were then opened. The residue was fractionated into four fractions by successive extractions with petroleum ether (bp $60-70^\circ$), toluene, and acetonitrile. The acetonitrile insoluble fraction (0.14 g) was identified as poly(vinylidene cyanide) by comparison of its ir spectrum with that of an authentic sample. The acetonitrile soluble fraction (0.68 g) was identified as a 1 to 1 alternating copolymer of dihydropyran and vinylidene cyanide (Table V). The toluene soluble fraction (0.25 g) was identified as 8,8-dicyano-2-oxobicyclo[4.2.0]octane, ¹H nmr, CDCl₃, see Table II. The petroleum ether soluble fraction (0.03 g) was identified as poly(dihydropyran) by comparison of its ir spectrum with that of an authentic sample. **Preparation** of 7,7,8,8-Tetracyano-2-oxabicyclo[4.2.0]oc-

Preparation of 7,7,8,8-Tetracyano-2-oxabicyclo[4.2.0]octane. A solution of 0.96 g (1.0 ml, 11.4 mmol) of dihydropyran in 3 ml of tetrahydrofuran was added to a solution of 0.65 g (5.1 mmol) of tetracyanoethylene in 20 ml of tetrahydrofuran. A red color developed immediately. After 6 hr, the color faded and the solvent was removed under reduced pressure. The white solid residue was washed with ether and recrystallized from acetonitrile-dichloromethane to yield 1 g (92%) of 7,7,8,8-tetracyano-2-oxobicyclo[4.2.0]octane: mp 169–170° (lit.¹⁸ 173–176°); ¹H nmr data are reported in Table II. Anal. Calcd for C₁₁H₈N₄O: C, 62.26; H, 3.80; N, 26.40. Found: C, 62.12; H, 3.48; N, 26.42.

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Poly(amine esters) Derived from Diethyl 1,4-Cyclohexanedione-2,5-dicarboxylate

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ABSTRACT: The reaction of diethyl 1,4-cyclohexanedione-2,5-dicarboxylate (SSE) with benzylamine was studied, and the product was fully characterized as diethyl 2,5-bis(benzylamino-3,6-dihydroterephthalate). This material was oxidized to the aromatic derivative under different conditions. The polycondensation of the title compound and several benzylic diamines to produce poly(aminodihydroterephthalates), and their subsequent oxidation, was investigated. The solubilities and thermal and spectroscopic properties of the polymers were studied.

The reaction between 1,4-cyclohexanedione-2,5-dicarboxylate (I) and amines to give diethyl 2,5-diamino-1,4dihydroterephthalates was first reported by Baeyer,¹ in 1886, when he synthesized diethyl 2,5-diamino-1,4-dihydroterephthalate. In 1914, Liebermann² synthesized a number of N-substituted diaminodihydroterephthalates. This reaction has subsequently been applied to polymer synthesis. In 1968, Kimura³ first synthesized aromatic poly(aminodihydroterephthalates) using I and *m*-phenylenediamine or 4,4'-diaminodiphenyl ether. These polymers were used as precursors for polyquinolones. Higashi, *et al.*,⁴ later reacted I with aliphatic diamines to obtain polymers which formed tough films of higher molecular weight than those reported by Kimura.

Diethyl 1,4-cyclohexanedione-2,5-dicarboxylate and its tautomer, diethyl 2,5-dihydroxy-3,6-dihydroterephthalate, have four electrophilic sites, the two ethyl carboxylate carbons, and the two enol α carbons. Under mild reaction conditions, e.g., 120°, in a polar solvent, reaction takes place exclusively at the enol sites.

Higashi, et al.,⁴ have shown that the reaction between I and amines occurs in steps (Figure 1).

At room temperature, an unstable ammonium salt (II) is

formed. Between 50 and 70°, the monoaminodihydroterephthalate ammonium salt, III, is formed. At temperatures greater than 100° II or III is converted to the diaminodihydroterephthalate, IV.

Oxidation of IV to the aromatic moiety, V, is easily accomplished with reagents such as pentachloronitrobenzene in potassium hydroxide,⁵ chloranil,⁶ air in glacial acetic acid,² and iodine dispersed in an organic solvent.⁷

When R (IV, V) is aryl, conversion to linear *trans*-quinacridones (VI, VII) is readily achieved. This transformation can be accomplished with aluminum chloride in trichlorobenzene,⁸ polyphosphoric acid,⁹ and phosphorous oxychloride in nitrobenzene,¹⁰ at elevated temperatures. This conversion can also be effected thermally in a high boiling inert solvent such as Dowtherm A¹¹ (biphenyl-biphenyloxide, 23.5:76.5) (the Conrad-Limpach reaction).

It was hoped that the introduction of the benzylic group in the polymer chain would increase the flexibility of the system, enhancing solubility in organic solvents, and lead to high molecular weight aromatic polyamines. Furthermore, introduction of the benzylic group might inhibit cyclization (to produce a seven-membered ring) and result in a cross-linked network, formed by intermolecular acyla-



Figure 1.

Figure 2. ¹H nmr spectrum of diethyl 2,5-bis(benzylamino-3,6dihydroterephthalate).

tion. Such materials might be valuable high-temperature thermosetting resins.

Results and Discussion

Diethyl 2.5-Bis(benzylamino-3,6-dihydroterephthalate). Compound I can exist in two tautomeric forms, the keto and enol (see Figure 1). Spectroscopic evidence has been presented that the enol is the preferred form.^{12,13} Presumably the enol is stabilized by internal hydrogen bonding between the hydroxyl group and the ester carbonyl group.

The reaction between I and benzyl amine was studied under a number of conditions in N-methylpyrrolidone (NMP) and m-cresol.

The observations of Kimura and Higashi, *et al.*, that the reaction proceeds well in a polar solvent under acid catalysis were confirmed.

Best results were obtained using a twofold excess of ben-

Figure 3. ¹³C nmr spectrum of diethyl 2,5-bis(benzylamino-3,6dihydroterephthalate).

zylamine in NMP with trifluoracetic acid or trifluoromethane sulfonic acid as catalysts, or in m-cresol (without added catalyst other than the solvent).

The product, diethyl 2,5-bisbenzylamino-3,6-dihydroterephthalate, is a crystalline, orange solid, stable to water.

Two tautomeric forms are possible, the enamine VIII or the imine IX.

Spectral Results. ¹H Nuclear Magnetic Resonance **Spectrum.** The proton nmr spectrum (Figure 2) unequivocally supports the structure of the reaction product between SSE and benzyl amine as the enamine (VIII) on the nmr time scale, at ambient temperature.

The ring methylene protons appear as a sharp singlet at 3.13 ppm downfield from TMS. The benzyl protons appear as a double at 4.26 ppm. Protons on nitrogen are known to split protons on adjacent carbons if the rate of exchange is slow.¹⁴ Nitrogen protons are seen at 8.86 ppm. Slow rate of exchange is suggested by the broadness of the peak at this frequency.

¹³C Nuclear Magnetic Resonance Spectrum. The carbon-13 nuclear magnetic resonance spectrum (Figure 3)

^a Downfield from TMS.

shows 11 types of carbon atoms. Eleven carbons would be expected in the enamine, VIII, or the imine, IX, tautomer. Levy and Nelson¹⁵ report that the range for substituted alkenes is 80 to 145 ppm relative to TMS. Aromatic carbons appear in the range of 110 to 170 ppm while ester carbonyls fall above 160 ppm. If the preferred form were the imine, the resonances of six carbons would appear above 80 ppm, while if the enamine were the preferred form, seven resonances would be above 80 ppm. The ¹³C nmr spectrum demonstrates that the enamine is the preferred tautomeric form because there are seven carbons appearing above 80 ppm. Shift assignments are shown in Table I.

Diethyl 2,5-Bis(benzylaminoterephthalate). The oxidation of diethyl 2,5-bis(benzylamino-3,6-dihydroterephthalate) (VIII) to diethyl 2,5-bis(benzylaminoterephthalate) (X) (Figure 4) was studied. In our system mild conditions were necessary, because the susceptibility of benzylic groups to oxidation is well known. Of the various chemical methods tried, oxygen in acetic acid at reflux, or bromine in carbon tetrachloride at reflux under a nitrogen atmosphere, were equally effective.

Spectral Results. ¹H Nuclear Magnetic Resonance

^a Downfield from TMS

а

b

С

d

e

f

Figure 5. ¹H nmr of diethyl 2,5-bis(benzylaminoterephthalate).

Figure 6. ¹³C of diethyl 2,5-bis(benzylaminoterephthalate).

Spectrum. The proton nmr spectrum is presented in Figure 5. Oxidation is confirmed by disappearance of the ring methylene absorption at 3.13 ppm. The integral of the aromatic band at 7.20 ppm indicates that two protons have been added to the aromatic region. The benzylic group appears as a sharp singlet at 4.32 ppm. If exchange is fast, the hydrogen on a nitrogen will not split hydrogen on adjacent carbon atoms.¹⁴ Fast rate of exchange is evidenced by a sharp singlet at 4.53 ppm.

Carbon-13 Nuclear Magnetic Resonance Spectrum. The ¹³C nmr spectrum (Figure 6) shows 11 types of carbon

	-	-					
Polymer	Diamine	Solvent	Catalyst T	Cemp, °C	Time, hr	Yield	$\eta_{ ext{inh}}$, dl/g
E	<i>m</i> -Xylyenediamine	NMP(insol)	TFA 8.6 \times 10 ⁻² M	120	5	100	0.14ª
F	m-Xylyenediamine	<i>m</i> -Cresol		120	3.75	95.6	$0.20,^{a}$ $0.22,^{b}$ 0.32^{c}
G	m-Xylyenediamine	m-Cresol	TFA 3.2 \times 10 ⁻¹ M	120	3.75	55.5	$0.17,^{a}$ 0.11^{b}
H	m-Xylyenediamine	m-Cresol		120	4.25	94.4	0.14^{a}
I	<i>m</i> -Xylyenediamine	m-Cresol		120	8	96.7	0.15^{a}
J	m-Xylyenediamine	m-Cresol	TFA 3.1 \times 10 ⁻¹ M	120	8	30.0	0.11^{a}
K	<i>m</i> -Xylyenediamine	m-Cresol		120	21	97.1	$0.15,^a$ 0.21^b
L	<i>m</i> -Xylyenediamine	$m-{\tt Cresol}$	TFA 3.1 \times 10 ⁻¹	120	21	66.7	0.07, ^a 0.05 ^c
М	p-Xylylenediamine			120	3.5	95.9	0.34^{c}
Ν	4,4'-Bis(amino- methylbiphenyl)	m-Cresol		120	3.5	95.1	0.25 ^c
0	4,4'-Bis(amino- methyldiphenyl ether)	m-Cresol		12 0	3.75	91.4	0.19 ^c

 Table III

 Preparation of Poly(diethyl 2,5-diaralkylamino-3,6-dihydroterephthalates)

^a Hexafluoro-2-propanol (HFP), 25°, 1 g/100 ml. ^b m-Cresol, 25°, 1 g/100 ml. ^c TFA, 25°, 1 g/100 ml.

Table IV Differential Scanning Calorimetry of Some Poly(diethyl 2,5-bis(benzylamino-3,6-dihydroterephthalates))

Figure 7. Thermal gravimetric analysis of poly(diethyl 2,5-*p*-xy-lylylamino-3,6-dihydroterephthalate).

atoms. Three carbons appear below 110 ppm, indicating three aliphatic carbons. Assignments appear in Table II.

Poly(diethyl 2,5-diaralkylamino-3,6-dihydroterephthalates). In contrast to the results of Higashi, *et al.*, *m*-cresol was found to be the best polymerization solvent. It has a high boiling point (202°), it retained all the polymers produced (including the oxidized, all aromatic ones) in solution, and it apparently functions as a catalyst. An external catalyst did not seem to increase molecular weight and decreased the yield.

Polymerization was not successful in trifluoroacetic acid (TFA), methanesulfonic acid, or antimony trichloride. In the case of TFA, starting material was recovered because the temperature at reflux (72.4°) was not sufficient to cause reaction. In the cases of methanesulfonic acid and antimony trichloride, addition of these solvents caused

Figure 8. ¹H nmr of poly(diethyl 2,5-bis(*p*-xylylylamino-3,6-dihydroterephthalate)).

fuming and immediate darkening of the reaction mixture, which yielded no product.

In general, the polymers obtained were insoluble in chloroform, NMP, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, and hexamethylphosphorous triamide. Addition of lithium bromide to these solvents did not enhance solubility. The polymers (E–O) were soluble in acids such as trifluoroacetic acid, methanesulfonic acid (with darkening), *m*-cresol, and 37% HCl. Polymers (E–L, O) were soluble in hexafluoro-2-propanol and hexafluoroacetone sesquihydrate. Dilute solutions of the polymers displayed polyelectrolyte behavior (viscosity measurements) in *m*-cresol and TFA. Polyelectrolyte behavior was not observed in hexafluoro-2-propanol. The polymers were isolated as orange colored powders, which formed cohesive films upon solution casting and subsequent evaporation of the solvent. The films displayed excellent adhesion to glass.

Thermal Behavior. The results of differential scanning calorimetry are reported in Table IV. The glass transition temperature (T_g) is seen to increase as rigid and symmetrical groups are introduced into the chain. The T_g of polymer O is between F and M presumably because introduction of the oxygen atom provides more flexibility to the chain. Apparent crystallization temperatures were observed in all four polymers. However, decomposition occurred before

 Table V

 Thermal Gravimetric Analyses (deg) for Some Poly(diethyl 2,5-bis(benzylamino-3,6-dihydroterephthalates))

	Initial wt loss		10% wt loss		25% wt loss		50% wt loss		75% \	wt loss
Polymer	N ₂	Air	\mathbf{N}_2	Air	\mathbf{N}_2	Air	N ₂	Air	\mathbf{N}_2	Air
F	130	130	280	300	350	370	490	500	a	580
М	110	110	285	320	350	375	515	540	а	590
Ν	110	110	270	300	360	390	480	565	а	600
0	200	200	300	300	385	400	500	565	а	605

^a 900°, 64% wt loss.

Table VI ¹H Nmr Spectra (δ) of Some Poly(diethyl 2,5-bis(aralkylamino-3,6-dihydroterephthalates))

Polyme	er -CH3	-OCH ₂ -	-CH2-	\mathbf{PhCH}_{2}	
F M	δ 1.10 1.10	δ 4.10 4.10	δ 3.48 3.47	δ 4.85 4.80	
N O	1.10 1.00	$4.15 \\ 4.17$	$3.45 \\ 3.43$	4.82 4.82	

melting was observed.

Thermal gravimetric analyses of the polymers revealed that all of the polymers lost at least 2% of their original weight in nitrogen and in air, before 200° (see Table V). Generally, the polymers lost all of their weight in air, and 45-50% of their weight in nitrogen, before 650°. A typical trace is shown in Figure 7.

Spectral Results. ¹H Nuclear Magnetic Resonance. The proton nmr spectra resemble those of the model compound (see Figure 8, Table VI). It can, therefore, be assumed that the polymers are polyenamines.

Poly(diethyl 2,5-diaralkylaminoterephthalates). The formation of poly(diethyl 2,5-diaralkylaminoterephthalates) from poly(diethyl 2,5-diamino-3,6-dihydroterephthalates) was best accomplished with oxygen in m-cresol at 120° (Table VII). Proton nmr studies showed that oxidation was complete in 0.5 hr.

The solubility of polymers P–S was similar to their dihydro precursors. All were insoluble in chloroform, DMF, DMAc, etc. Polymers P and S were soluble in hexafluoro-2-propanol, while all were soluble in TFA, *m*-cresol, and methanesulfonic acid (with darkening). Dilute solutions of the polymers exhibited polyelectrolyte behavior during viscosity measurements in TFA. This is in contrast to the results reported by Tai, Higashi, and Yokomiza for polymers obtained by oxidizing the products of reaction of aromatic diamines and $I.^{21}$ All their oxidized materials were completely insoluble.

Differential scanning calorimetry results are shown in Table VIII. The same trend in T_g seen in the poly(aminodihydroterephthalates) is observed. The T_g of each totally aromatic polymer is lower than the T_g of its dihydro precursor, indicating that, perhaps, the loss of the ring hydrogen atoms and the planarity of the aromatic ring in the fully aromatic polymer allow easier motion about the chain axis. Apparent crystallization temperatures were observed only for polymers P and Q, but decomposition occurred before melting was observed.

Thermal gravimetric analyses of the totally aromatic polymer were made (see Table IX). A typical analysis is presented in Figure 9.

Spectral Results. ¹H Nuclear Magnetic Resonance. The proton nmr spectra are presented in Table VII. A typical spectrum is shown in Figure 10. Disappearance of the

Figure 9. Thermal gravimetric analysis of poly(diethyl 2,5-p-xy-lylylaminoterephthalate).

Figure 10. ¹H nmr of poly(diethyl 2,5-*p*-xylylylaminoterephthalate).

ring methylene protons confirms aromatization.

Experimental Section

¹H nmr spectra were recorded on a Varian Model T-60 nmr spectrometer. ¹³C nmr spectra were recorded on a Varian Model XL-100 nmr spectrometer. All nmr spectra are relative to TMS. Infrared spectra were recorded on Perkin-Elmer Model 457 (Nujol mulls) and Model 521 (KBr pellets) grating infrared spectrophotometer. Visible and ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer. Mass spectra were obtained on a Du Pont Model 21-104 mass spectrometer. Melting points (uncorrected) were determined on a Thomas-Hoover capillary melting point apparatus. Intrinsic viscosity measurements were made with a Ubbelohde viscometer in a constant temperature water bath at 25°. Differential scanning calorimetry was done on a Perkin-Elmer Model DSC-1B apparatus. Thermal analysis of the polymers was done on a Du Pont Model 950 thermogravimetric analyzer.

Diethyl 1,4-Cyclohexanedione-2,5-dicarboxylate. Compound I was prepared according to the procedure of Moore:¹² yield, 82.0%; mp 127-128°.

Benzylamine (Eastman Organics) was stored over molecular sieves (4A) prior to use.

N-Methylpyrrolidone (NMP) (Aldrich Chemical Co.) was stored over molecular sieves (4A) prior to use.

m-Cresol (Aldrich Chemical Co.) was dried by azeotropic distil-

S (0)°

0.16

Preparation of Poly(diethyl 2,5-diaralkylaminoterephthalates)										
Polymer	Diamine	Solvent	Oxidizing agent	T, °C	Time, hr	Yield,ª %	$\eta_{inh}, \ dl/g^b$			
P (F) ^c	<i>m</i> -Xylylenediamine	<i>m</i> -Cresol	O ₂	120	0.5	99	0.28			
$Q (M)^c$	p-Xylylenediamine	m-Cresol	O_2	120	0.5	98	0.34			
$R(N)^{c}$	4,4'-Bis(amino-	m-Cresol	0,	120	0.5	98	0.17			

 Table VII

 Preparation of Poly(diethyl 2,5-diaralkylaminoterephthalates

ether)

^a Based on the amount of material recovered after precipitation into CH₃OH-H₂O-NaOH. Nmr shows only aromatic ring hydrogen atoms. ^b TFA, 25°, 1 g/ml. ^c Derived from this dihydro polymer (see Table VI).

 O_2

120

m-Cresol

Table VIII Differential Scanning Calorimetry of Some Poly(diethyl 2,5-bis(aralkylaminoterephthalates))

methylbiphenyl)

methyldiphenyl

4,4'-Bis(amino-

Polymer	T_{g} , deg C	$T_{\rm c}, \deg \mathbf{C}$	T_{m} , deg C	
 Р	86	175	Not observed	-
R	90 115	217	Not observed	

lation with toluene. The *m*-cresol was then distilled at 185° in vacuo.

Diethyl 2,5-Bis(benzylamino-3,6-dihydroterephthalate).¹⁸ A 500-ml three-neck round-bottom flask was fitted with a stirrer, nitrogen inlet tube, and heating mantle. The flask was charged with I (25.00 g, 0.0976 mol) and 300 ml of NMP. To this was added benzyl amine (45.00 g, 0.4206 mol) and trifluoroacetic acid (4.6 g). The reaction was carried out in a nitrogen atmosphere at 120° for 1.25 hr. Upon completion of the reaction, the mixture was allowed to cool. Colorless needles crystallized from the reaction solution. After cooling to room temperature, the mixture was poured into 3.5 l. of water. The precipitated product, now orange colored, was filtered, washed with water, and dried in vacuo. The product is soluble in chloroform and methylene chloride. It is soluble in hot cyclohexane, tetrahydrofuran, methanol, and toluene. Upon recrystallization from cyclohexane, the yield was 88.1%: mp 169-173°; ir (KBr) 3260 (NH), 1648, 1238 (-C(O)O-), 1591 (>C=C<), 1072, 1042, 773, 692 cm⁻¹; λ_{max} (CH₃CN) 288 (ϵ 2.40 × 10⁵), 469 nm (ϵ 1.83 × 10²); nmr (CDCl₃) δ 1.23 (t, 6 CH₃), 3.13 (s, 4 CH₂), 3.97 (q, 4 -OCH₂-), 4.26 (d, 4 PhCH₂), 6.94 (10 Ph-), 8.86 (s, 2 NH). Anal. Calcd for C₂₆H₃₀N₂O₄: C, 71.88; H, 6.95; N, 6.45. Found: C, 72.0; H, 7.0; N, 6.3.

Diethyl 2,5-Bis(benzylaminoterephthalate). A 50-ml roundbottom flask was fitted with a water condenser, oxygen inlet tube, magnetic stirrer, and heating mantle. The flask was charged with diethyl 2,5-bis(benzylamino-3,6-dihydroterephthalate) (2.00 g, 4.60 mmol) and 25 ml of glacial acetic acid. At reflux, a stream of oxygen was bubbled into the solution for 0.5 hr. Upon completion of the reaction (TLC), the obtained solution was allowed to cool and was diluted with 25 ml of chloroform. The acetic acid was neutralized with a sodium bicarbonate solution and the chloroform layer was evaporated to dryness. The product is soluble in tetrahydrofuran, methylene chloride, chloroform, acetic acid, dimethylformamide, and hot alcohol and hot cyclohexane. Upon recrystallization from 2-propanol, the yield was 95% of bright red needles: mp 149.5–152.5°; ir (KBr) 3391 (NH), 1670, 1205 (–C(O)O–), 1520 (1,2,4,5-tetrasubstituted phenyl), 1411, 1100, 782, and 689 cm⁻¹; λ_{max} (CH₃CN) 243 nm (ϵ 4.77 × 10³), 468 nm (ϵ 4.77 × 10³); nmr (CDCl₃) δ 1.46 (t, 6 CH₃), 4.2 (q, 4 OCH₂), 4.32 (s, 4 PhCH₂), 4.53 (s, 2 NH), 7.2 (s, 12 aromatic).

96.7

0.5

Anal. Calcd for $C_{26}H_{28}N_2O_4$: C, 72.21; H, 6.52; N, 6.48. Found: C, 71.1; H, 6.68; N, 6.4.

m-Xylylenediamine (Aldrich Chemical Co.) was purified by distillation, bp 146-148° (17 mm) (lit.¹⁹ bp 140° (14 mm)), and stored under nitrogen.

p-Xylylenediamine (Diamond Shamrock Co.) was purified by distillation, bp 217-220° (10 mm) (lit.¹⁹ 230° (10 mm)), mp 34-35.5° (lit.²⁰ 35°), and was stored under nitrogen.

4,4'-Bis(aminomethylbiphenyl) was prepared by hydrogenation of 4,4'-dicyanobiphenyl (Eastman Chemical Co.) according to the method of Albert:²⁰ yield, 32%; mp 144–146.5° (lit.²⁰ 144– 145°).

4,4'-Bis(aminomethyldiphenyl ether) was prepared by the hydrogenation of 4,4'-dicyanodiphenyl ether according to the method of Albert:²⁰ yield, 51%; bp 186–188° (0.2 mm) (lit.²⁰ 186° (0.3 mm)).

Poly(diethyl 2,5-*p***-xylylamino-3,6-dihydroterephthalate).** A 100-ml round-bottom two-neck flask was fitted with a stirrer, nitrogen inlet tube, and an oil bath. The flask was charged with *p*-xylylenediamine (1.7845 g, 13.5028 mmol) and I (3.3576 g, 13.5028 mmol). To this mixture was added 30 ml of *m*-cresol. The reaction was carried out at 120° for 3.75 hr under a nitrogen atmosphere. Upon completion of the reaction, the resulting polymer solution was poured with stirring into a mixture of 75 ml of H₂O, 225 ml of methanol, and 2 g of sodium hydroxide to precipitate 4.58 g of polymer (97.1% yield): T_g , 120°; T_c , 222°; η_{inh} , 0.34 dl/g (TFA, 1 g/100 ml, 25°); nmr (TFA) δ 1.1 (6 CH₃), 4.1 (4 –OCH₂–), 3.47 (4 – CH₂–), 4.8 (4 PhCH₂), 7.3 (8 Ph); ir (Nujol mull) 3280 (NH), 1650 (C = 0), 1600 cm⁻¹ (>C==C<).

Poly(diethyl 2,5-*p***-xylylylaminoterephthalate).** A 50-ml twoneck round-bottom flask was fitted with a stirrer, oxygen inlet tube, and an oil bath. The flask was charged with poly(diethyl 2,5*p*-xylylylamino-3,6-dihydroterephthalate (1.5 g) and *m*-cresol (15 ml). The reaction mixture was stirred at room temperature until a polymer solution was obtained. The resulting solution was heated to 120° at which temperature a stream of oxygen was introduced into the solution for 0.5 hr. Upon completion of the reaction, the polymer solution was poured with stirring into a mixture of 40 ml of H₂O, 110 ml of methanol, and 1 g of sodium hydroxide to precipitate 1.45 g of polymer (97% yield): T_g , 90°; T_c 217°; η_{inh} , 0.34

Table IX
$Thermal\ Gravimetric\ Analyses\ (deg)\ for\ Some\ Poly(diethyl\ 2,5-bis(aralkylaminoterephthalates))$

	Initial wt loss		$10\%~{ m wt~loss}$		25% wt loss		50% wt loss		$75\%~{ m wt~loss}$	
Polymer	N ₂	Air	N ₂	Air	\mathbf{N}_2	Air	$\overline{\mathbf{N}_2}$	Air	\mathbf{N}_2	Air
P	110	110	320	235	358	350	440	455	850	558
Q	220	220	335	335	358	362	430	510	850	565
R	170	170	335	340	360	410	490	540	a	575
S	110	110	295	325	360	405	475	560	a	600

^a At 900°, 65% wt loss.

dl/g (TFA, 1g/100 ml, 25°); nmr (TFA) δ 1.06 (6 CH₃), δ 4.20 (4 -OCH₂-), δ 4.53 (4 PhCH₂), δ 7.3 (4 amine aromatic), δ 8.2 (2 1,2,4,5-tetrasubstituted phenyl); ir (Nujol mull) 3380 (NH), 1630 (-C(O)O-), 1,2,4,5-tetrasubstituted phenyl 1525 cm⁻¹.

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Thermal Polymerization of Dimethylaminoethyl Methacrylate

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ABSTRACT: The existence of a self-catalyzed or "thermal" polymerization is reported for dimethylaminoethyl methacrylate. Evidence is provided to indicate that the polymerization is free radical in mechanism. The kinetics are observed to be: $R_p = k [\text{monomer}]^{3/2}$. A mechanism for the polymization is proposed.

The preparation of aminoalkyl acrylates was first reported in the patent literature. A British patent was awarded to E. I. du Pont deNemours and Co. in 1937 for the preparation of dimethylaminoethyl methacrylate (DMAEM) from dimethylaminoethanol and methyl methacrylate by heating in benzene in the presence of p-phenylenediamine as an inhibitor of polymerization and sodium methoxide.¹ In 1938, Graves prepared several monomeric amino acrylates by treating acrylyl halide with amino alcohol in the presence of a polymerization inhibitor and an inert solvent such as benzene, toluene, or dioxane.² A Swiss patent was issued to Voelker. Hering, and Zweifel in 1968 for the preparation of aminoacrylic esters in a high yield by the butyl orthotitanate catalyzed transesterification of isopropyl acrylate with the appropriate amino alcohol.^{3,4} Agadzhanyan and Amboyan described the preparation of DMAEM in 60–80% yield by the reaction of β -chloroacyl chloride with dimethylaminoethanol.5

$$CH_2 = C(CH_3) - C - O - CH_2 - CH_2N(CH_3)_2$$

DMAEM

The first attempt to homopolymerize DMAEM was in 1949. It was found that benzoyl peroxide would not readily initiate the polymerization of DMAEM,² but that uv light⁶ or azo-type initiators⁷ were successful. Dimethylaminoethyl methacrylate and acrylate were radical polymerized in bulk, the acrylate giving higher initial rates.⁸

DMAEM was selected for study becuase of the presence of a tertiary amino group which could come into the vicinity of the double bond thereby exerting an effect on the polymerization reaction. The kinetics of the polymerization with azo initiator in bulk and in solution were studied by Griswold,⁹ Ling,¹⁰ and Dewey.¹¹ The rate law for initiated radical polymerization of DMAEM was given by the following equation.

$$R_{\rm p} = k [{\rm monomer}] [{\rm initiator}]^{1/2}$$

They observed that DMAEM polymerized without the free radical initiator at a significant rate. At 60°, DMAEM showed a self-initiation rate of polymerization of 1.2%/hr in bulk.¹⁰ We now report an extended study of this self-initiation.

Experimental Section

Purification of Monomer. The monomer, DMAEM, was donated by Rohm and Haas Co. and contained 2,000 ppm of the monomethyl ether of hydroquinone (MEHQ) as an inhibitor of polymerization for shipping.

The method described by Griswold for the extraction of the inhibitor⁹ was modified. The inhibited monomer was shaken five times with solutions each 5% in sodium hydroxide and 25% in sodium chloride. The monomer was then centrifuged for 15 min to remove turbidity and stored at 0° over anhydrous sodium sulfate. The infrared spectrum of the monomer at this point showed a strong absorption band indicating the presence of water. The wet monomer was mixed with cyclohexane and stored over anhydrous calcium chloride for at least 12 hr. No detectable water then remained in the monomer solution. Where desired the cyclohexane was removed by distillation under vacuum (15 mm and 18°) without polymerization. Purified DMAEM was stored at -5° in a brown glass bottle covered with aluminum foil.

Polymerization of Monomer. All glassware was boiled with nitric acid, rinsed several times with distilled water, and then dried in an oven. Reaction tubes were prepared from 12-mm Pyrex tubing constricted in the center to facilitate closing the tube with a torch later. The tubes were wrapped in aluminum foil to exclude light. Samples of DMAEM were prepared by weight at desired dilutions in redistilled reagent grade cyclohexane, and approximately 3 ml of the sample was placed in each of the reaction tubes. The tubes were connected to a high vacuum manifold, frozen with liquid nitrogen, evacuated, and sealed with a torch. At zero time the tubes were placed in a constant temperature bath at 60° and each was incubated for an appropriate period of time. The reaction was stopped by freezing the tube.