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DEVELOPMENT OF SPACE STABLE SEMITRANSPARENT POLYQUINOXALINE FILMS

by

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FOREWORD

This report was prepared by The Boeing Company, Aerospace Group, under NASA Contract NAS1-11255, "Development of Space Stable Semitransparent Polyquinoxaline Films." The work was administered under the direction of The National Aeronautics and Space Administration, Langley Research Center, with Mr. Wayne S. Slemp, as the Project Engineer.

The period of performance was from December 10, 1971 to November 24, 1972, including approval and distribution of The Final Report. The work was performed in The Materials Section of The Aerospace Group, The Boeing Company. Dr. R. G. Cheatham was Program Supervisor and Mr. P. M. Hergenrother was the Principal Investigator, with Mr. Sylvester Hill assisting.

SUMMARY

Three polyphenylquinoxalines underwent preliminary study for potential use as coatings on aircraft and spacecraft. These polymers were prepared from the reaction of 3,3',4,4'-tetraaminodiphenyl ether with p,p'-oxydibenzil and with m -bis (phenylglyoxalyl) benzene and from the reaction of 3,3',4,4'-tetraaminodiphenylsulfone with p,p'-oxydibenzil. High purity reactants and solvents were used in polymer preparation to minimize color in the polymer films. High molecular weight polymers (e.g. η_{inh}=1.5 to 2.1 dl/g) were prepared at ambient temperature at 12 to 15% concentration by upsetting the stoichiometry by 0.5 to 1.0% in favor of the bis (1,2-dicarbonyl) reactant. A portion of each polymer was endcapped with benzil and with o-phenylenediamine. Certain properties of the endcapped and unendcapped versions of each polymer are compared. Uniform films of 2.0 and 0.1 mil thickness were cast from solutions of the unendcapped and endcapped versions of each of the three polymers.

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1.0 INTRODUCTION

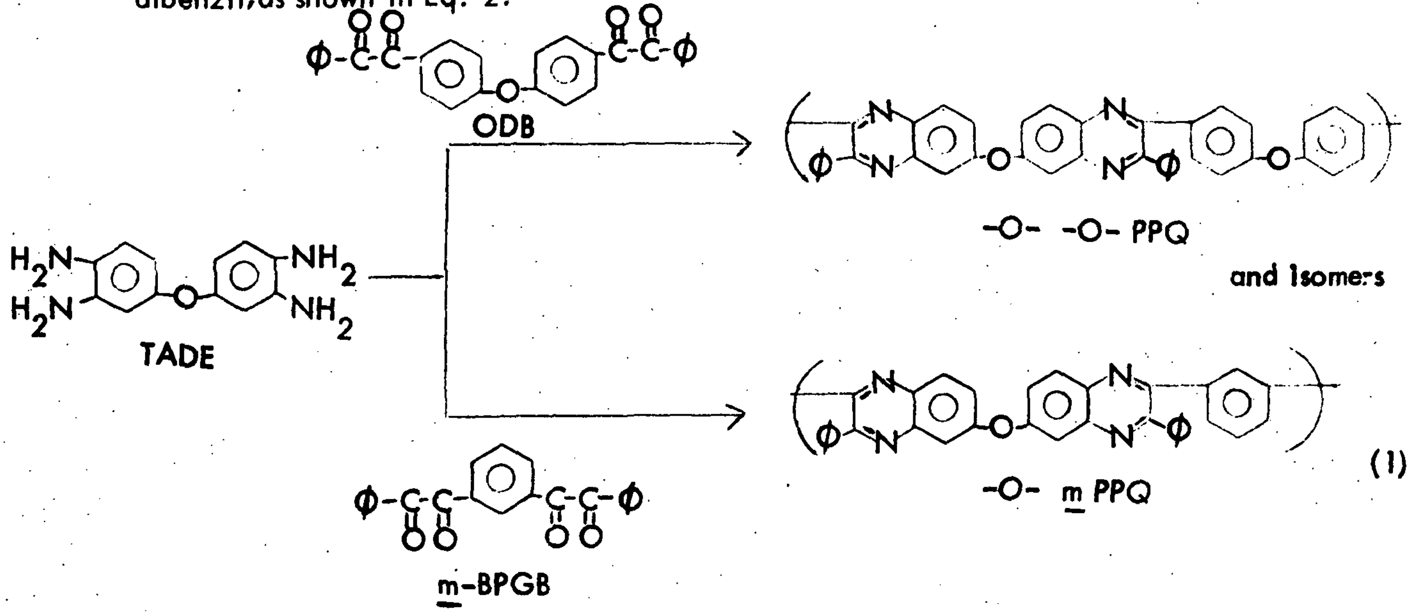
The need for improved coating materials capable of performing for long lifetimes in extreme environments such as that encountered in deep space, has served as the impetus for this research program on polyphenylquinoxalines (PPQ). These new improved polymeric materials should exhibit high stability towards ultraviolet and charged particle radiation as evidenced by good retention of color and mechanical properties (e.g., adhesion). The principal potential applications for these polymers are as surface coatings on spacecraft and aircraft as well as on space components such as solar cell covers and substrates for second surface mirrors.

The objective of this program was to develop PPQ films which would have a maximum transparency between 0.25 and 2.5μm in wavelength and exhibit high stability towards ultraviolet and particulate radiation for use as spacecraft and aircraft coatings. Prior work at Boeing showed that a PPQ film retained good color, flexibility, and toughness after exposure to relatively high level of particulate radiation whereas a polyimide film (H-film), exposed simultaneously, underwent embrittlement.

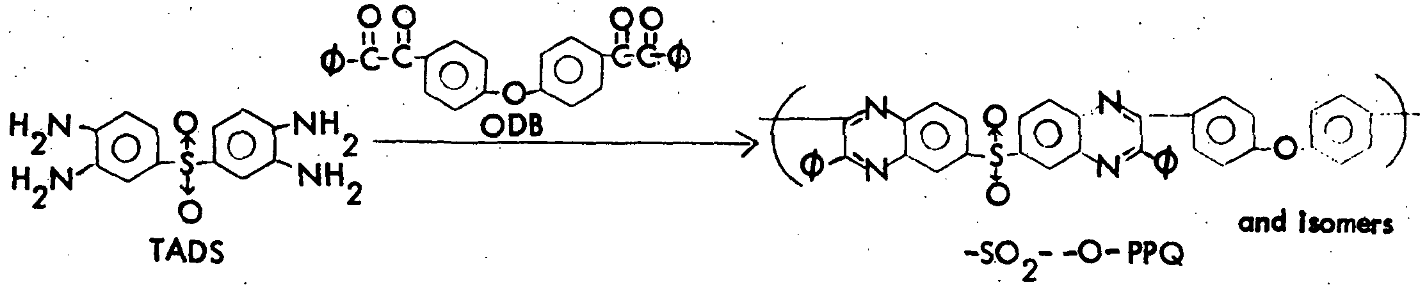
In this program, three PPQ were selected from a list of more than forty different PPQ which have been prepared and characterized at Boeing (Ref. 1 and 2). It was thought that these PPQ would provide near-colorless thin films which would retain good color and mechanical properties after exposure to ultraviolet and particulate radiation.

2.0 DISCUSSION

The major effort in this program concerned the preparation of three PPQ from the reaction of 3,3', 4,4'-tetraaminodiphenyl ether (TADE) with p,p'-oxydibenzil (ODB) and with m-bis(phenylglyoxalyl)benzene (m-BPGB) as shown in Eq. 1,and from the reaction of 3,3',4,4'-tetraaminodiphenyl sulfone (TADS) with p,p'-oxydibenzil,as shown in Eq. 2.



(1)

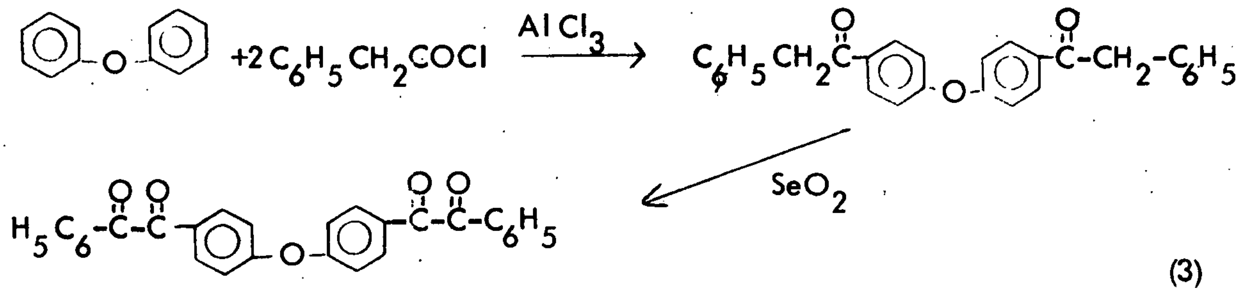


(2)

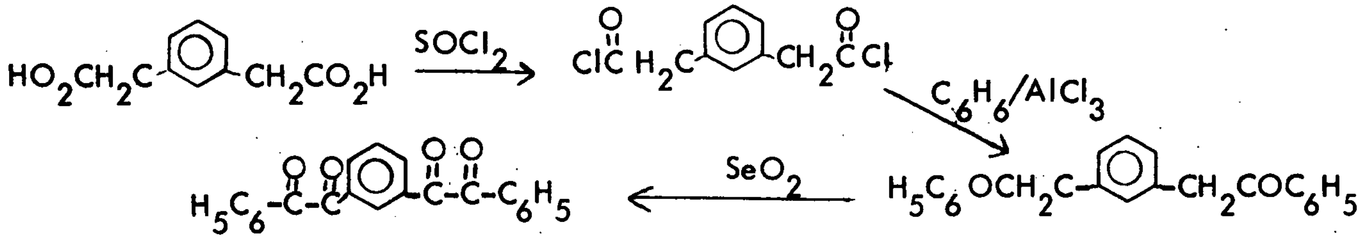
Originally,the PPQ from the reaction of 3,3',4,4'-tetraaminodiphenyl sulfone and m-bis(phenylglyoxalyl)benzene was proposed. However, as discussed in the following section, problems were encountered in consistently obtaining high molecular weight polymer and, as a result, the PPQ shown in Eq. 2 was substituted with approval of the NASA Project Engineer.

2.1 Reactant Synthesis

Following a known procedure (Ref. 3), p,p'-oxydibenzil was prepared as shown in Eq. 3.


(3)

Meta-bis(phenylglyoxalyl)benzene was prepared following a modification of a known procedure (Ref. 4) as shown in Eq. 4.


(4)

The two aromatic tetramines, 3,3', 4,4'-tetraaminodiphenyl ether and 3,3',4,4'-tetraaminodiphenyl sulfone, were obtained commercially and recrystallized (see Experimental Section).

Since one of the objectives of this program was to prepare near colorless thin PPQ films, it was necessary to purify each of the reactants and polymerization solvents prior to use in polymer formation to eliminate impurities which may contribute to color. The purity of the refined reactants was examined by differential scanning calorimetry at a heating rate of $2^{\circ}C$ per minute (Figure 1). Each reactant exhibited a single sharp melting endotherm, indicating high purity.

The endcapping agents, *o*-phenylenediamine and benzil, were obtained commercially and the diamine was recrystallized prior to use in endcapping studies. Both reactants were of high purity, as indicated by DSC and visual melting point.

2.1 Reactant Synthesis (Continued)

The melting points for each of the reactants as determined visually and by DSC are given in Table 1.

TABLE 1

CHARACTERIZATION OF REACTANTS

Reactant	DSC m.p., °C	Visual m.p., °C	Lit m.p., °C (Ref.)
3,3',4,4'-tetraaminodiphenyl ether	151	152.5-153.5	150-151 (5)
p,p'-oxydibenzil	105	106-107	106.4-107.4 (6)
m-bis(phenylglyoxalyl) benzene	98	99-100	98-99.5 (4)
3,3',4,4'-tetraaminodiphenyl sulfone	176	178-179	173-147 (7)
o-phenylenediamine	99	101-102	102-103 (8)
benzil	94	95-96	95 (8)

2.2 Solvents

The solvents employed for the recrystallization of the reactants were obtained commercially in high purity (98+%). The solvents used for polymer formation were obtained commercially in high purity and redistilled prior to use in polymer formation. Those solvents most commonly used, m-cresol and sym-tetrachloroethane, were analyzed by gas chromotography using a 6'x1/8" SE 30 column. Redistilled sym-tetrachloroethane had six minor components which constituted 1.97%. The major impurity (1.56%) exhibited the same retention time as pentachloroethane. Redistilled m-cresol had two minor components which boiled higher than m-cresol and constituted 0.26%. The major impurity (0.18%) was thought to be a dimethylphenol.

2.3 Polymer Synthesis

2.3.1 General Procedure

The general procedure for polymer preparation involved the addition of the bis (1,2-dicarbonyl) compound as a fine powder during ~3 minutes to a stirred slurry of the aromatic bis (o-diamine) in various solvents at room temperature.

2.3.1 General Procedure (Continued)

In some cases as shown in Table 2, the reaction temperature was increased and maintained at an elevated temperature for a given time period. Past work on polyphenyl-as-triazines (Ref. 9), as well as on polyphenylquinoxalines, showed that when stoichiometric quantities of high purity reactants are used on a 0.010 mole scale at 15 to 20% (W/V concentration), the resulting polymer solution is generally extremely viscous and, in some cases, forms an irreversible gel. The high viscosity or gelling phenomenon can be alleviated without any appreciable detrimental effect upon the polymer by upsetting the stoichiometry of the reactants. The stoichiometry should be upset in favor of the bis(1,2-dicarbonyl) compound since PPQ with o-amino end groups tend to discolor more readily than PPQ with 1,2-dicarbonyl end groups.

2.3.2 Chlorinated Solvent Studies

Therefore, initial polymer work involved the preparation of PPQ on a small scale (generally 0.010 mole) by using exact stoichiometry as well as upsetting the stoichiometry of the reactants in favor of the bis(1,2-dicarbonyl) monomer. Since phenolic solvents (e.g., m-cresol) are known to undergo oxidation in air to yield colored products, it was desirable to use solvents other than m-cresol in the polymerization. As shown in Table 1, relatively high molecular weight polymers, as indicated by inherent viscosities (0.5% H_2SO_4 solution at 25°C) of 1.39 and 1.49 dl/g, were obtained from the reaction of TADE and ODB in chloroform (Expt. No. 120) and from the reaction of TADS and m-BPGB in chloroform (Expt. No. 141). However, the films prepared by doctoring a portion of these solutions onto glass plates followed by air drying were turbid. Various attempts to obtain clear, uniform 1.0 mil films from chloroform PPQ solutions were unsuccessful. The preparation of PPQ (Expt. No. 127 and 126) in sym-tetrachloroethane (TCE) provided lower molecular weight polymer and also turbid films. The turbidity in the films cast from chloroform or TCE solution is presumably due to the presence of water from the condensation reaction. The turbidity could probably be alleviated by more careful control of solvent removal or by precipitating the polymer, then drying, redissolving, and recasting it from the new solution. Regardless, past work had shown that PPQ prepared in a 1:1 mixture of m-cresol and xylene provided clear yellow films. Therefore, further polymer synthesis employed a 1:1 mixture of m-cresol and xylene as the solvent.

2.3.3 Meta-Cresol-Xylene Studies

a. Reaction of TADS and m-BPGB

In a 1:1 mixture of m-cresol and xylene, the reaction of TADS and m-BPGB (Expt. No. 121, 126, 132, 135, 137, and 144) on a 0.010 mole scale failed to form high molecular weight polymer ($\eta_{inh} > 0.92$ dl/g) under various conditions. At exact stoichiometry (Expt. No. 132), a PPQ with an η_{inh} of 0.92 was obtained after 18 hours at room temperature. However, when this reaction was repeated (Expt. No. 135, 137, and 144), low molecular weight polymer was obtained even when the reaction temperature was increased and maintained at 190°C for 20.5 hours (Expt. No. 137). These results were surprizing since each of these reactants (from the same batch) could be readily polymerized with other PPQ monomers to yield high molecular weight polymers. Instead of devoting additional effort in an attempt to obtain high molecular weight polymer from the reaction of TADS with m-BPGB, the PPQ from the reaction of TADS and ODB was substituted with the approval of the NASA Langley Project Engineer.

b. Reaction of TADS and ODB

The first reaction (Expt. No. 145) of TADS and ODB at exact stoichiometry in a 1:1 mixture of m-cresol and xylene at ambient temperature provided a high molecular weight polymer ($\eta_{inh} = 2.4$, 0.5% m-cresol solution at 25°C). However, the viscous clear light yellow solution gelled after standing for 24 hours at room temperature. In an attempt to alleviate the gelling problem, the stoichiometry was upset by 1% in favor of ODB (Expt. No. 146) to provide a polymer of relatively low molecular weight ($\eta_{inh} = 0.51$). After repeating this reaction several times (Expt. No. 149, 151, 153, 155, and 156), it became apparent that the reaction of TADS with ODB, under the conditions indicated in Table 1, proceeded relatively slow. For example, when the stoichiometry was upset by 0.5% in favor of ODB (Expt. No. 153), the polymer required a reaction time of 148 hours at 26°C to attain an η_{inh} of 1.55. Gelation occurred after 264 hours at 26°C, even though the solution had been diluted from 20 to 13.1%. A repeat of this reaction (Expt. No. 155) at 15% concentration resulted in gelling after 96 hours at 26°C. A stable solution of relatively high molecular weight polymer ($\eta_{inh} = 1.10$) was finally obtained by upsetting the stoichiometry 1% in favor of ODB. The final polymer solution had a solids content of 12% (Expt. No. 156-2). Based upon work on polypheny-as-triazines

(Ref. 9) and other work on phenylquinoxaline polymers (Ref. 10), the gelling phenomenon is tentatively attributed to a combination of two factors, a small amount of branching and the presence of very high molecular weight species.

c. Scale-up

Although somewhat erratic results were experienced in preliminary polymer synthesis, it was thought that some of the problems could be overcome by increasing the size of the reaction. If successful, this would provide sufficient polymer for endcapping studies and preparation of samples required on this contract. Therefore, as shown in Table 3, the three PPQ (Expt. No. 143, 154, and 164) were prepared on a 0.20 mole scale by upsetting the stoichiometry by 1% in favor of the bis(1,2-dicarbonyl) compound. The reaction temperature was maintained at 26°C except for an initial surge in temperature to ~35°C when the bis(1,2-dicarbonyl) compound was added to the stirred slurry of tetraamine. The increase in molecular weight of the polymer was followed by Brookfield viscosity measurements on the solution. For example, a plot of viscosity in centipoises (cps) versus time is presented in Fig. 2 for the polymer from the reaction of TADS and ODB (Expt. No. 164). The viscosity increased gradually from 1150 cps after 24 hours to 11,100 cps after 240 hours with very little increase after an additional 240 hours. It was apparent that the reaction of TADS with ODB or with m-BPGB proceeds at a relatively slow rate; whereas the reaction of TADE with ODB or with m-BPGB proceeds much faster. The lower reactivity of TADS is due to the strong electron withdrawing power of the sulfone group, thereby decreasing the nucleophilicity of the amino groups.

d. Further Studies of the Reaction of TADS and m-BPGB

With this observation, the reaction of TADS with m-BPGB was repeated on a 0.010 mole scale at 15% solids content in a 1:1 mixture of m-cresol and xylene. After stirring at 26°C for 12 days, a polymer with an η_{inh} of 1.64 was obtained. Apparently, low molecular weight polymer was obtained in the earlier attempts because the reaction time was too short to permit adequate chain growth.

2.4 Polymer Endcapping

Each of the three PPQ in Table 3 was treated in the following manner. The original polymer solution was poured slowly into methanol in a Waring Blender to precipitate a fibrous solid which was thoroughly washed in boiling methanol. After drying at 130°C *in vacuo* for 4 hours, the polymer was redissolved in a 1:1 mixture of *m*-cresol and xylene at 11 to 13.8% solids content and filtered through a 30 to 50μ sintered glass funnel. An excess of *o*-phenylenediamine was added to about half of the filtered solution which was then stirred at ambient temperature under nitrogen for 28 hours. The polymer was isolated as before by precipitation in methanol, thoroughly washed and dried at 130°C *in vacuo*. The resulting near-white solid was redissolved in TCE at ∼10% solids content and then treated with an excess of benzil by stirring under nitrogen at ambient temperature for 26 hours. The resulting polymer solution was again isolated in methanol, washed thoroughly with hot methanol and benzene, dried at 130°C *in vacuo*, and redissolved in a 1:1 mixture of *m*-cresol and xylene. The resulting solution was filtered again. The solution properties of the polymers listed in Table 2 are those after precipitating and redissolving the polymer before and after endcapping.

Endcapping work was performed in an attempt to reduce the presence of end groups which may contribute to color in the polymer. For example, amino groups are known to undergo oxidation to yield highly colored products. The end groups in PPQ would be *o*-diamino and 1,2-dicarbonyl groups. Upon reaction with benzil, the o-amino groups should be converted to a 2,3-diphenylquinoxaline, while the 1,2-dicarbonyl groups should undergo reaction with *o*-phenylenediamine to form a quinoxaline moiety.

2.5 Polymer Characterization

In an attempt to determine the quantity of amino end groups in the PPQ obtained from the reaction of TADE with ODB, the following acetylation was attempted in an argon atmosphere. A 4.0g portion of the unendcapped diether PPQ (Expt. No. 143-1) was dried at 210°C *in vacuo* for 24 hours and redissolved in 100 ml of dry TCE. Acetic anhydride was added and the TCE solution stirred for 48 hours. The TCE solution was thoroughly washed with water and the aqueous fractions titrated with standard base. The titrations showed a 100% recovery of acetic acid, indicating no detectable amino end groups. This was not unexpected since the polymer was prepared with a 1% excess of ODB and the weight average molecular weight of the polymer is probably > 200,000 (Ref. 11). As shown in Table 3, the unendcapped and endcapped versions of each of the three polymers exhibited almost identical η_{inh} which indicated high molecular weight. This means that no loss in viscosity (and molecular weight) was incurred by the endcapping treatments.

The glass transition temperature (Tg) of the unendcapped and endcapped versions of each of the three PPQ were also very similar. A representative DSC curve for the diether PPQ is shown in Fig. 3. The two versions of the diether PPQ (Expt. No. 143) exhibited a difference in Tg of 3°C while the difference in Tg for the two versions of TADE-m-BPGB and TADS-ODB polymers were 1 and 0°C, respectively. It should be noted that the Tg values of the diether PPQ (Expt. No. 143) and sulfone ether PPQ (Expt. No. 164) were previously reported (Ref. 12) to be 258°C (found 254°C) and 290°C (found 293°C), respectively.

Ultraviolet and visible spectroscopic analyses were performed to determine differences which could result from polymer endcapping. The ultraviolet and visible spectra of sulfuric acid solutions of the unendcapped and endcapped versions of each of the three PPQ are presented in Table 3. The wavelengths of maximum absorption (λ max) in the ultraviolet and visible region for the unendcapped and endcapped versions of each of the three PPQ are essentially identical. The molar absorptivity (ϵ, molar extinction coefficient) for the two versions of the ether m-phenylene PPQ (Expt. No. 154) and the sulfone ether PPQ (Expt. No. 164) agree favorably, whereas ϵ for the two versions of the diether PPQ (Expt. No. 143) differ. These values were found to be valid upon rechecking and no reasonable explanation can be offered to account for this difference.

2.6 Films

Films of 2.0 and 0.1 mil thickness having a minimum area of 144 sq. in. were cast from solutions of the unendcapped and endcapped versions of each of the three PPQ listed in Table 3 (Expt. No. 143, 154, and 164). These films were prepared at Gulf Energy and Environmental Systems, San Diego, California, with the assistance of Mr. Wolfgang Wrasidlo. A specially designed chamber used for the preparation of membranes for evaluation in reverse osmosis was used in the PPQ film preparation. This chamber was designed to control the various parameters such as humidity, casting speed, drying temperature and particle contamination (e.g. dust) necessary to prepare membranes for molecular separations. Prior to the large scale casting, the parameters required to obtain 2.0 and 0.1 mil thick films from each of the six PPQ solutions were determined experimentally by preparing small films. These conditions varied with each of the six PPQ solutions, primarily due to different solids content and viscosity.

The solutions were cast on mirror plate glass surface which had been thoroughly cleaned (acetone, windex and acetone) and preconditioned by applying a very thin coat of solvent (1:1 mixture of m-cresol and xylene). After applying the polymer solution with a doctor blade, the wet films were dried at ~ 50°C in a dust-free air environment for 2 days. Prior work with similar solutions had shown that the atmosphere (air or inert gas) failed to exhibit any detectable effect upon the color of PPQ films. After drying at ~ 50°C, the 2.0 mil films were still slightly tacky whereas the 0.1 mil films appeared dry. The films were further dried in air (dry) at 110°C for 8 hours, then stripped from the glass plate using water, rolled in white paper, and carefully stage-dried *in vacuo* (<5 mm) continuously for 1 week until a final temperature of ~ 150°C was maintained for 13 hours. The volatile content of the 2.0 mil films was $<1\%$.

The method previously described was used to cast a film of ~ 3.8 mils in thickness having an area of ~ 180 sq. in. from the TADE-m-BPGB polymer described in Table 3 (Expt. No. 162). The initial drying cycle was identical to that of the other films. However, the final drying cycle *in vacuo* was two weeks until a final temperature of ~ 150°C was maintained for 36 hours.

Each of the six PPQ solutions defined in Table 3 (Expt. No. 143, 154, and 164) were also used to coat 1.0 mil films on one side of three 7/8 inch-diameter aluminum discs which had been specially polished and supplied by NASA Langley. The coating and drying operation was performed as previously described for the films.

2.6 Films (Continued)

The ultraviolet and visible spectra as measured on a Cary 14 spectrophotometer of 2.0 and 0.1 mil thick films of the endcapped and unendcapped versions of the diether PPQ (Table 3, Expt. No. 143) were essentially identical. The percent light transmission of the unendcapped film at various wavelengths is presented in Table 4.

TABLE 4

PERCENT LIGHT TRANSMISSION OF POLY-2,2'-(p,p'-OXYDIPHENYLENE)-6,6'-OXYDI (3-PHENYLQUINOXALINE) FILM (TABLE 3, EXPT. NO. 143-1)

	Film Thickness, mils	
Wavelength, mμ	2.0	0.1
700	94	98
500	91	95
450	85	94
430	68	93.5
420	0	88
410	0	50
405	0	0
380	-	0
200	-	0

3.0 EXPERIMENTAL

p,p'-Oxydibenzil A solution of diphenyl ether (170g, 1.0 mole) and phenylacetyl chloride (309g, 2.0 mole) in methylene chloride (500 ml) was added during 3 hr. to a stirred suspension of anhydrous aluminum chloride (266g, 2.0 mole) in methylene chloride (1.5ℓ) at 5-10°C. After complete addition, the resulting brown mixture was stirred at 5-10°C for 2 hr. and at ambient temperature for 18 hr. The brown mixture was poured onto crushed ice and hydrochloric acid. The organic phase was separated, washed twice with water, and concentrated to dryness. The cream-colored residual solid was pulverized, washed with aqueous sodium bicarbonate, and recrystallized from N,N-dimethylformamide (20% solid content) to afford p-phenylacetylphenyl ether as white crystals (303g, 75% yield) m.p. 169-170.5 [lit m.p. 169-170°C (Ref. 6)]. To a stirred slurry of selenium dioxide (111g, 1.0 mole) in glacial acetic acid (1.4) at 60°C, powdered p-phenylacetylphenyl ether (203g, 2.0 mole) was added. The stirred reaction mixture was refluxed for 7 hours followed by a hot filtration. The hot clear yellow filtrate was treated with charcoal, filtered through celite, and concentrated to ~1ℓ under vacuum. Upon cooling, a semi-crystalline yellow solid separated (174g, 80% yield) m.p. 104.5-106°C. Recrystallization from ethanol (~4.5ℓ) afford p,p'-oxydibenzil as yellow crystals (148g, 85% recovery) m.p. 105.5-107°C [lit. m.p. 106.4-107.4 (Ref. 6)] . This material was recrystallized again from ethanol to afford yellow crystals, m.p. 106-107°C. The melting point by DSC was 105°C.

***m*-Bis(phenylglyoxalyl)benzene** *m*-Phenylenediacetic acid (500g, 2.57 mole) was stirred in thionyl chloride (2.3ℓ) containing a few drops of N, N-dimethylformamide at ambient temperature for 2 days. The resulting orange brown solution was concentrated to dryness at temperature < 50°C *in vacuo* to yield a crystalline yellowish orange solid (602g). To a stirred slurry of anhydrous aluminum chloride (863g, 6.5 mole) in a dry benzene (1.6ℓ) at 5 to 10°C, a solution of the diacid chloride of *m*-phenylenediacetic acid (602g, 2.6 mole) in dry benzene (1.2ℓ) was added during 3 hr. After complete additon, the brown reaction mixture was stirred at 5 to 10°C for 2 hr. and at ambient temperature for 18 hrs. The brown reaction mixture was *m-Bis(phenylglyoxalyl)benzene* (Continued)

poured onto ice and hydrochloric acid. The organic phase was separated, washed with water, concentrated to ~1.2ℓ, and cooled to yield a tan solid (619g). Recrystallization from alcohol (4ℓ) provided a tan crystalline solid (400g) m.p. 89-92°C. This material was recrystallized again from alcohol to afford *m*-diphenacylbenzene as tan crystals (321g) m.p. 90-92°C [lit m.p. 90.5-91 (Ref. 4)]. To a stirred slurry of selenium dioxide (222g, 2.0 mole) in glacial acetic acid (1.5ℓ) at 60°C, *m*-diphenacylbenzene (314g, 1.0 mole) was added. After refluxing for 6 hr., the reaction mixture was filtered hot, and the hot filtrate treated with charcoal and celite and refiltered. Upon cooling, yellowish orange needles separated (254.7g) m.p. 98-99.5°C. Recrystallization from ethanol provided yellow crystals m.p. 99-100°C [lit. m.p. 98-99.5°C (Ref. 4)]. The melting point by DSC was 98°C.

3,3',4,4'-Tetraaminodiphenyl ether Crude tetraamine (178g) melting at 150-153.5°C was recrystallized from deoxygenerated water (2.1ℓ) containing a pinch of sodium dithionite under argon using charcoal. Upon cooling the pale yellow filtrate, white crystals (160g) were isolated which melted at 152-153.5°C after drying *in vacuo* over phosphorus pentoxide. Recrystallization again from water provided TADE as white crystals, m.p. 152.5-153.5°C. [lit. m.p. 150-151°C (Ref. 5)]. The DSC melting point was 151°C.

3,3',4,4'-Tetraaminodiphenyl sulfone - Crude tetraamine (122g) melting at 176-179°C was recrystallized from deoxygenated water (4.0ℓ) using a pinch of sodium dithionite and charcoal under argon to afford white crystals (95g), m.p. 178.5-180°C, after drying *in vacuo* over phosphorus pentoxide. Recrystallization a second time afforded TADS as white crystals, m.p. 178-179 [lit. m.p. 173-174 (Ref. 7)]. The DSC melting point was 176°C.

o-Phenylenediamine - The diamine (100g) was recrystallized from deoxygenated water (0.5ℓ) using a pinch of sodium dithionite and charcoal under argon to afford white crystals (74g), m.p. 101-102°C. By DSC, the melting point was 99°C.

Polymer - The general procedure for polymer synthesis was previously described under the Polymer Synthesis Section of this report. The experimental details for each polymer prepared in this program are provided in Tables 2 and 3.

Polymer Endcapping - Polymer endcapping was performed for each of the three PPQ in Table 3 by the following procedure. The PPQ solution, as prepared in a 1:1 mixture of m-cresol and xylene, was poured slowly into methanol in a Waring blender. The fibrous polymer was boiled twice in methanol (~1ℓ), then dried in vacuo at 130°C for 4 hours. The polymer was redissolved in a 1:1 mixture of m-cresol and xylene at the solids content indicated in Table 3. This solution was filtered through a 30 to 50μ sintered glass funnel. To half of the filtered solution, excess o-phenylenediamine (10g) was added and the solution stirred at ambient temperature under nitrogen for 28 hr. The polymer was isolated and dried as before and redissolved in TCE at ~10% solids content. An excess of benzil (25g) was added and the solution stirred at ambient temperature under nitrogen for 26 hr. The polymer was isolated as before, thoroughly washed successively with hot methanol and benzene, dried as before, and redissolved in a 1:1 mixture of m-cresol and xylene at the solids content indicated in Table 3. The resulting solution was then filtered through a 30 to 50μ sintered glass funnel.

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TABLE 2 - PRELIMINARY SYNTHESIS AND CHARACTERIZATION OF POLYPHENYLQUINOXALINES

Exp't. No. PH-1	Reactants	Stoich. NH_2:CO [1]	R_x Scale, Mole	Solvent	R_x Condition		Solution, (% Solids Content)	η_{inh}, dl/g [2]	Film Properties		Color of ppt Polymer
					Temp.,°C	Time, hr.			Color	Remarks	
120	TADE, ODB	0.985:1.000	0.01	$CHCl_3$	61	8	dk. or. br. med. vis. (20)	1.39	lt. Tan, turbid	Tough & Flexible	lt. tan
127	TADE, ODB	0.985:1.000	0.01	TCE	70 90	4 3	or. brown low vis. (20)	-- 0.69	lt. tan turbid	low strength	near white
133	TADE, m-BPGB	0.985:1.000	0.01	m-cresol & xylene (1:1)	26	18	lt. or. br. med. vis. (20)	0.87	pale yel., clear	tough & flexible	near white
136	TADE, m-BPGB	0.99:1.00	0.10	m-cresol & xylene (1:1)	65-80	2	cl. yel. (20)	0.80	cl. yel.	tough & flexible	near white
141	TADE, m-BPGB	1.00:1.00	0.10	$CHCl_3$	26	48	yel., turbid (20)	1.49	yel, turbid	tough & flex.	--
121	TADS, m-BPGB	0.99:1.00	0.01	$CHCl_3$	61	12	or. brown, low vis. (20)	0.58	lt. tan, turbid	brittle	lt. tan
126	TADS, m-BPGB	0.99:1.00	0.01	TCE	70 146	8 3	or. brown, low vis. (20)	0.50	lt. Tan turbid	brittle	near white
132	TADS, m-BPGB	1:00:1.00	0.01	m-cresol xylene (1:1)	26	18	cl. yel. med. vis. (20)	0.92	Pale yel., Clear	tough & flexible	near white
135	TADS, m-BPGB	1.00:1:00	0.01	m-cresol xylene (1:1)	160	2	yel., turbid (20)	0.38	cl. yel.	brittle	--
137	TADS, m-BPGB	1:00:1.00	0.01	m-cresol	190	20.5	cl. yel. or. (20)	0.50	cl. yel.	brittle	--
144-1 144-2	TADS, m-BPGB	1.00:1.00	0.01	m-cresol xylene (1:1)	80 190	7 6	cl. lt. yel. (20) cl. lt. yel. (20)	0.47 0.49	-- --	brittle brittle	-- --
145	TADS, ODB	1.00:1.00	0.01	↑	26	72	gelled (20)	(2.04)	cl. lt. yel.	Tough & felx.	--
146	TADS, ODB	0.99:1.00	0.01	│	26	72	cl. lt. yel. (20)	(0.51)	--	brittle	
149-1 149-2	TADS, ODB TADS, ODB	0.995:1.000	0.01	│	26 26	27 99	cl. lt. yel (20) cl. lt, yel. vis. (20)	(0.65) (1.60)	yel, turbid cl. yel.	low strength tough	--
151	TADS, ODB	0.9975:1.000	0.01	│	26	120	gelled (20)	Insol.	--	--	--
153-1 153-2	TADS, ODB	0.995:1.000	0.01	│	26 26	148 264	vis. cl. yel (20) yel., gelled (13.1)	(1.55) --	cl. lt. yel. --	tough & flex. --	pale yellow --
155	TADS, ODB	0.995:1.000	0.01	↓	26	96	yel., gelled (15)	--	--	--	--
156-1 156-2	TADS, ODB TADS, ODB	0.990:1.000	0.01	m-cresol xylene (1:1)	26 26	72 144	cl. lt. yel. (15) cl. lt. yel. (12)	(0.90) (1.10)	cl. lt. yel. --	tough & flex. --	pale yellow --

1. Stoichiometry NH_2:CO = Tetraamine: bis(1,2-dicarbonyl)compound, molar ratio (e.g. 0.985 mole TADE: 1.000 mole ODB for Expt No. PH-1-120)

2. Inherent Viscosity as 0.5% H_2SO_4 Solution @ 25°C, in parenthesis as 0.5% m-cresol solution @ 25°C

TABLE 3 - SYNTHESIS AND CHARACTERIZATION OF POLYPHENYLQUINOXALINES

				R_x Condition [2]			Solution					Spectral Data [8]			
												Ultraviolet		Visible	
Expt. No. PH-1	Reactants	Stoich.[1] NH_2:CO	R_x Scale, Mole	Temp., °C	Time hr.	Solids[3] Content % 1	Solids[4] Content, %	Color	Viscosity,[5] cps,	ηinh,[6] dl/g	Tg,[7] °C	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ
143-1	TADE, ODB	0.99:1.00	0.18	26	27	12.3	11.0	cl. lt. yel.	6000	2.06	254	288	50,523	569	41,238
143-2	Endcapped	--	--	-	-	--	11.8	cl. lt. yel.	8000	2.06	257	288	44,269	570	38,544
154-1	TADE, m-BPGB	0.99:1.00	0.20	26	72	15.0	12.8	cl. lt. yel.	9850	1.89	278	282	47,439	523	38,242
154-2	Endcapped	--	--	-	-	--	12.0	cl. lt. yel.	8350	1.93	279	282	47,481	522	37,095
164-1	TADS, ODB	0.99:1.00	0.20	26	240	15.0	13.8	cl yel.	11,100	1.50	293	283	33,528	573	26,548
164-2	Endcapped	--	--	-	-	--	12.0	cl. yel.	4200	1.51	293	283	33,831	572	26,234
162	TADE, m-BPGB	0.995:1.000	0.20	26	96	15.0	13.5	cl. lt. yel.	9150	1.72	-	-	--	-	--

1. Stoichiometry NH_2:CO = Tetraamine: bis(1,2-dicarbonyl) compound, molar ratio (e.g. 0.99 mole TADE: 1.00 mole ODB for Expt. No. PH-1-143)
2. Upon addition of bis(1,2-dicarbonyl) compound, exotherm to ~35° C (except for Expt. No. PH-1-164)
3. Solids content based upon weight of reactants and volume of solvent (1:1 mixture of m-cresol and xylene)
4. Solids content based upon weight of polymer and volume of solvent
5. Brookfield viscosity at 25° C, centipoises
6. Inherent viscosity as 0.5% m-cresol solution at 25° C
7. Tg = Glass Transition temperature, determined by differential scanning calorimetry at ΔT = 20° C/min, N_2
8. Measured in sulfuric acid, λ_{max} = wavelength of maximum absorption, ϵ = molar extinction coefficient

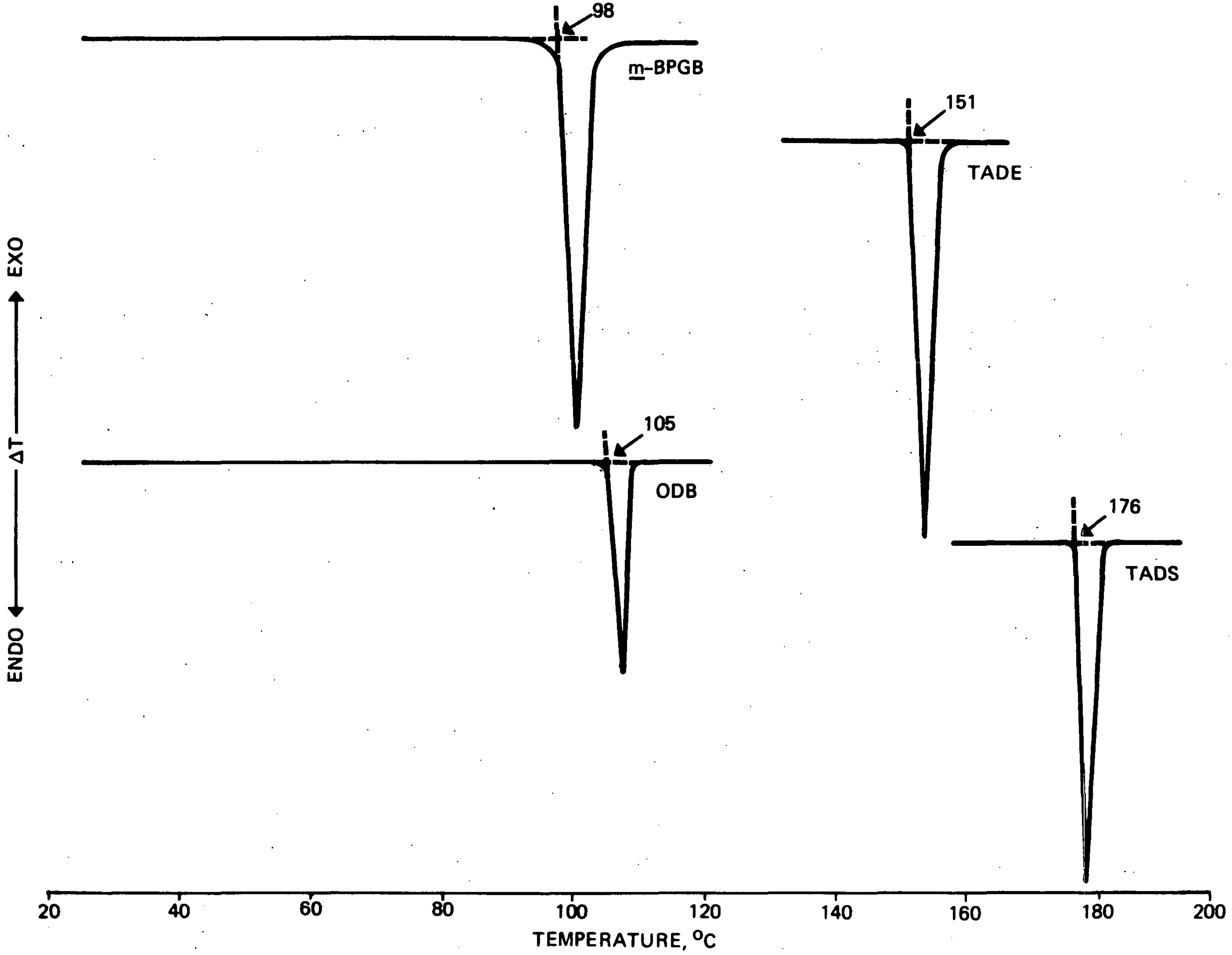

Fig. 1 Differential Scanning Calorimetry of Reactants ($\Delta T = 2°C/min$, N_2)

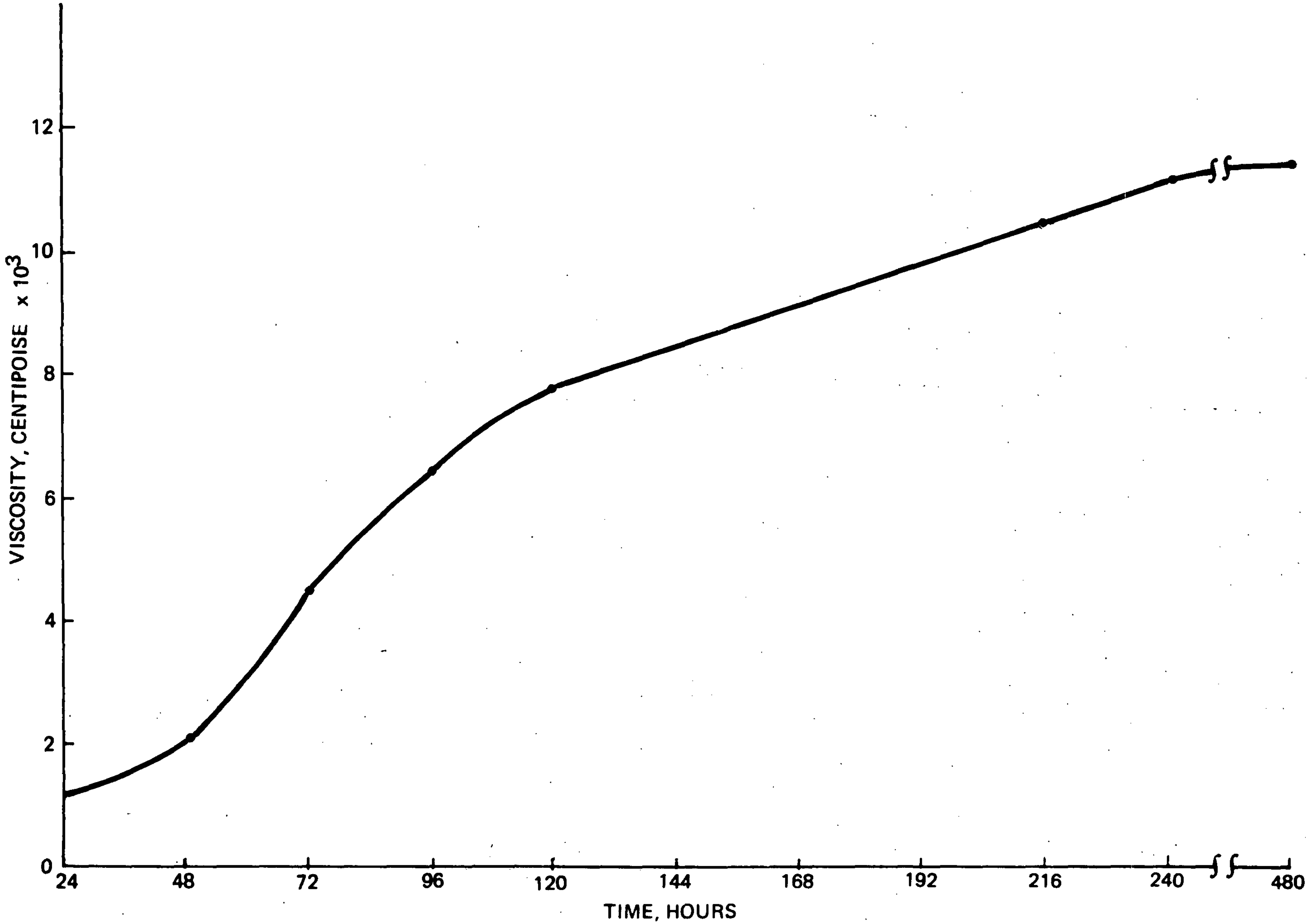

Fig. 2 Plot of Solution Viscosity of Poly-2,2'-(p,p'-oxydiphenylene)-6,6'-sulfonyldi(3-phenylquinoxaline) versus Time

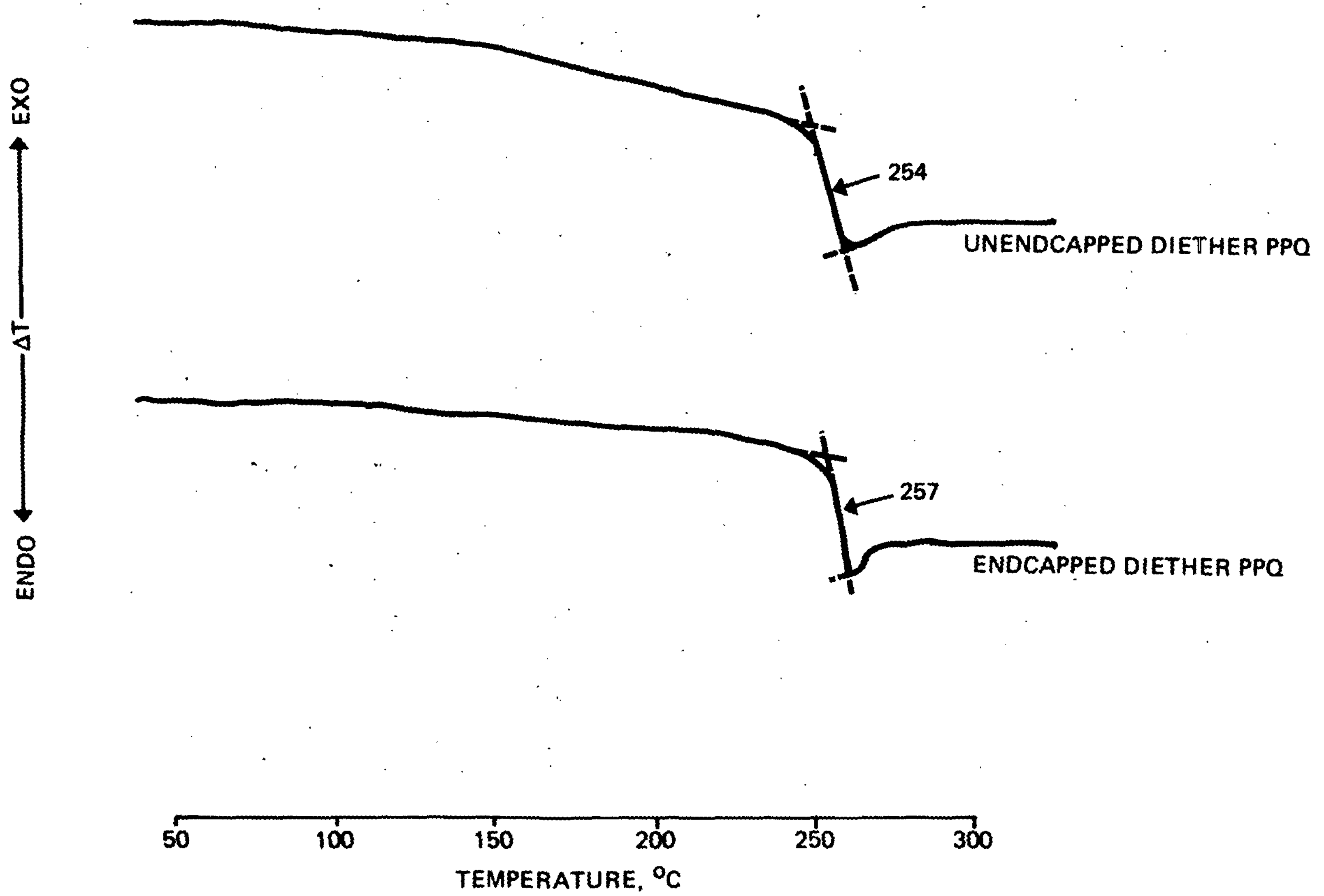

Fig. 3 Differential Scanning Calorimetry of Poly-2,2'-(p,p'-oxydiphenylene)-6,6'-oxydi(3-phenylquinoxaline) (T = 20°C/min, N_2)