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Thermally Stable Spiropolymers*

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SUMMARY

The condensation of the aliphatic spirotetraamine 2,2-bis(aminomethyl)-1,3-diaminopropane (I) or 1,4-bis(aminomethyl)-1,4-diaminocyclohexane (II) with pyromellitic dianhydride (III) or 1,4,5,8-naphthalenetetracarboxylic dianhydride (IV) was studied. It was found that in polyphosphoric acid at temperatures greater than 200°C and after long reaction times, either tetraamine produced the desired spiropolymer with the dianhydride (IV), but only tars could be isolated when the dianhydride (III) was used. Although these condensations proceed through a polyimide precursor which then cyclizes by elimination of water, condensations of (II) with (IV) only yielded the fully cyclized material and all attempts to isolate the imide precursor failed. Strong evidence for total cyclization was obtained by comparing the infrared and ultraviolet spectra of the polymer and of model compounds that were representative of the fully cyclized and imide forms. Condensations of (I) and (IV) yielded polymers that were only 50% cyclized. The polymer based on spirotetraamine (I) started to lose weight at 300°C in both air and vacuum, while the polymer based on amine (II) showed no weight loss until 500°C in vacuum and 400°C in air.

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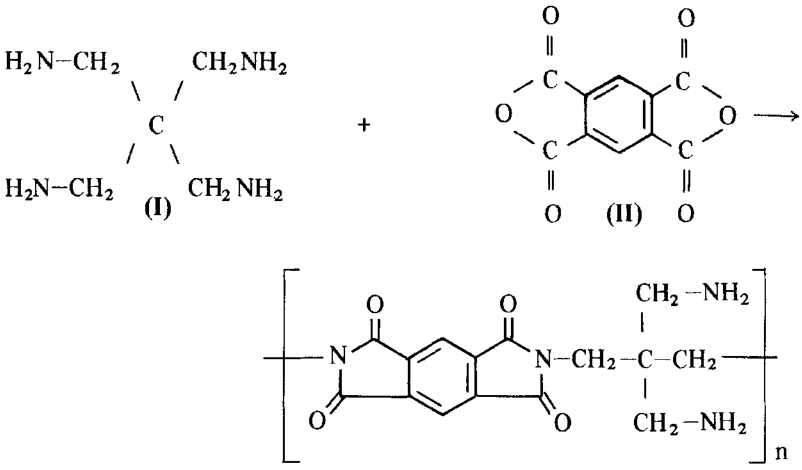
INTRODUCTION

In recent years considerable work has been done on the synthesis of ladder polymers which by virtue of their double-stranded structure show a very high degree of thermal stability. Much less attention has been paid to double-stranded polymers that are joined at regular intervals by a backbone spirocarbon. In fact, apart from polymers that have a spirostructure around a metal atom in the backbone, the few reported examples of all-organic spiropolymers are the polyspiroketals and thioketals, which have been synthesized by condensation of pentaerythritol derivatives with alicyclic diketones [1, 2].

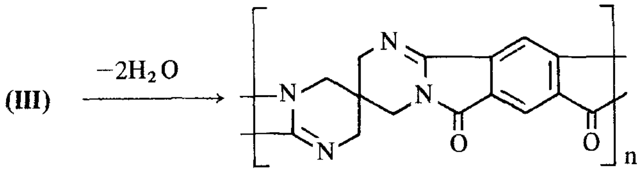
In a preliminary communication [3] we described the synthesis of spiropolymers by the condensation of aliphatic spirotetraamines and aromatic dianhydrides. In this paper we describe in some detail the synthesis and characterization of these polymers.

DISCUSSION

Initial synthetic efforts were concerned with the condensation of 2,2-bis(aminomethyl)-1,3-diaminopropane (I) and pyromellitic dianhydride (II) using melt condensation, interfacial polymerization, and polymerization in various high-boiling solvents. At temperatures above 180°C, black, intractable powders were obtained, but in polyphosphoric acid solution


(I) (II)

(III)



(IV)

at slightly lower temperatures, colorless, formic acid-soluble polymers were produced. These, however, readily decomposed in hot water. Similar low-molecular-weight materials were also produced by interfacial polycondensation techniques. Elemental analyses agreed well with an imide structure **(III)**, but the polymer instability in weak base and the very broad nature of the peaks in the infrared spectrum suggested that amide and amino acid groups were present. A typical infrared spectrum is shown in Fig. 1.

These polymers were converted by heating (at 305°C/0.01 Torr) to dark-tan, insoluble solids which analyzed reasonably well for the fully cyclized

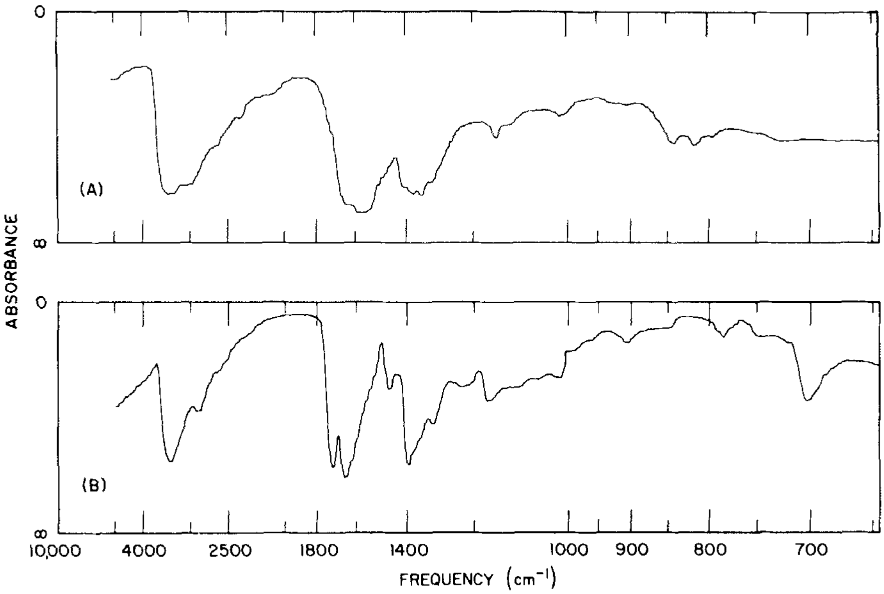
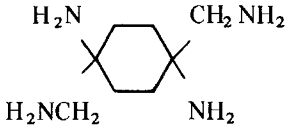


Fig. 1. Infrared spectra of 2,2-bis(aminomethyl)-1,3-diaminopropane/pyromellitic dianhydride polymer: (A) uncyclized polymer; (B) cyclized polymer (potassium bromide disk).

structure (**IV**). The infrared spectrum (Fig. 1) showed fairly sharp peaks and was similar to those of ladder polymers produced from pyromellitic dianhydride and aromatic tetraamines [4]. Since the polymer was completely insoluble, no detailed structural characterization could be carried out. Thermogravimetric analysis in vacuum showed a continuous weight loss above 300°C, but about 60% of the material remained even above 800°C.

Since 2,2-bis(aminomethyl)-1,3-diaminopropane was difficult to prepare and its condensation products did not yield useful materials, another spirotetraamine (V) was prepared via a Strecker synthesis from 1,4-cyclohexanedione.



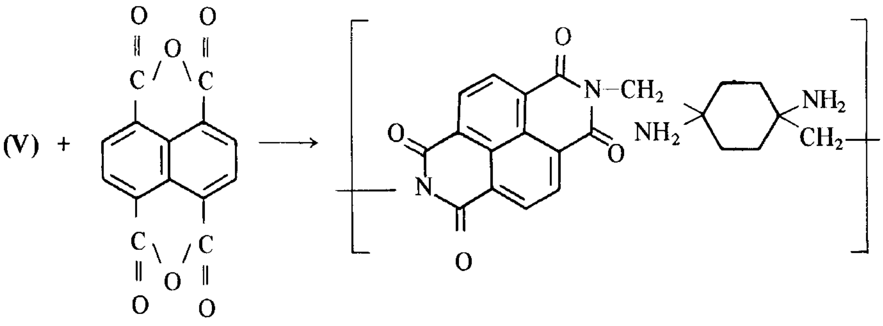
(V)

The overall yield of the trans-1,4-bis(aminomethyl)-1,4-diaminocyclohexane (V) was quite high (60%), and the amine was easy to prepare and purify as the tetrahydrochloride salt.

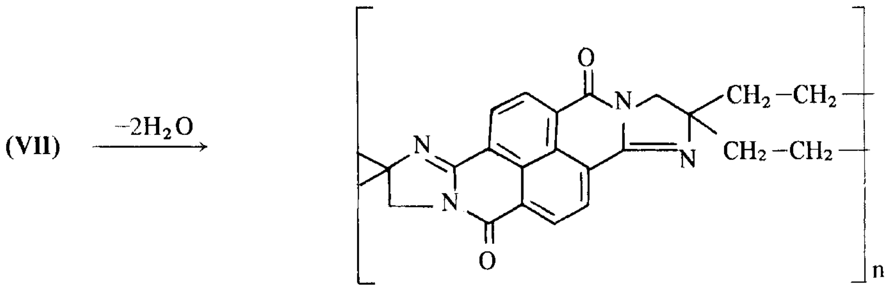
Attempts to prepare spiropolymers from pyromellitic dianhydride and the tetraamine (V) were even less successful than with (I) and no reaction at all was noted below 150°C. Polymerizations in polyphosphoric acid above 170°C only produced black tars, but polymerization at 160°C, for 3 weeks, produce 50% yield of polymer with properties very similar to those of polymer (III). However, attempts to cyclize this material only produced intractable tars.

Model compound studies using phthalic anhydride and either tetraamine (I) or (V) have shown that in solution complex mixtures of amido-amino acids, imides, imidazoles, and other compounds are produced. When these mixtures are heated to induce cyclization, various cross-linking and decomposition reactions can occur. Thus, it is not unexpected that the reaction of pyromellitic dianhydride with these tetraamines produces complex intractable mixtures.

A consideration of the stereochemical requirements of the condensation reaction and studies of molecular models suggested that use of 1,4,5,8-naphthalenetetracarboxylic dianhydride should lead to less complex reaction products since the peri position of the carboxyl groups greatly favors the formation of a cyclic imide over the various amino acid and imidazole structures which are possible and which would cause cross-linking. Therefore, the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride **(VI)** with the spirotetraamine **(V)** was investigated in some detail. The condensation of these monomers should proceed through the imide **(VII)** to the final cyclized polymer **(VIII)**.



(VI) **(VII)**

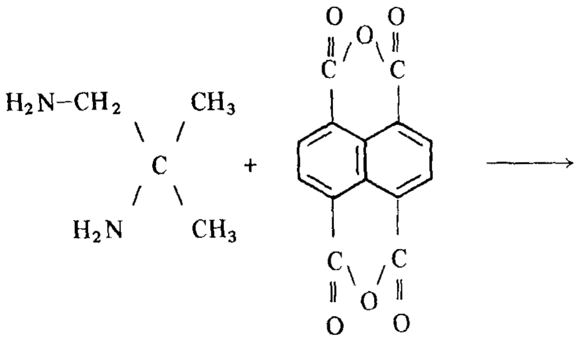


(VIII)

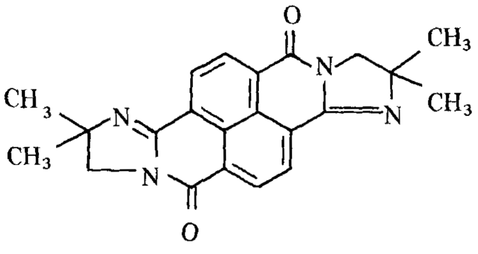
This study has shown that high-molecular-weight polymers could be produced in good yields when reactions were carried out in polyphosphoric acid at temperatures in excess of 200°C and when reaction times were at least 72 hr. Under optimum conditions (90 hr at 210°C) dark-green polymers were obtained in good yields (95%); intrinsic viscosities were as high as 1.7. The polymers were completely soluble in formic acid and their elemental analysis indicated that they existed mainly in the fully cyclized form **(VIII)**.

Attempts to prepare the noncyclized polymer by carring out the condensation in polyphosphoric acid at 160°C for 4 weeks produced only a low yield of light-green polymer, and a large amount of starting material could be recovered. Reactions carried out in solvents other than polyphosphoric acid below 170°C were not successful. Thus, this particular system appears to be unique in that the three steps leading to the final cyclized product (amino-amido acid → imide → cyclized structure) only take place at elevated temperatures and at not very different rates.

Additional information about the condensation reaction and further confirmation of the polymer structure were obtained from model compound studies. Thus, by use of 1,2-diamino-2-methylpropane (IX) as a model for one half of the tetraamine (V) and by its condensation with 1,4,5,8-naphthalenetetracarboxylic dianhydride (VI) in polyphosphoric acid at 180°C, a high yield (90%) of a compound having structure (X) was obtained.



(IX) (VI)



(X)

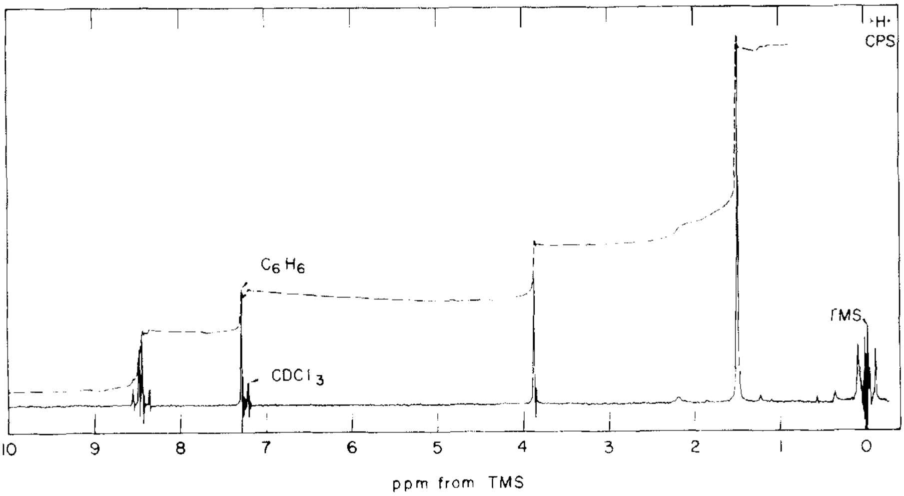
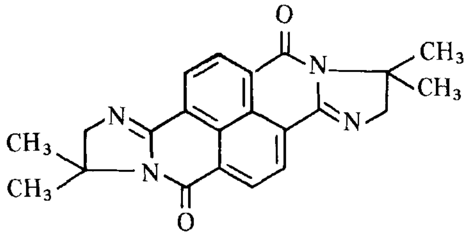


Fig. 2. NMR spectrum of model compound (X) in deuterochloroform.

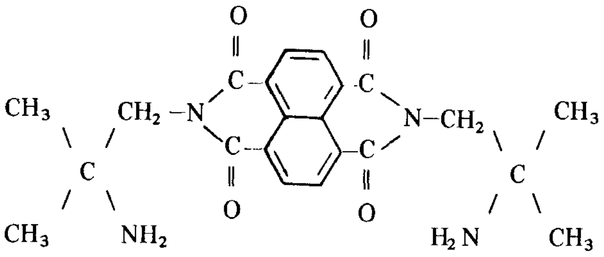
Of considerable interest was the fact that the nuclear magnetic resonance (NMR) spectrum of (X) (Fig. 2) showed that this compound was obtained exclusively as the trans-isomer, as evidenced by the AB pattern of the aromatic protons. Another possible—although unlikely—trans-isomer (XI) was ruled out by a NMR spectrum in trifluoroacetic acid which showed no broadening of the methylene signal, indicating that the imide nitrogen was attached only to the methylene group. Considerable broadening would be expected if the methylene were attached to the imine nitrogen.

When the condensation of (IX) with (VI) was carried out in ethylene glycol monomethyl ether at 120°C for 6 hr, a high yield of a yellow



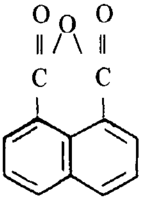
(XI)

compound was obtained which was shown to be a mixture of about 70% (X) and 30% of another compound which on attempted isolation by extraction with hot benzene was converted to (X). The facile conversion of this compound, along with the visible and infrared spectra of the mixture, indicates that it was very likely the imide (XII).



(XII)

In contrast, attempts to form model compounds from spirotetraamine (V) and 1,8-naphthalenedicarboxylic anhydride (XIII) yielded only starting



(XIII)

materials even in polyphosphoric acid at temperatures up to 190°C. This result and the fact that a high temperature is needed for polymerization indicate that the spirotetraamine (V) is very sterically hindered, and, unlike syntheses involving aromatic tetraamines [3] or the spirodiamine (IX), no reaction takes place except at higher temperatures.

Spectral comparison of polymer (VIII) with model compounds confirmed the assigned structure for the polymer and provided additional insight into certain structural details. The similarity in the infrared spectra of polymer (VIII) and model compound (X) is apparent in Fig. 3. It is to be noted that the strong imide bands at 1710 and 770 cm^{-1} which are present in

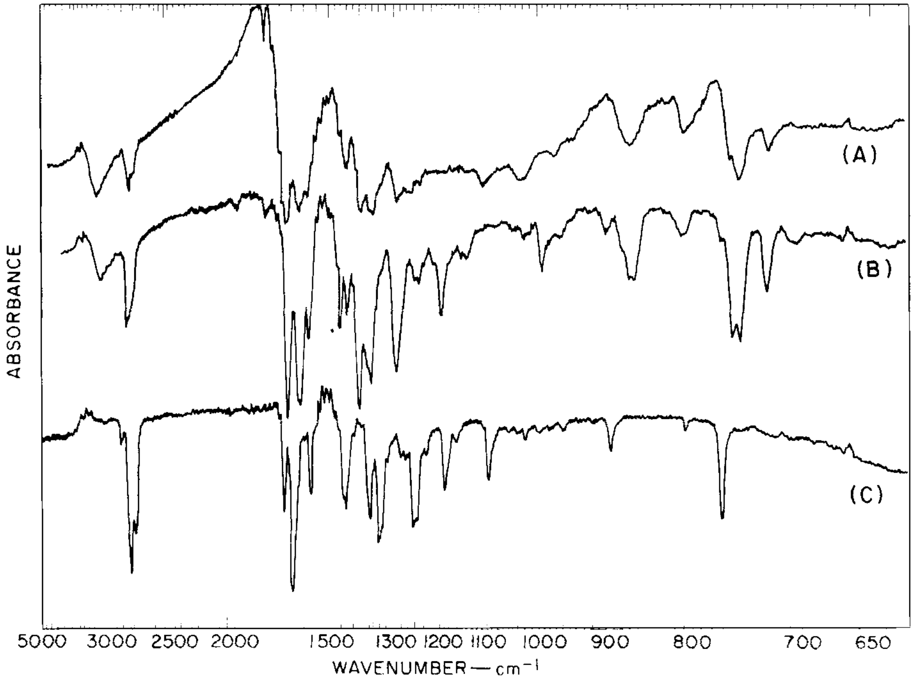
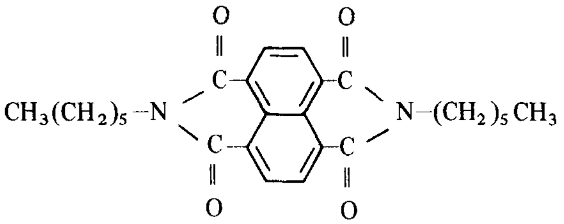


Fig. 3. Infrared spectra of (A), 1,4-bis(aminomethyl)-1,4-diaminocyclohexane/1,4,5,8-naphthalenetetracarboxylic dianhydride polymer; (B) model compound (**X**); (C) model compound (**XIV**) (potassium bromide disk).

model compound (**XIV**) are absent in polymer (**VIII**), indicating that within the accuracy of infrared measurements polymer (**VIII**) is completely cyclized.



(XIV)

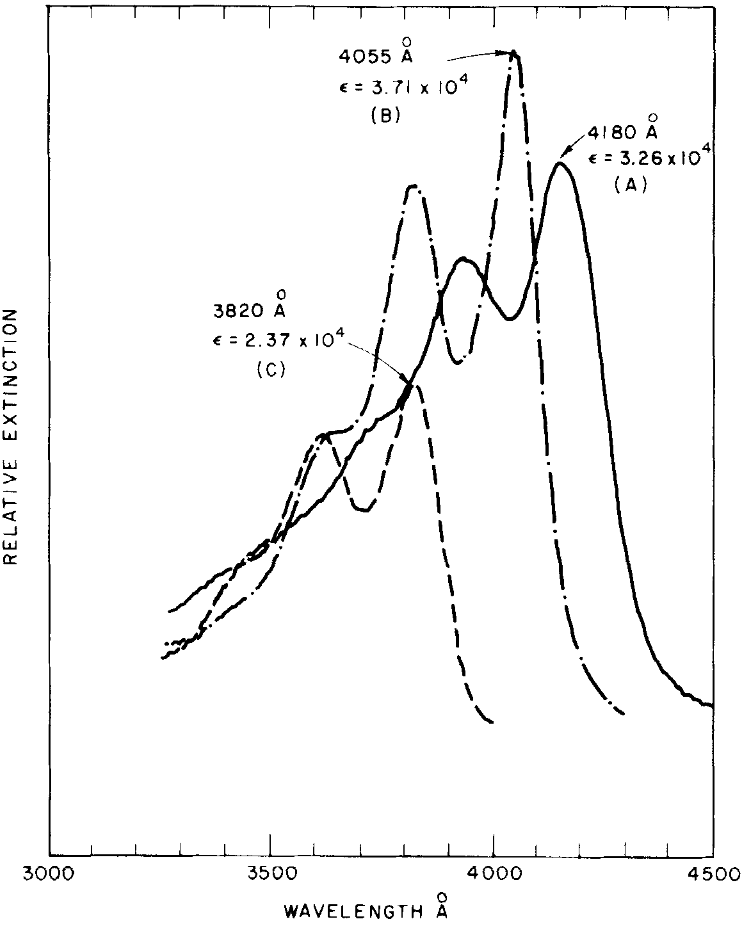
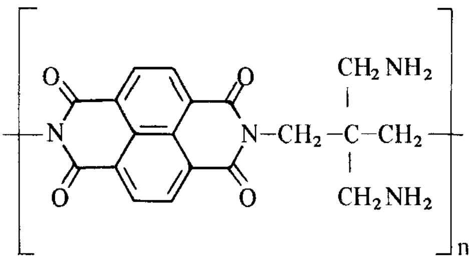


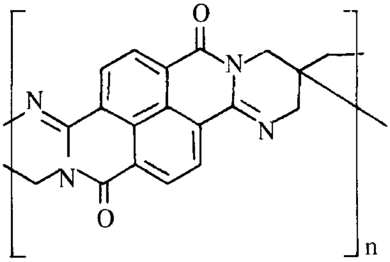
Fig. 4. Electronic spectra of (A) 1,4-bis(aminomethyl)-1,4-diaminocyclohexane/1,4,5,8-naphthalenetetracarboxylic dianhydride polymer; (B) model compound (X); (C) model compound (XIV) in formic acid.

The electronic spectra of polymer (VIII) and model compound (XI) (Fig. 4) were also similar, but they were distinctly different from the spectrum of the model imide (XIV). The slight differences noted between the spectra of (VIII) and (X) are very likely caused by the presence of a cyclohexane ring instead of two methyl groups. Samples of the polymer having quite different elemental analyses had identical electronic spectra, indicating that the differences were due to adsorbed water and not to extent of cyclization as had been assumed previously [3]. Also, the sharpness of the peaks in the electronic spectrum of the polymer and its close similarity to the spectra of model compound (X) again indicate very strongly that there are virtually no uncyclized segments in the polymer and that a stereospecific trans-polycondensation has occurred.

Because the condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride (VI) and the tetraamine (V) proceeded smoothly to yield a fully cyclized polymer, a condensation between this anhydride and 2,2-bis(aminomethyl)-1,3-diaminopropane (I) was studied to determine if the polyimide (XV) or a fully cyclized material (XVI) could be formed.



(XV)



(XVI)

It was found that a condensation reaction could be carried out in polyphosphoric acid at 200°C, over a 50-hr reaction time, and that a good yield of dark-green polymer ($\eta_{inh} = 0.35$) could be obtained. However, elemental analysis and infrared spectra of the polymer indicated that unlike the polymer prepared with tetraamine (V) this material was not fully cyclized. The infrared spectrum showed an additional sharp peak at about 1725 cm^{-1} and a broad peak at about 775 cm^{-1}, which indicates that portions of the polymer were in the uncyclized form (XV). The electronic spectrum (Fig. 5) indicated that the material was a 50:50 mixture of the fully cyclized polymer (XVI) and the imide (XV). Heating the material at 250°C (10^{-3} Torr) did not change the degree of cyclization.

Thermogravimetric analyses of polymers (VIII) and (XVI) are shown in Figs. 6 and 7. The polymer from 2,2-bis(aminomethyl)-1,3-diaminopropane (XVI) shows weight loss starting at about 300°C in both air and vacuum, whereas the polymer from 1,4-bis(aminomethyl)-1,4-diaminocyclohexane (VIII) shows no weight loss until about 500°C in vacuum and 400°C in air. The difference is even more noticeable when the differential weight loss

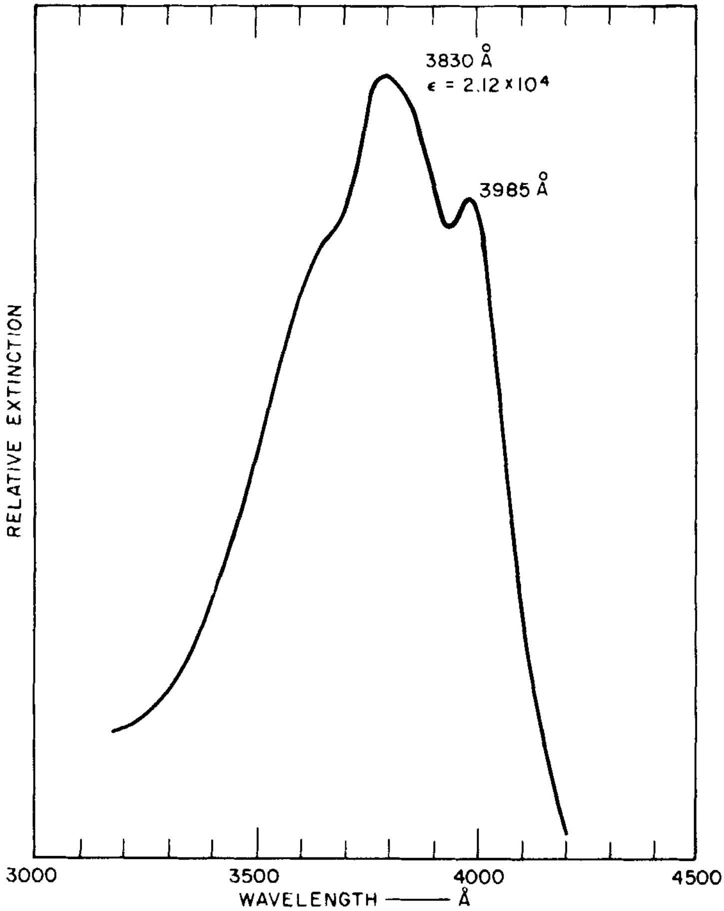


Fig. 5. Electronic spectrum of 2,2-bis(aminomethyl)-1,3-diaminopropane/1,4,5,8-naphthalenetetracarboxylic dianhydride polymer in formic acid.

curves are compared. The peaks at relatively low temperatures which are present in both of the curves for the 2,2-bis(aminomethyl)-1,3-diaminopropane polymer may be due either to a cyclization reaction or to a decomposition of the uncyclized units. In either case it would appear that if this polymer could be obtained in the completely cyclized form it would be a very stable material.

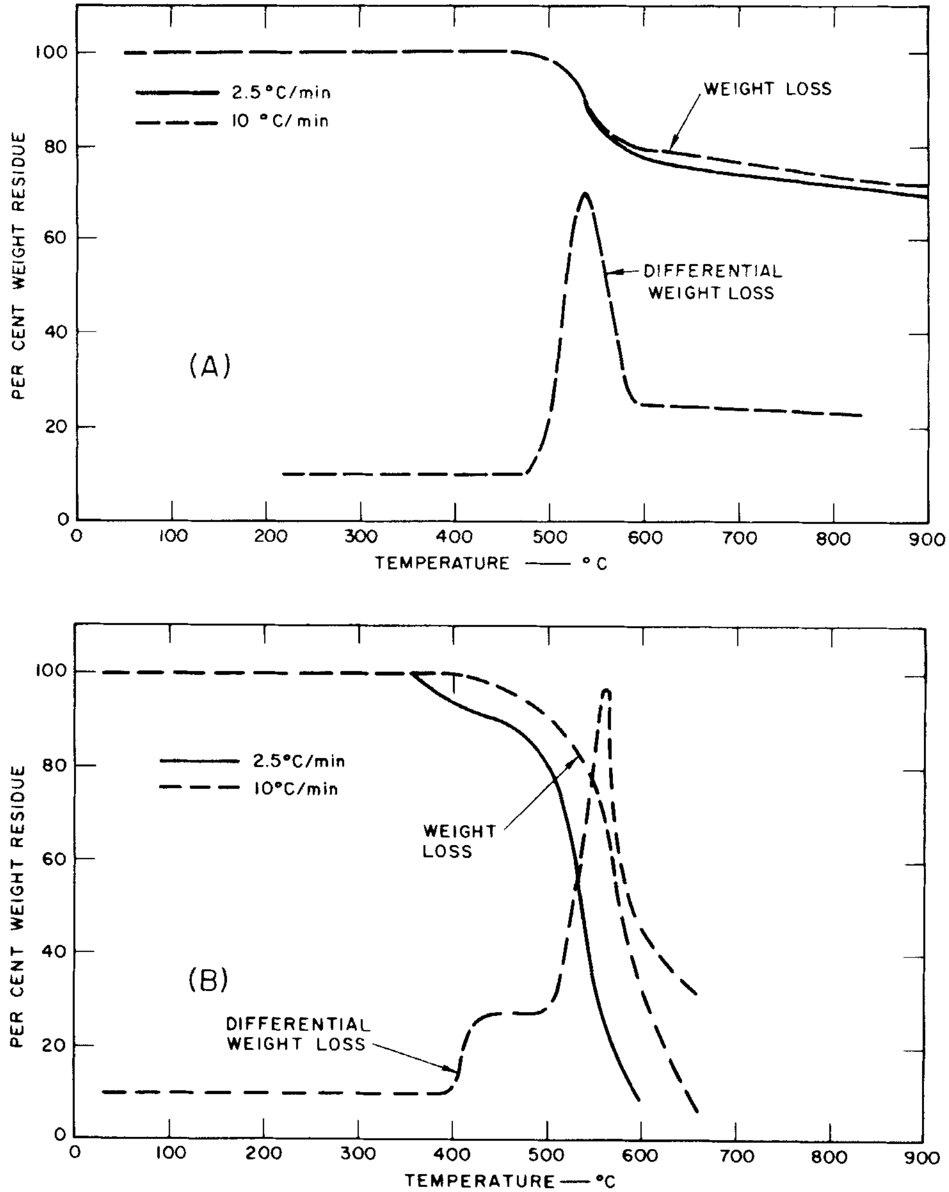


Fig. 6. Thermogravimetric analysis of 1,4-bis(aminomethyl)-1,4-diaminocyclohexane/1,4,5,8-naphthalenetetracarboxylic dianhydride polymer: (A) vacuum (10^{-2} Torr); (B) air at 0.05 liter/min.

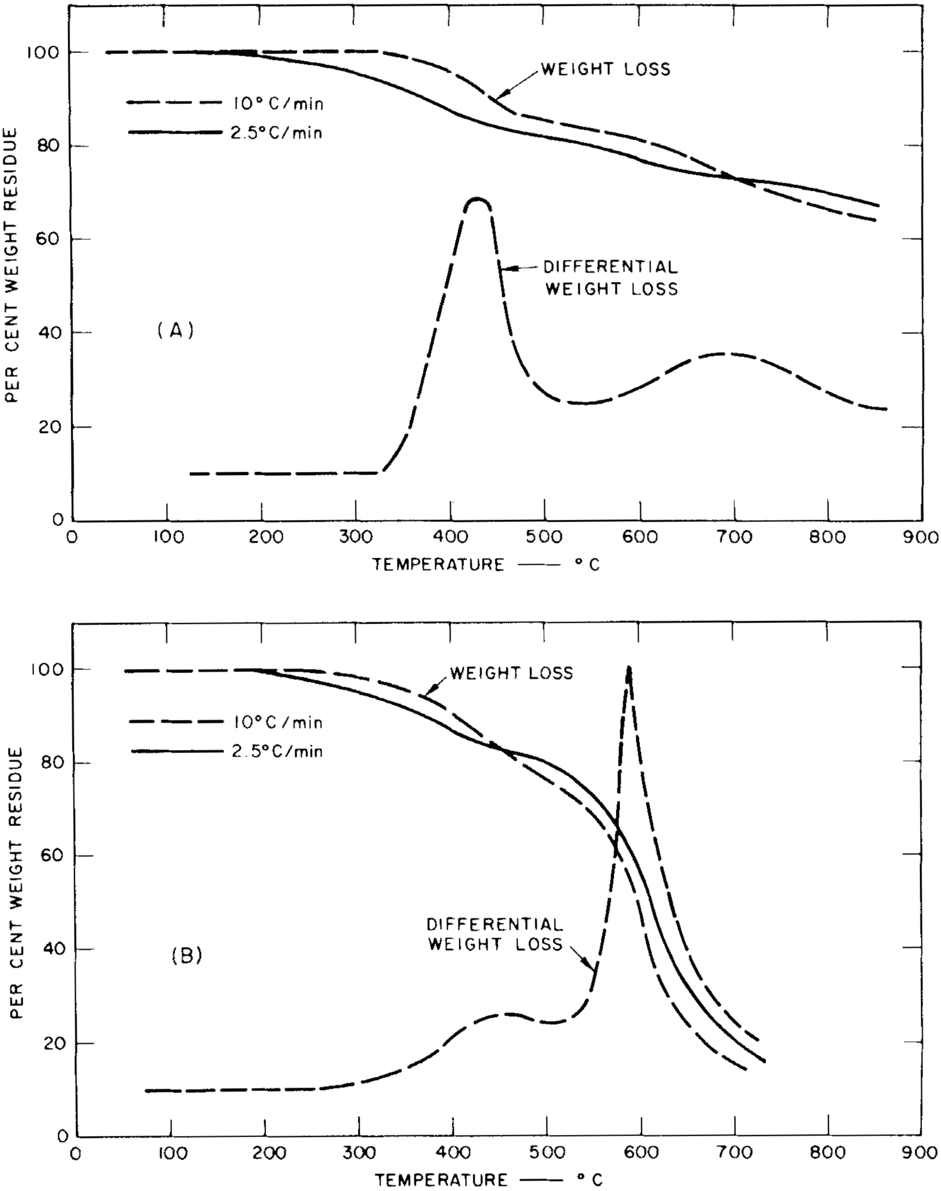


Fig. 7. Thermogravimetric analysis of 2,2-bis(aminomethyl)-1,3-diaminopropane/1,4,5,8-naphthalenetetracarboxylic dianhydride polymer: (A) vacuum (10^{-2} Torr); (B) air at 0.05 liter/min.

EXPERIMENTAL SECTION*

Preparation of Monomers

2,2-Bis(aminomethyl)-1,3-diaminopropane (I). This monomer was prepared by a modification of a previously described procedure [5]. Pentaerythritol tetrabromide (25 g, 0.065 mole) and sodio-p-toluenesulfonamide (50 g, 0.27 mole) were thoroughly powdered and then heated with vigorous stirring under nitrogen at 220-224°C for 10 hr. The crude product was ground and washed with hot water, collected, washed again with water, and finally extracted with boiling acetic acid (100 cc) diluted with water (5 cc). The insoluble residue was separated and crystallized from acetic acid to give the tetrasulfonamido compound (tetrakis-p-toluenesulfonamidomethylmethane) as colorless crystals (21.1 g, 45%), mp 247-248°C. The powdered sulfonamide (30 g) was heated with 70% sulfuric acid (100 cc) at 200°C for 3 hr and then cooled and diluted with water (ca. 500 cc) and ethanol (250 cc). The crude disulfate salt (6.7 g, 51%) slowly precipitated and was collected and purified by dissolution in sodium hydroxide solution, filtration, and reprecipitation with dilute sulfuric acid. This disulfate salt (8.0 g) was suspended in water and mixed with Dowex 1-X anion exchange resin (in OH^- form) until all the solid dissolved. The solution was then passed through a column of the same resin, the water was evaporated under vacuum, and the product was crystallized from benzene. The tetraamine was obtained as fine needles (4.5 g, 90%), mp 98-100°C (Lit. [5] 98-100°C).

Trans-1,4-Bis(aminomethyl)-1,4-diaminocyclohexane Tetrahydrochloride (V). 1,4-Diamino-1,4-dicyanocyclohexane [6] (5 g, 0.03 mole) was dissolved in 10% hydrochloric acid (150 ml), and 0.2 g of rhodium catalyst (5% on alumina) was added. The mixture was shaken under hydrogen at 50 psi until hydrogen uptake ceased. The catalyst was then filtered off and the solvent was removed under vacuum at room temperature. The resulting solid was recrystallized from concentrated hydrochloric acid to yield colorless crystals, mp ≃ 265°C (dec). Calculated for $C_8H_{24}N_4Cl_4$: C, 30.20, H, 7.60; N, 17.62; Cl, 44.48. Found: C, 30.24; H, 7.53; N, 17.75; Cl, 43.95.

The NMR spectrum of the amine hydrochloride was determined in deuterium oxide after all the amino hydrogens had been exchanged. There

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*Names of polymers and model compounds were suggested by Dr. K. L. Loening, Director of Nomenclature, Chemical Abstracts Service.

were two sharp peaks in the ration of 1:2 at 6.31 τ and 7.71 τ corresponding to the methylene hydrogens adjacent to the amine groups and the methylenes in the cyclohexane ring. The free amine was obtained by passing an aqueous solution of the hydrochloride through a column of anion exchange resin (in the OH^- form) and removing the water under vacuum. However, a stable, anhydrous product could not be obtained, so the amine hydrochloride was used in all polymerizations.

1,4,5,8-Naphthalenetetracarboxylic Dianhydride (VI). The monomer was purchased from Aldrich Chemical Co. and purified by continuous extraction with and crystallization from glacial acetic acid containing a little acetic anhydride. The initial, highly colored extracts were discarded and the crystalline anhydride was dried under vacuum at 250°C.

Pyromellitic Dianhydride (II). This monomer was purchased from Aldrich Chemical Co. and was used as received (mp 285-287°C).

Model Compound Synthesis

1,2,8,9-Tetrahydro-2,2,9,9-tetramethylbenzo [*l m n*]-diimidazo [1,2-*c*: 1′,2′-*j*] [3,8]phenanthroline-6,13-dione (X). 1,4,5,8-Naphthalenetetracarboxylic dianhydride (5.36 g, 0.02 mole) was suspended in polyphosphoric acid (100 ml) at 160°C, and 1,2-diamino-2-methylpropane (5.40 g, 0.06 mole) was added dropwise. The mixture was vigorously stirred at 190°C for 6 hr, allowed to cool, and poured into distilled water (400 ml). The solution was then filtered and basified with sodium hydroxide. The resulting yellow precipitate (6.7 g, 90.0%) was crystallized from benzene to give fine yellow needles, mp 284°C (dec). Calculated for $C_{22}H_{20}N_4O_2$: C, 70.95; H, 5.41; N, 15.05. Found: C, 71.03; H, 5.40; N, 14.89.

The NMR (in deuterochloroform) showed single peaks at 8.51 τ (gem dimethyl) and 6.13 τ (methylene adjacent to nitrogen) and a quartet centered at 1.53 τ (aromatic protons).

2,7-Bis(2-amino-2-methylpropyl)-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo [*l m n*][3,8]phenanthroline (XII). 1,4,5,8-Naphthalenetetracarboxylic dianhydride (5.36 g, 0.02 mole) and 1,2-diamino-2-methylpropane (5.40 g, 0.06 mole) were refluxed in ethylene glycol monomethyl ether (100 ml) for 6 hr. The solution was then poured into water and the resulting yellow precipitate was filtered and dried. The infrared spectrum of this material showed that it was a mixture of 70% (X) and a new compound with major peaks at 1735 and 1760 cm^{-1}. On extraction with hot benzene, compound (X) was extracted as a pure product, but the second material could not be obtained pure and appeared to change slowly into compound (X).

2,7-Di-n-hexyl-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*l m n*][3,8] phenanthroline (XIII). n-Hexylamine (3 g, 0.03 mole) was dissolved in ethylene glycol monomethyl ether (50 ml), and 1,4,5,8-naphthalenetetracarboxylic dianhydride (3 g, 0.015 mole) was added with stirring. The solution was heated for 6 hr on a steam bath and then poured into cold water. The resulting precipitate was crystallized from benzene or methanol to yield fine pink needles, mp 210-212°C (3.8 g, 78%). Calculated for $C_{26}H_{30}N_2O_4$:C, 71.86; H, 6.96. Found: C, 71.92; H, 6.88.

Polymer Synthesis

Poly [(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-*c*:4,5-*c'*]dipyrrole-2,6 (1H,3H)-diyl)-6-[2,2-bis(aminomethyl)trimethylene]] (III). *Method 1.* Pyromellitic dianhydride (2.17 g, 0.01 mole) and 2,2-bis (aminomethyl)-1,3-diaminopropane disulfate (3.28 g, 0.01 mole) were dissolved in polyphosphoric acid (100 ml) and heated in a sealed tube at 160°C for 3 weeks. The solution was then cooled and poured into water to give a high yield of white precipitate. However, when the precipitate was washed with hot water to remove inorganic impurities, it decomposed to a brown tar. Attempts to cyclize this material by heating at 250°C (10^{-3} Torr) gave a black, intractable solid. Attempts to conduct the polymerization in polyphosphoric acid at higher temperatures, even for much shorter times, led to black tarry solutions from which it was not possible to isolate tractable products. Experiments in other solvents were also unsuccessful.

Method 2. A solution of 2,2-bis (aminomethyl)-1,3-diaminopropane tetrahydrate (0.32 g, 0.0015 mole) in distilled water (5.0 ml) was placed in a micro attachment of a Waring Blendor. A solution of pyromellitic dianhydride (0.32 g, 0.0015 mole) in methyl ethyl ketone (5.0 cc) was then added and the mixture was stirred vigorously for 1 min. A white solid was formed which was filtered and then dried under vacuum at 114°C. Calculated for $C_{15}H_{14}N_4O_4$: C, 57.4; H, 4.5; N, 17.8. Found: C, 57.5; H, 5.6; N, 17.6. η_{inh} = 0.08 in formic acid.

Poly [(2',6'-dihydro-6'-oxospiro[pyrimidine-5(4H),3'(4'H)-pyrimido-[2,1-*a*]isoindole[-1,2:8',9'(6H)-tetrayl)-8'-carbonyl] (IV). Reaction product

(III) was placed in a tube, evacuated to 5×10^{-4} Torr, and heated at 305°C for 6 hr. A progressive color change from white to light brown to dark brown was noted. Calculated for $C_{15}H_{10}N_4O_2$: C, 64.7; H, 3.6; N, 20.1. Found: C, 64.7; H, 4.3; N, 18.8.

Poly[(6,13-dihydro-6,13-dioxobenzo[*l m n*]diimidazo[1,2-*c*:1′,2′-*j*][3,8] phenanthroline-2,9(1H,8H)-diylidene)-9,9-diethylene] (VIII). The procedure used was essentially that reported by Dawans and Marvel [4]. A three-necked flask was equipped with a nitrogen inlet and outlet, a magnetic stirrer, and an apparatus to introduce solid reagents under an inert atmosphere. Polyphosphoric acid (116%, 100 ml) was added and heated at 200°C for 2 hr and then cooled to 140°C under nitrogen. The tetraamine or the amine hydrochloride was added and the solution was kept at this temperature for 2 hr until all the water or hydrogen chloride had been eliminated. One equivalent of the dianhydride or tetraacid was then added and the reaction mixture was heated under nitrogen with vigorous stirring. The polymer was isolated by pouring the hot reaction mixture into water, centrifuging, and washing the precipitate thoroughly with water. The solid was then dispersed in dilute ammonium carbonate overnight before washing and drying under vacuum. The results are shown in Table 1.

Table 1. Polymerization of 1,4-Bis(aminomethyl)-1,4-diaminocyclohexane and 1,4,5,8-Naphthalenetetracarboxylic Dianhydride in Polyphosphoric Acid (116%)[a]

Reaction conditions		Analysis			Properties		
Time, hr	Temp., °C	% C	% H	% N	η_{inh}[b]	% Yield	Solubility[b]
672	160					< 5	Soluble
120	175	68.98	4.52	14.20	0.45	15	Soluble
28	200	69.15	4.54	15.10	0.38	70	Soluble
144	200	69.52	4.55	13.74	0.56	85	Soluble
28	240	71.73	4.48	13.00	0.30	80	50%
72	210	70.04	4.33	12.75	0.59	90	Soluble
96	210	69.39	4.13	14.40	–	70	70%
96	210	70.12	4.41	13.89	1.55	95	Soluble

[a] Calculated for polyaminoamido acid $C_{22}H_{24}N_4O_6$: C, 59.99; H, 5.49; N, 12.72. Calculated for uncyclized polymer $C_{22}H_{20}N_4O_4$: C, 65.33; H, 4.99; N, 13.85. Calculated for cyclized polymer $C_{22}H_{16}O_4N_2$: C, 71.72; H, 4.38; N, 15.21.

[b] In formic acid.

Poly[(7,15-dihydro-7,15-dioxobenzo[*l m n*]dipyrazo[1,2-*c*:1′,2′-*j*][3,8] phenanthroline-2,10(1H,3H,9H,11H)-diylidene)-10,10-dimethylene] (XVI). 2,2-Bis(aminomethyl)-1,3-diaminopropane disulfate (1.0417 g, 3.18 mole) was dissolved in polyphosphoric acid at 205°C and stirred under nitrogen with 1,4,5,8-naphthalenetetracarboxylic acid (0.965 g, 3.18 mmole) for 50 hr. The solution was then cooled and poured into water; the resulting precipitate was centrifuged and washed repeatedly with distilled water. The material was next washed with dilute ammonia, rewashed with distilled water, and dried under vacuum at 114°C to give a dark-green formic acid-soluble produce (0.83 g, $\eta_{\mathrm{inh}} = 0.35$ at 30°C). Calculated for polymide $C_{19}H_{16}N_4O_4$: C, 62.64; H, 4.43; N, 15.38. Calculated for cyclized polymer $C_{19}H_{12}N_4O_4$: C, 69.50; H, 3.68; N, 17.07. Found: C, 64.22; H, 3.75; N, 15.56. The polymer was then heated at 255°C (10^{-3} Torr) for 48 hr to give a dark-green product with infrared and visible spectra similar to those of the unheated material.

Polymer Characterization

Infrared spectra were obtained as potassium bromide pellets on a Beckman IR 5 infrared spectrometer.

Ultraviolet and visible spectra were obtained in 97% formic acid solutions on a Cary Model 14 recording spectrophotometer.

Thermal gravimetric analyses were obtained on an assembly based on a Cahn electrobalance, a Cahn time derivative computer, and a modified Leeds and Northrup temperature programmer.

Nuclear magnetic resonance spectra were obtained on a Varian HR 100 spectrometer.

Inherent viscosities of all polymer samples were obtained in 0.25% formic acid (97-100%) solution at 31°C.

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Discussion of Paper by J. H. Hodgkin and J. Heller

Thermally Stable Spiropolymers

C. L. Segal:	The polymer remains 50% cyclized even on additional heating in polyphosphoric acid, but appears to cyclize in TGA heating. If weight loss in TGA was due to water evolution and ring closure, why can you not achieve more than 50% ring closure during synthesis?
J. Heller:	Additional cyclization can very likely be achieved by heating the polymer to sufficiently high temperatures. The TGA trace seems to indicate that about 400°C is required. What I have described with this particular system were only some preliminary experiments.
D. J. O'Neil:	In the infrared spectrum shown as evidence for a fully cyclized polymer, there appeared evidence of an amino and/or hydroxyl group. Doesn't this suggest incomplete cyclization?
J. Heller:	The hydroxyl group comes from water in the KBr pellet used to obtain the spectrum. No amino group is evident.
A. Rembaum:	Is the elemental analysis of the same sample reproducible?
J. Heller:	Yes, analyses are reasonably reproducible.