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REACTIVE PLASTICIZERS FOR HIGH TEMPERATURE QUINOXALINE THERMOPLASTICS

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

JUNE 1976

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FINAL REPORT FOR PERIOD NOVEMBER 1974 - OCTOBER 1975

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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NOTICE

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, Work Unit No. 73400469, "Polymers for Matrix Resins and Adhesives with Improved Processibilities and Performance". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Project Scientist.

This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

F. E. Arnold

F. E. ARNOLD
Project Scientist

FOR THE COMMANDER

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

AIR FORCE - 28 SEPTEMBER 76 - 150

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, Work Unit No. 73400469, "Polymers for Matrix Resins and Adhesives with Improved Processibilities and Performance". It was administered under the direction of Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFML Project Scientist. This report describes work conducted from March 1975 to October 1975.

The work described in this report was conducted in the Polymer Branch laboratory by Dr. R. L. Kovar of the University of Dayton Research Institute, Dr. G. F. L. Ehlers and Dr. F. E. Arnold of the Air Force Materials Laboratory. The manuscript was released by the authors in January 1976 for publication as a Technical Report.

The authors wish to thank Mr, K. R. Fisch for the determination of glass transition temperatures.

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SUMMARY

This report is concerned with a novel approach to the processing of high temperature thermoplastics. A series of bis(ethynylquinoxaline) monomers were prepared to demonstrate the feasibility of using reactive plasticizers in the processing of polyphenylquinoxaline thermoplastics. The monomers were prepared by the reaction of 4(3-ethynylphenoxy)-o-phenylenediamine with various aromatic 1,2-dicarbonyl compounds in m-cresol. The reactive plasticizer lowers the effective softening point of the thermoplastic resin during processing and then becomes dormant by reacting with itself or the host thermoplastic. Mixtures of monomer and thermoplastic were studied with respect to compatibility, Tg depression and plasticizer deactivation.

SECTION I
INTRODUCTION

In recent years there has been an increasing interest in the utilization of thermoplastic resins to reduce the processing cost of fiber-reinforced composites. Thermoplastic matrices offer the possibility of lessening the fabrication costs of advanced structures, thereby making them cost competitive. The cost reductions are possible because faster and lower cost manufacturing procedures can be employed. Manufacturing methods which have been investigated (References 1-6) for fabrication of graphite/thermoplastic composites have demonstrated cost savings from 25 to 80% over conventional epoxy composites.

Processing of a thermoplastic material as a fiber reinforced composite involves essentially two steps, consolidation of boardy prepreg into sheet stock and thermoforming the sheet stock into structural components. A problem associated with the fabrication process is the high temperatures required in both the consolidation and thermoforming operations. High processing temperatures are required to provide adequate flow and wetting of the fibers. Temperatures in the range of (200-300°F) above the glass transition temperature of the thermoplastic material are necessary to decrease its bulk viscosity for the consolidation process. The problem becomes more critical as the use-temperature of the structural composite is extended, since higher use-temperatures require thermoplastics with higher glass transition and therefore must be fabricated at high temperatures. The disadvantages of using very high fabrication temperatures (800-1000°F) are the unfavorable economics of high temperature tooling and the danger of the material to thermally degradate during processing.

The use of plasticizers is an approach to reduce the high temperatures required for fabrication. A plasticizer lowers the glass transition temperature of the thermoplastic and also reduces its bulk viscosity. Although plasticizers are very attractive for the processing of thermoplastics they will also lower the use-temperature of the fabricated structural component.

The ideal plasticizer would be one which lowers the effective softening point of the thermoplastic resin during processing, and then becomes dormant by reacting with itself or the host thermoplastic. The type of reaction deactivating the plasticizer will undoubtedly have different effects on the mechanical performance of the structural laminate. A reactive plasticizer which becomes dormant by a reaction with itself would generate an organic filler, whereas, reaction with the host thermoplastic could encompass a crosslinking of the thermoplastic matrix. The mechanism and kinetics by which the reaction takes place will also determine the success or failure of an individual reactive plasticizer.

The objective of this work is to synthesize various reactive plasticizers of specific molecular structure which would be compatible with high temperature thermoplastic resins. The purpose of the work is to demonstrate the feasibility of using reactive plasticizers in the processing of high temperature thermoplastic resins into fiber reinforced composites. This report describes a phase of the current effort directed toward attaining this goal.

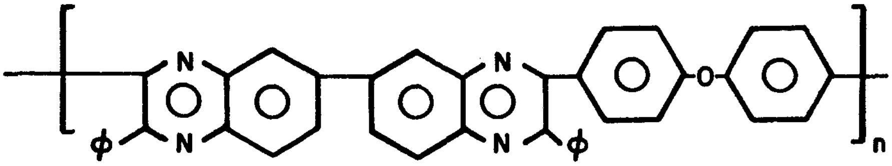
SECTION II
DISCUSSION AND RESULTS

An effective reactive plasticizer is one which is completely compatible with the thermoplastic, both before and after it reacts to become dormant in the system. The success or failure of any plasticizer is primarily dependent on its compatibility with the host thermoplastic. The reaction, by which the plasticizer becomes dormant must proceed by addition without the evolution of volatile by-products. Any volatiles produced during processing would result in the formation of voids in the composite and would detract from the mechanical performance of the structural component.

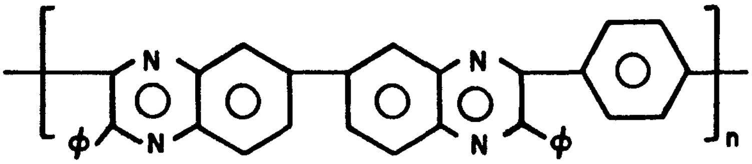
The plasticizer could become deactivated by three different types of addition reactions.

1. Polymerization of the plasticizer with itself leading to a network structure imbedded in the thermoplastic.
2. Intramolecular cycloaddition reactions of the plasticizer generating a simple organic filler.
3. Addition reactions of the plasticizer with the thermoplastic, leading to both branching and crosslinking of the thermoplastic. Each type of reaction would give a different material with respect to its physical and mechanical properties.

The approach utilized in this work was to structurally tailor the plasticizer to closely resemble the molecular structure of the thermoplastic resin. This would assure the highest probability of obtaining compatibility with the mixtures. Deactivation of the plasticizer was accomplished by its homopolymerization via aromatic acetylene groups. The same type of addition polymerization is employed in the ATQ polymer system (Reference 7), currently under development as a high temperature, moisture resistant matrix resin. The high temperature thermoplastics chosen for this study were from the family of polyphenylquinoxaline (A & B) with glass transition temperatures in the 280 - 350°C range.



A

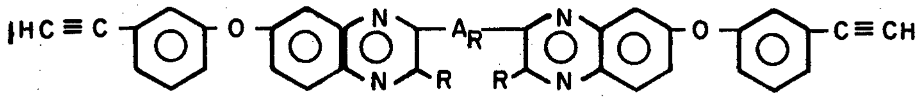


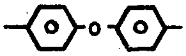
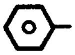
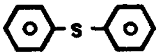
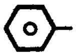
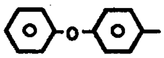
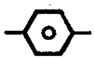
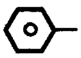
B

A series of bisphenylquinoxaline monomers were prepared (Table 1) containing primary acetylene groups. The molecular structure of the monomers was varied in an effort to obtain polymerizable plasticizers with low softening points. The monomers were prepared by the condensation of 3-(3,4-diaminophenoxy)acetophenone (I) with aromatic bis(1,2-dicarbonyl) compounds to give bis-phenoxyacetylquinoxaline intermediates.

TABLE 1

REACTIVE PLASTICIZERS

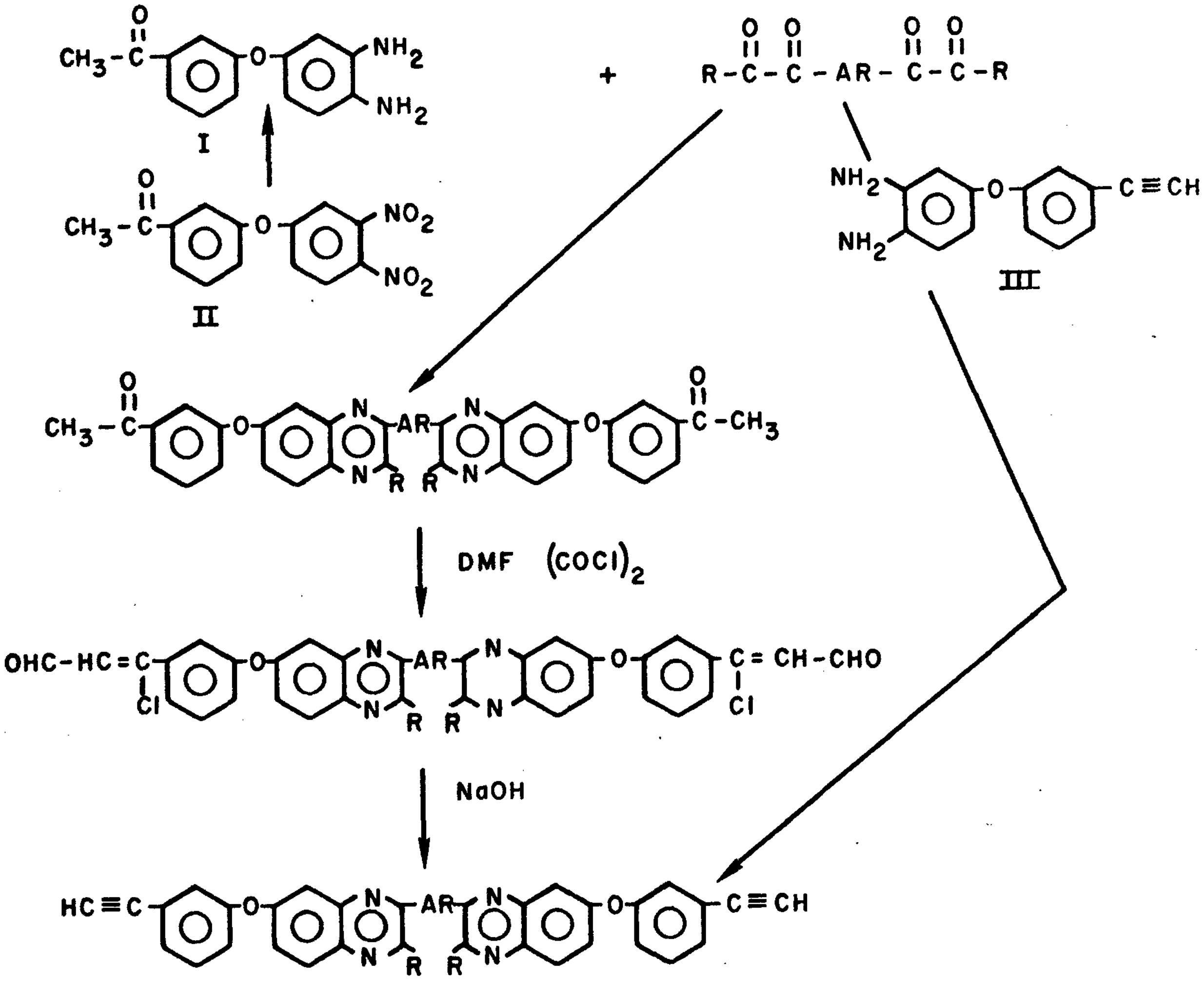


Plasticizer	Ar	R	Tg. °C	T_{pi} (1) °C	Tp max(2) °C	Tg(3) °C
IV			100	220	250	280
V			140	225	263	337
VI			95	180	263	278
VII			205	205	255	348

(1) Tpi = Temperature of polymerization (initial) as determined by DSC (ΔT = 20°C/min).

(2) Tp max = Temperature of polymerization (maximum) as determined by DSC (ΔT = 20°C/min).

(3) Tg = Glass transition temperature after heating at 280°C for 12 hrs.



The 3-(3,4-diaminophenoxy)acetophenone was prepared and used in situ by catalytic reduction of 3-(3,4-dinitrophenoxy)acetophenone (II) with platinum oxide in absolute ethanol. Conversion of the bis-acetyl intermediates to acetylenes was carried out by formation of chlorocinnamaldehyde groups with oxalyl chloride in dimethylformamide (DMF) and their subsequent hydrolysis using aqueous sodium hydroxide. An alternate route to the monomers was provided by the direct condensation of aromatic bis(-1,2-dicarbonyl) compounds with 4-(3-ethynylphenoxy)-o-phenylene-diamine (III) in m-cresol. Compound III is the end-capping agent used in the synthesis of ATQ oligomers (Reference 7).

Solid phase homopolymerization of the monomers were carried out in the differential scanning calorimeter (DSC) at a fixed heating rate of 20°C/min. DSC scans provided the glass transition temperatures of the monomers (Table 1) and the temperatures at which the polymerizations were initiated and reached a maximum. Samples of each monomer were also heated under nitrogen at 280°C for 12 hours to surmise what Tg could be expected after a complete cure. Two of the four monomers prepared had Tgs in the 100°C range and could be used to demonstrate the feasibility of the process. It was felt that monomer (IV), containing pendant phenyl groups would be more compatible with the PPQ thermoplastics A & B; therefore, it was selected as the plasticizer used in this study.

Samples of plasticizer (IV) were mixed in various percentages with different molecular weight PPQ thermoplastics. To assure homogeniety in mixing, the plasticizer and thermoplastic were dissolved in chloroform and either coprecipitated into methanol or cast into film by removal of the chloroform.

Film samples of the mixtures were heated at different temperatures and the deactivation of the plasticizer was followed by the disappearance of the acetylenic hydrogen absorption 3.2μ (Figure 5) in the infrared spectra. After an eight-hour cure at 280°C no acetylenic hydrogen absorption could be detected (Figure 6). The light yellow films containing the plasticizer were transparent (without haze) both before and after heat treatment, which was a good indication of compatibility of the system.

The films (after the heat treatment) were no longer soluble in the solvent from which they were cast. The deactivation reaction of the plasticizer presumably resulted in both reaction with itself and also the host thermoplastic forming a small percentage of crosslinks in the system. The insolubility of the films could also be explained by the fact that the high molecular weight material is entwined in an imbedded network structure generated from the plasticizer. Further work will be required to clarify the actual mechanism by which insolubility results.

Further proof of compatibility is provided by the DSC data (Table 2). The data indicate only one Tg for the mixture plasticizer/thermoplastic (A), incompatible components would display their inherent Tg's, while a partially compatible mixture would show a Tg of the mixture along with more or less strong signals for the original Tg's. It should be stated, however, that the extent of compatibility can only be ascertained on the basis of the sensitivity of the method, in this case DSC.

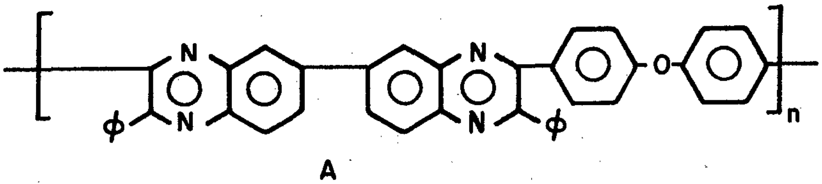
Polymerization temperatures (initial as well as maximum) increase with increasing "dilution" of the reactive plasticizer with the polymer. The Tg's of the cured mixtures are about 20°C higher than that of the polymer, and about 26°C higher than the Tg of the cured plasticizer. This may be the result of entanglement of the cured plasticizer network with the polymer chains, but it may also suggest that some crosslinking between the plasticizer and the polymer occurs.

Slightly lower Tg's and polymerization temperatures were observed for the lower molecular weight polymer, but the Tg's of the cured mixtures are practically the same as those of the mixtures with the high molecular weight polymer.

Figure 7 demonstrates the effect of the plasticizer not only on the softening temperature or Tg, but also on the degree of flow or viscosity indicated by the depth of penetration. With increasing plasticizer content, the uncured mixtures show decreasing softening temperatures and increasing flow. The cured mixtures not only have a higher Tg, but also less flow than the polymer itself.

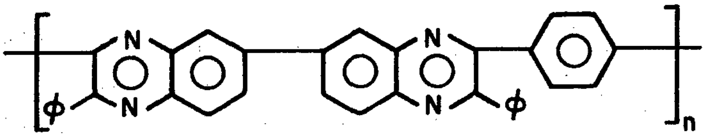
No glass transition temperatures have been found for the mixtures of plasticizer with the polymer (B) in Table 2. As a result of the high Tg of the polymer, Tg's of compatible mixtures of this polymer with plasticizer are expected to fall within the polymerization temperature range of the plasticizer and cannot be detected by DSC or TMA. Consolidation of prepregs would not be possible with such a system without premature curing occurring. Excessive amounts of plasticizer would be needed to lower the Tg of the mixture below the onset of polymerization.

TABLE 2
PLASTICIZATION OF PPQ THERMOPLASTICS



A

(a) N_{inh}	% Plasticizer	% PPQ	Tg Mixture	(b) Tpi	(c) Tpm	(d) Tg Cured
2.19	0	100	286°			
	100	0	100°	220°	250°	280°
	20	80	243°	253°	310°	304°
	30	70	226°	235°	300°	307°
0.91	0	100	285°			
	20	80	234°	245°	294°	306°
	30	70	213°	225°	286°	308°



B

2.7	0	100°	349°			
	20	80	-	200°	280°	357°
	30	70	-	205°	266°	354°

(a) Inherent viscosity determined in m-cresol (0.5% at 25°C)

(b) Tpi = Temperature of polymerization (initial) as determined by DSC, 20°C/min.

(c) Tpm = Temperature of polymerization (maximum) as determined by DSC 20°C/min.

(d) Tg after heating at 280°C, 8 hours.

SECTION III

EXPERIMENTAL

1. GLASS TRANSITIONS

Glass transition and polymerization temperatures have been determined by differential scanning calorimetry (DSC). Samples were subjected to a heating rate of $\Delta T = 20°C/min$ in nitrogen in the Dupont 990 Differential Scanning Calorimeter. The extrapolated onset of the baseline shift was taken as Tg. Onset and peak of the polymerization exotherm were considered as the initial (Tpi) and the maximum (Tpm) temperature of polymerization, respectively.

The cured samples gave frequently unsatisfactory DSC signals. Thermomechanical Analysis (TMA) was used to determine the Tg of the cured samples. These were subjected to programmed heating at $\Delta T = 20°C/min$ in air using the Dupont Thermomechanical Analyzer, with the penetration probe and 5g load. The highest rate of penetration (peak of the derivative curve) was taken as Tg.

2. MONOMERS

a. p,p'-Bis[3-phenyl-6-(3-ethynylphenoxy)-quinoxaline-2-yl]-diphenylether (IV)

(1) p,p'-bis[3-phenyl-6-(3-acetylphenoxy)-quinoxaline-2-yl]diphenylether.

To a hydrogenation bottle was added 10.0 g (28.6 mmole) of 3-(3,4-dinitrophenoxy)acetophenone and 250 ml of absolute ethanol. The suspension was purged with nitrogen, and then 150 mg of platinum oxide catalyst was carefully added. The flask was shaken under a hydrogen pressure of 55 psi until no further pressure drop was noticeable (four hours). TLC at that point (SiO_2,eluted with ethylacetate) showed one major spot of reduced product (3-[3,4-diaminophenoxy]acetophenone) and only a small amount of impurity. The solution was filtered under nitrogen pressure, and the filtrate purged with nitrogen for ten minutes. Then, 5.2 g (12 mmole) of p,p'-bis(phenyl-glyoxaloyl)diphenylether was added along with 5 ml of acetic acid, and the mixture refluxed under nitrogen for one hour. At that point the solvent was evaporated in vacuo and the residue refluxed with

25 ml of m-cresol to complete the reaction. The m-cresol was distilled off in vacuo and the residue dissolved in a minimum volume of methylene chloride. This solution was poured into 50 ml of refluxing ethanol and the methylene chloride boiled off. The precipitated product was filtered and air-dried. TLC (S_iO_2-elution with CH_2Cl_2) showed a highly fluorescent first spot of high Rf which was subsequently identified as the product. The solid product was purified by repeated recrystallization from methanol/CH_2Cl_2 mixtures in which the methylene chloride was boiled away. High purity material was obtained by chromatography on a dry column of silica gel (quartz column). Elution of the column with methylene chloride afforded a first band (fluorescent) containing the product. Evaporation of solvent in vacuo yielded p,p'-bias[2-phenyl-6-(3-acetylphenoxy) quinoxaline-2-yl]-diphenylether as an amorphous pale yellow solid, m.p. 100°C (foaming).

Calc'd for $C_{56}H_{38}N_4O_5$:	C, 79.42; H, 4.52; N, 6.62
Found:	C, 79.08; H, 4.33; N, 6.51

(2) p,p'-bis(3-phenyl-6-(3-ethynylphenoxy)-quinoxaline-2-yl]-diphenylether

A 250 ml round bottomed one-necked flask equipped with magnetic stirrer and nitrogen inlet adapter was thoroughly flamed and purged with nitrogen. To this was added 25 ml of anhydrous DMF. The flask was cooled with stirring under nitrogen to -78°C, and then 2.5 g (20 mmole) of freshly distilled oxalyl chloride was added dropwise to the flask to minimize the violent reaction. A white precipitate of Vilsmeyer complex formed in the flask. After the addition the reaction mixture was stirred at 0°C for 15 minutes at which time 5.0 g (6.9 mmole) of p,p'-bis[3-phenyl-6-(acetylphenoxy)-quinoxaline-2-yl]-diphenyl-ether was added to the flask. The flask was allowed to warm to room temperature, and was then stirred at 50°C for one-half hour. The contents of the flask were poured into 500 ml of cold, saturated sodium bicarbonate solution, and the crude product which precipitated was filtered, washed with water, and dried. The material thus obtained could be used directly for the next step, or could be purified by chromatography on a column of silica gel (elution with methylene chloride).

To a refluxing solution of sodium hydroxide (5.0 g) in 40 ml of water was added a solution of p,p'-bis[3-phenyl-6-(3-chlorocinnaldophenoxy)-quinoxaline-2-yl]-diphenylether (4.0 g) dissolved in 10 ml of dioxane. The mixture was refluxed for one-half hour, at which time TLC showed the reaction to be virtually complete. The reaction mixture was poured into one liter of water and the solution acidified with 50% sulfuric acid. The cooled solution was extracted with several portions of methylene chloride, and the combined extracts evaporated to near dryness in vacuo. The residue was chromatographed on a 1" x 12" dry column of silica gel (quartz column) (eluted with CH_2Cl_2/hexane). Band 1 (highly fluorescent in UV) contained the desired product, m.p. 98-99°C. I.R. (Figure 1).

Calc'd for $C_{56}H_{34}N_4O_3$:	C, 82.95; H, 4.23; N, 6.91
Found:	C, 82.53; H, 4.20; N, 6.67

b. 4-(3-Ethynylphenoxy)-o-phenylenediamine (III)

The precursor (III) was prepared (Reference 7) by the reaction of m-hydroxyace-tophenone with 3,4-dinitro-fluorobenzene to give 3'-acetylphenyl-3,4-dinitrophenyl ether. The acetyl group was then converted to a chlorocinnamaldehyde group followed by hydrolysis to the ethynyl and subsequent reduction of the nitro groups to amines.

c. p,p'-Bis[3-phenyl-6-(3-ethynylphenoxy)quinoxaline-2-yl]diphenylsulfide

To a solution containing 1.25 g (2.77 mmoles) of 4,4'-(phenylglyoxaloyl)diphenylsulfide and 1 ml of glacial acetic acid dissolved in 25 ml of m-cresol was slowly added, under a nitrogen atmosphere, a solution containing 1.24 g (5.55 mmoles) of 4-(3-ethynylphenoxy)-o-phenylenediamine dissolved in 25 ml of methylene chloride. After completion of the addition, the reaction mixture was heated at reflux for one hour, at which time the methylene chloride was distilled out of the reaction mixture. The mixture was further heated to 150°C and maintained at that temperature for one hour. The cooled reaction mixture was then placed on a rotary evaporator and the cresol was removed under reduced pressure.

The residual solid was recrystallized from dioxane/water to give 2.0 g (87.3%) of product, m.p. 140-141°C, I.R. (Figure 2).

Analysis Calc'd for $C_{56}H_{34}N_4O_2S$: C, 81.33; H, 4.14; N, 6.77

Found: C, 81.53; H, 3.89; N, 6.93

d. 1,3-Bis[3-(p'-phenoxyphenyl)-6-(3-ethynylphenoxy)-quinoxaline-2-yl]benzene(VI)

To a solution containing 1.3 g (2.71 mmoles) of meta-bis(p'-phenoxyphenylglyoxalyl)benzene dissolved in 25 ml of dioxane and 0.5 ml of glacial acetic acid was added, under a nitrogen atmosphere, a solution containing 1.21 g (5.43 mmoles) of 4-(3-ethynylphenoxy)-o-phenylenediamine, dissolved in 25 ml of methylene chloride. The reaction mixture was heated to reflux to remove the methylene chloride then heated to 100°C and maintained at that temperature for one hour. The cooled reaction mixture was precipitated into water and the resulting pale yellow solid was isolated by filtration and dried under reduced pressure. The product was recrystallized from dioxane/water to give 2.1 g (87% yield), I.R. (Figure 3).

Analysis: Calc'd for $C_{62}H_{38}N_4O_4$: C, 82.86; H, 4.24; N, 6.20

Found: C, 82.13; H, 4.01; N, 5.91

e. 1,4-Bis[3-phenyl-6-(3-ethynylphenoxy)quinoxaline)-2-yl]benzene (VII)

To a solution containing 1.3 g (3.79 mmoles) of para-bis(phenylglyoxalyl)benzene and 0.5 ml of glacial acetic acid was added, under a nitrogen atmosphere, 1.7 g (7.59 mmoles) of 4-(3-ethynylphenoxy)-o-phenylenediamine dissolved in 20 ml of methylene chloride. The reaction mixture was heated to reflux to remove the methylene chloride, then heated to 150°C and maintained at that temperature for one hour. The cooled reaction mixture was precipitated into methanol and the resulting white solid was isolated by filtration and dried under reduced pressure. The solid product was purified by chromatography on a dry column of silica gel (quartz column). Elution of the column with methylene chloride afforded a first band (fluorescent) containing the product. Evaporation of solvent in vacuo yielded 2.1 g (77%) of the product m.p. 204-205°C, I.R. (Figure 4).

Analysis: Calc'd for $C_{50}H_{30}N_4O_2$: C, 83.54; H, 4.22; N, 7.79

Found: C, 83.21; H, 4.23; N, 7.54

3. POLYMERS

The polyphenylquinoxaline thermoplastics, poly[2,2'-diphenyl[6,6'-diquinoxaline]3,3'-diyl)-p-phenylene] A, and poly[2,2'-diphenyl [6,6'-diquinoxaline]3,3'-diyl)-p-phenylene] B were obtained from the Research and Development Division of Whittaker Corporation.

SECTION IV

CONCLUSIONS

This work was performed to demonstrate the feasibility of using reactive plasticizers in the processing of high temperature thermoplastics. The reactive plasticizer lowers the effective softening point of the thermoplastic during processing and then becomes dormant by reacting with itself or the host thermoplastic.

A series of bis(ethynylquinoxaline) monomers was prepared and used as reactive plasticizers for the polyphenylquinoxaline class of high temperature thermoplastic resins. It has been shown that tailoring the molecular structure of the plasticizer to resemble the structure of the thermoplastic results in a completely compatible system. Further, the homopolymerization reaction of bisethynyl compounds does provide an addition process for the deactivation of the plasticizers. It was also observed that after deactivation of the plasticizer, the mixtures were insoluble in conventional solvents used for the thermoplastic. This phenomenon is not clearly understood but should provide improvement in the creep and craze resistance of the fabricated thermoplastic resin. The results are positive and encouraging, although it is recognized that future work will be required to define more clearly the possible potential of such a process for Air Force use.

Future research in this area should be directed toward the following goals:

1. To synthesize new reactive plasticizers which will be compatible with commercially available thermoplastic resins, and exhibit low Tgs (0-20°C) for high plasticizer efficiency.

2. To investigate the influence of thermoplastic molecular weight and plasticizer on the initial Tg and bulk viscosity of the uncured mixture as well as the mechanical properties of the thermoplastic after the plasticizer has been cured.

3. To demonstrate the process with the actual fabrication of fiber reinforced thermoplastic composites.

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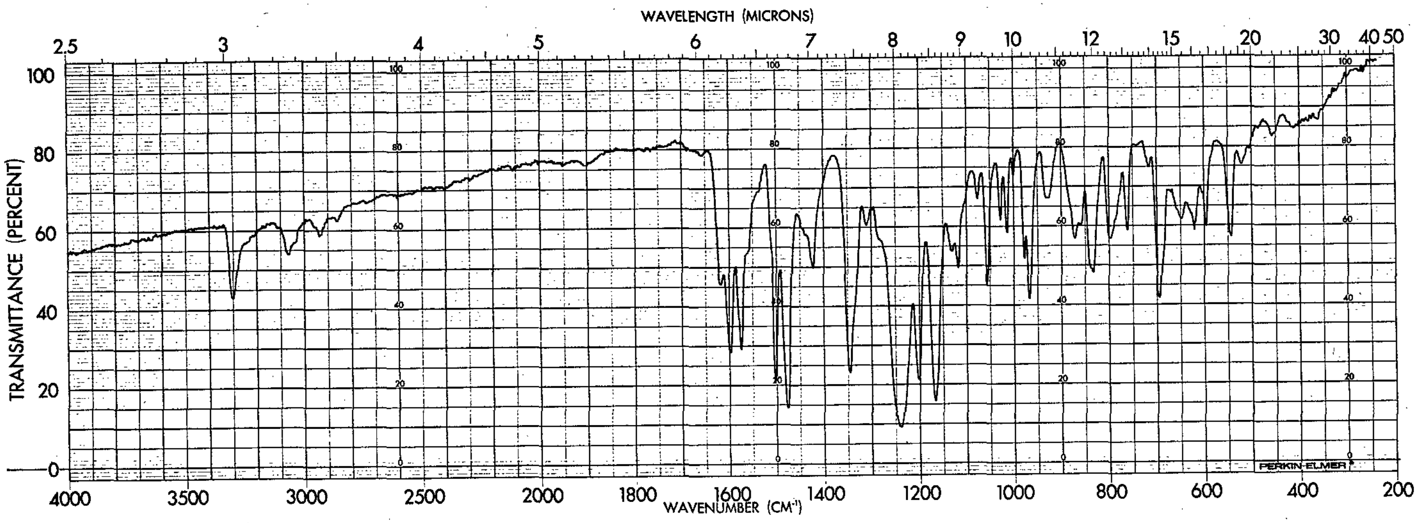

Figure 1. Infrared Spectrum of 4,4'-Bis[3-Phenyl-6-(3-Ethynylphenoxy)-Quinoxaline-2-yl]Diphenylether (Kbr)

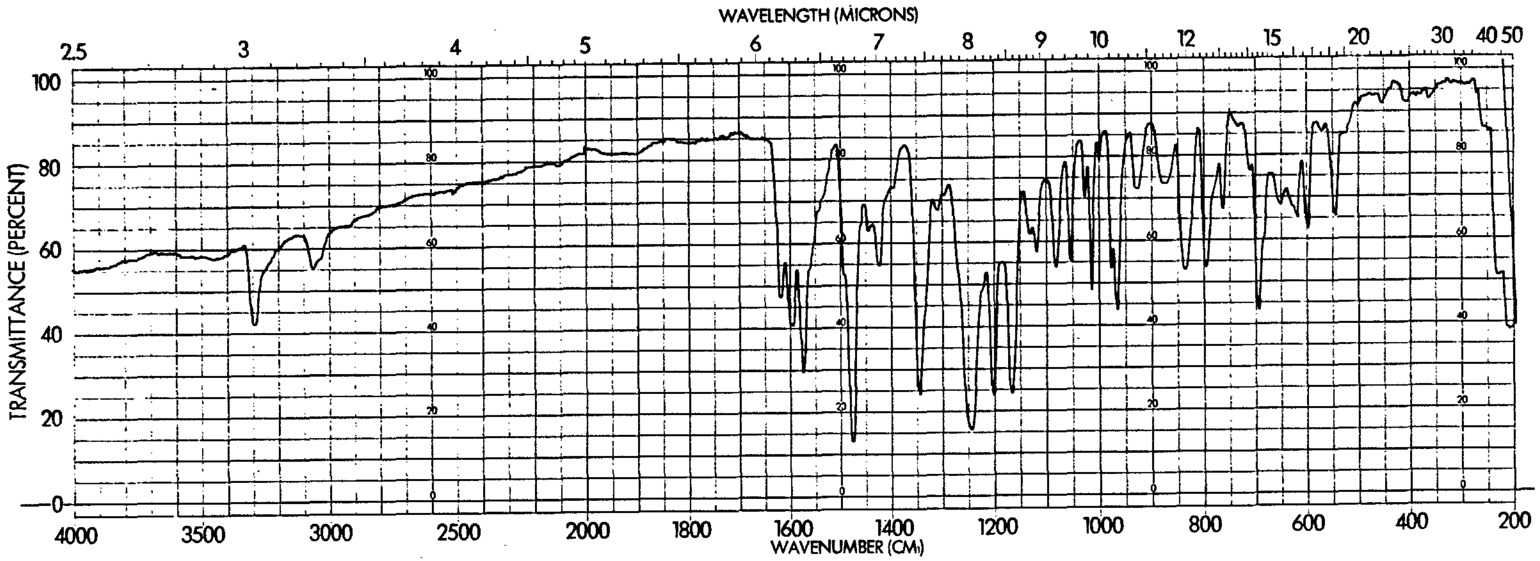

Figure 2. Infrared Spectrum of 4,4'-Bis[3-Phenyl-6-3-Ethynylphenoxy) Quinoxaline-2-yl]Diphenylsulfide (Kbr)

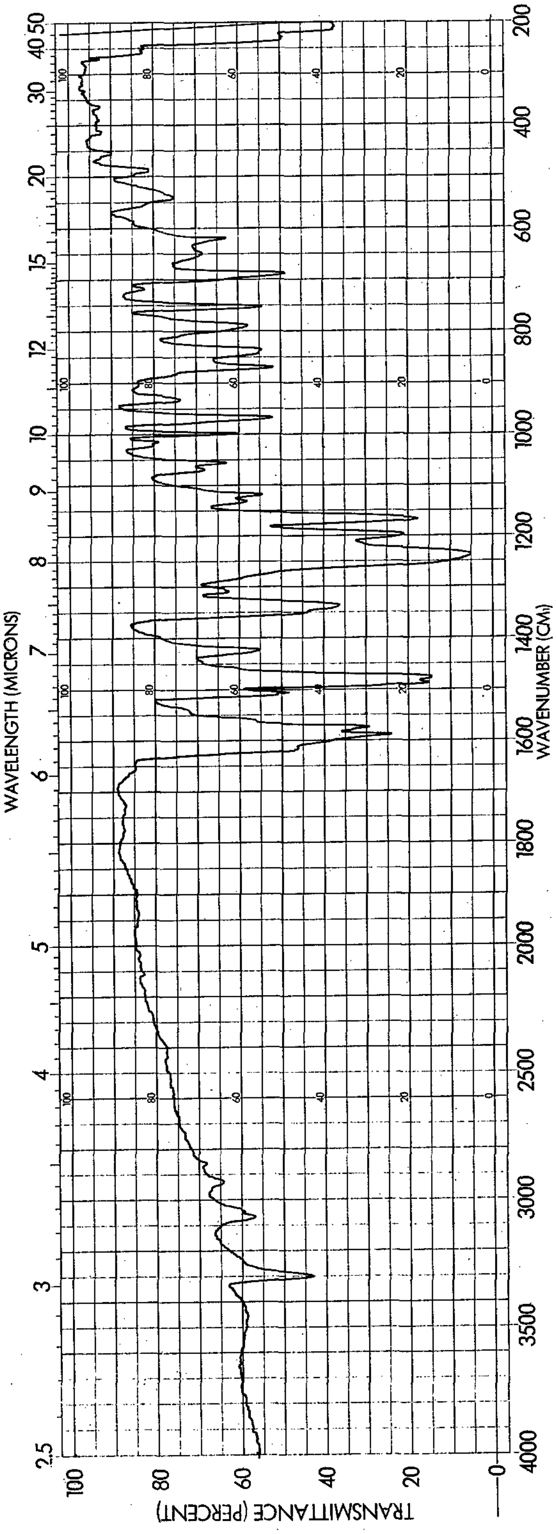

Figure 3. Infrared Spectrum of 1,3-Bis[3-(p'-Phenoxyphenyl)-6-(3-Ethynylphenoxy) Quinoxaline-2-yl]Benzene (Kbr)

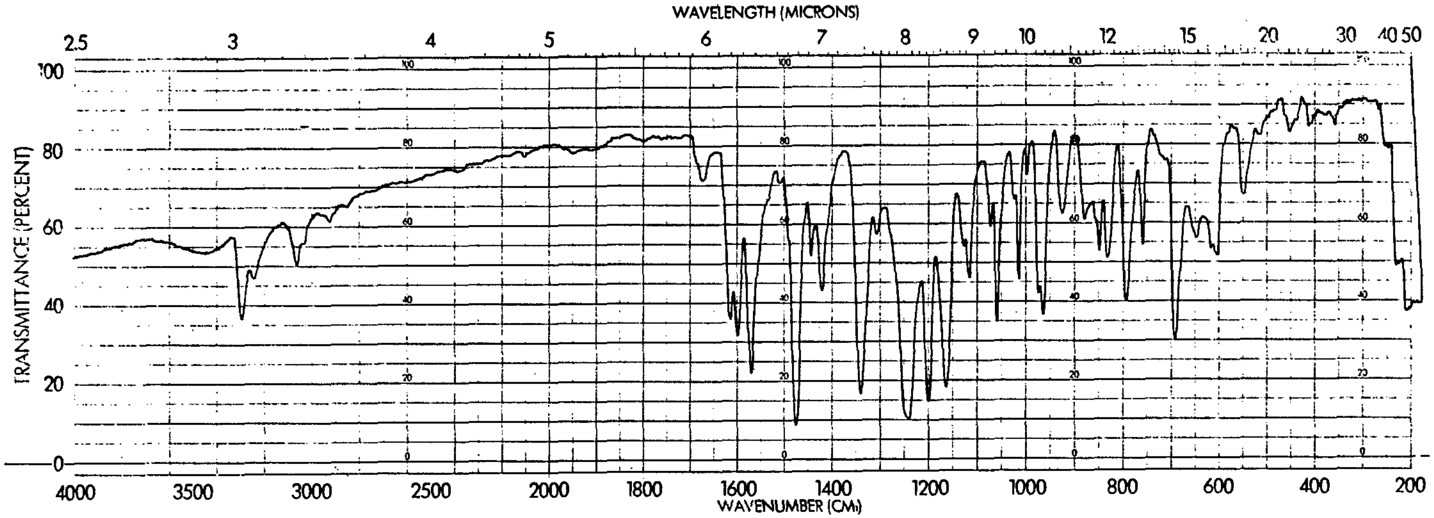

Figure 4. Infrared Spectrum of 1,4-Bis[3-Phenyl-6-(3-Ethynlphenoxy) Quinoxaline)-2-yl]Benzene (Kbr)

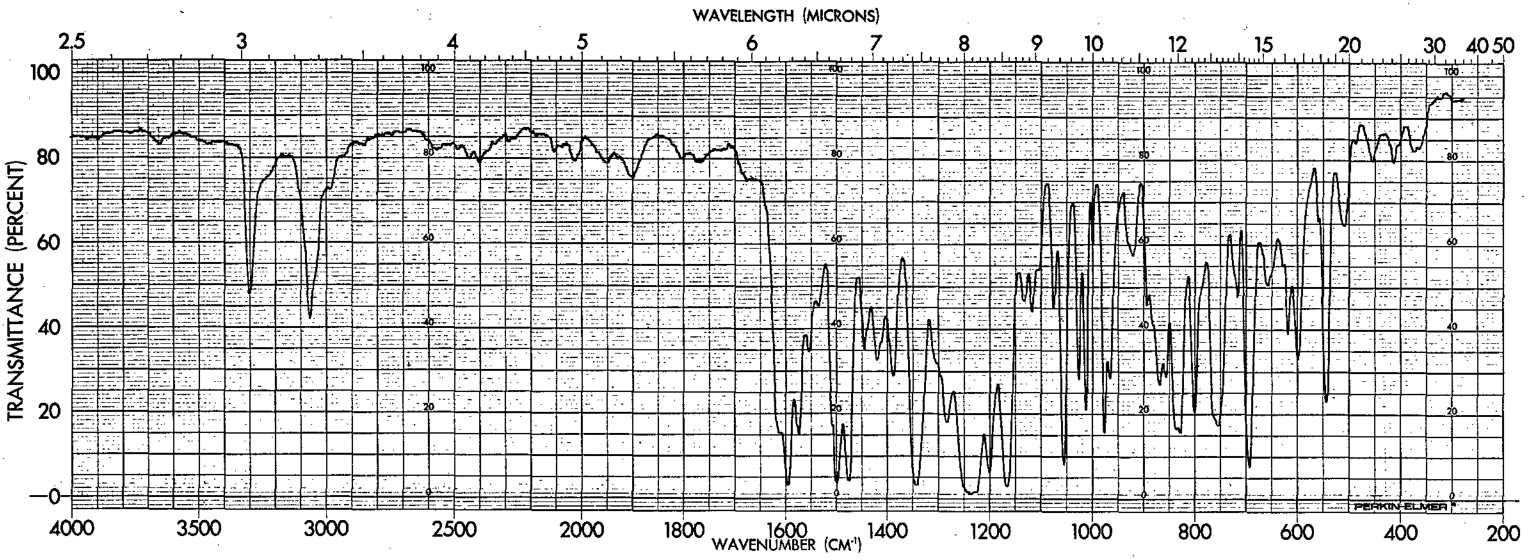

Figure 5. Infrared Spectrum of Poly[2,2'-Diphenyl[6,6'-Diquinoxaline]-3,3'-Diyl)-p-Phenyleneoxy-p-Phenylene] (Containing 30%) Plasticizer (Film)

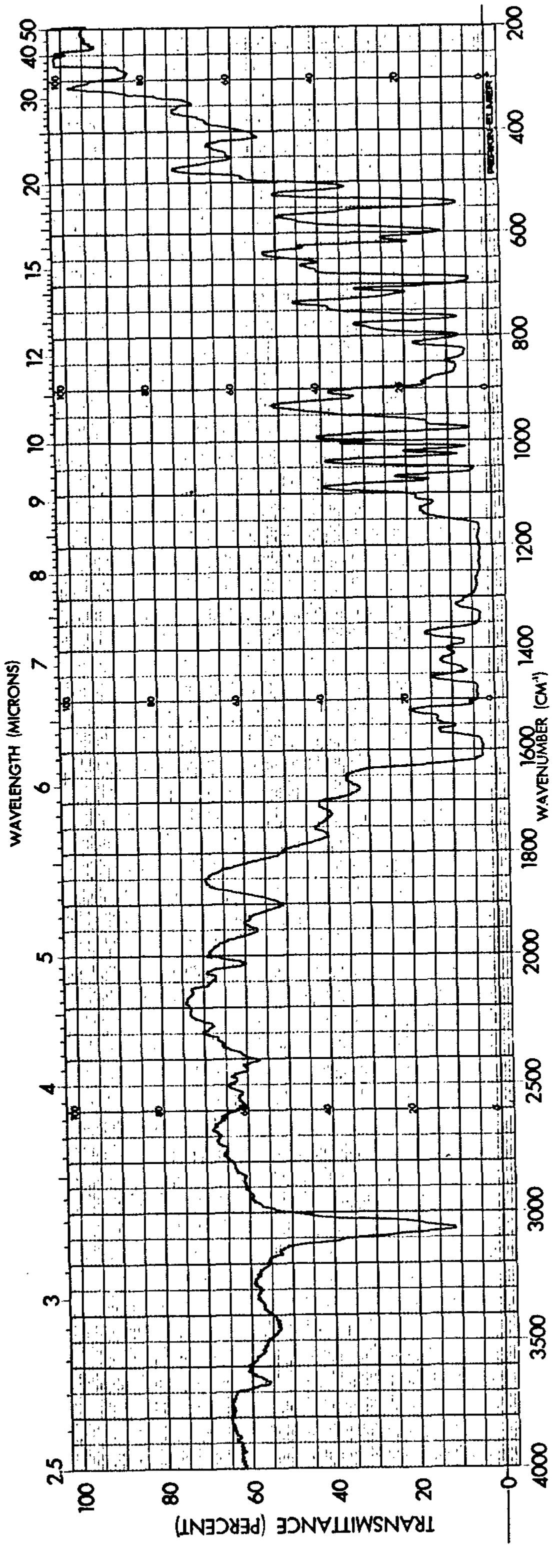

Figure 6. Infrared Spectrum of Poly[2,2'-Dipheny(6,6'-Diquinoxaline]-3,3'-Diyl)-p-Phenyleneoxy-p-Phenylene] (Containing 30%) Plasticizer; Heated at 280°C for 12 hours

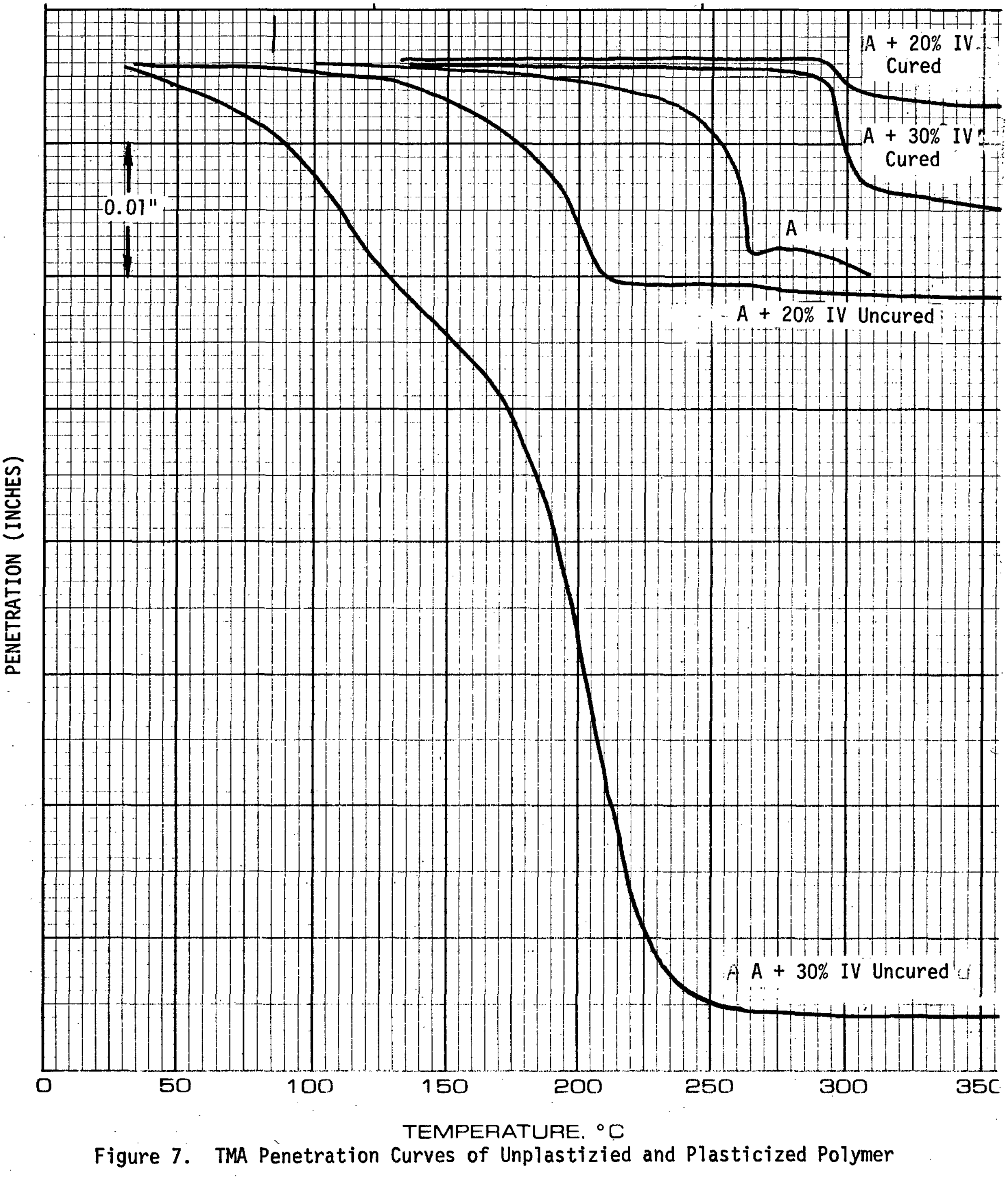

Figure 7. TMA Penetration Curves of Unplastizied and Plasticized Polymer
a. Uncured and Cured .

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