH as the styrene content of the system increases. As can be seen, the molecular weight of the *Pm*DAS samples has little effect on the value of ΔH obtained.

Kinetic Studies

Comparative studies were made using TG and DSC. Activation energies were derived from dynamic TG data by the method of MacCallum and Tanner¹⁰ (method I) and from isothermal data (method II), and the results are shown in Table IX. Similar studies were made using DSC by the methods of Friedman¹¹ and Reich¹²; the results obtained are shown in Table X. The results obtained are subject to the limitations previously discussed for *p*-N,N-diethylaminostyrene polymers.² However, it is apparent that these systems have the same general order of stability, with PS being slightly less stable.

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