RIA-76-U664

POLYPHENYLQUINOXALINE/POLY-p-TOLYLQUINOXALINE COPOLYMERS: THE SEARCH FOR A CROSS-LINKABLE PPQ

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September 1976

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: AMMRC TR 76-33

2. GOVT ACCESSION NO.:

3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): POLYPHENYLQUINOXALINE/POLY-p-TOLYLQUINOXALINE COPOLYMERS: THE SEARCH FOR A CROSS-LINKABLE PPQ

5. TYPE OF REPORT & PERIOD COVERED: Final Report

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): Stanley E. Wentworth

8. CONTRACT OR GRANT NUMBER(s):

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Army Materials and Mechanics Research Center
Watertown, Massachusetts 02172
DRXMR-RA

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
D/A Project: 1T162105AH84
AMCMS Code: 612105.11.H8400
Agency Accession: DA OF4696

11. CONTROLLING OFFICE NAME AND ADDRESS:
U. S. Army Materiel Development and Readiness Command
Alexandria, Virginia 22333

12. REPORT DATE: September 1976

13. NUMBER OF PAGES: 6

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report):

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

18. SUPPLEMENTARY NOTES:

19. KEY WORDS (Continue on reverse side if necessary and identify by block number):

High-temperature polymers
Polyquinoxalines
Cross-linking
Torsional braid analysis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

(SEE REVERSE SIDE)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

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Block No. 20

ABSTRACT

As part of a continuing effort to reduce or eliminate the thermoplasticity long associated with polyphenylquinoxalines, a series of phenylquinoxaline/p-tolylquinoxaline copolymers has been prepared and their thermal stability and cross-linkability evaluated. Previous studies have indicated poly-p-tolylquinoxaline (PTQ) to be significantly more cross-linkable but also markedly less thermo-oxidatively stable than polyphenylquinoxaline (PPQ). Thus, an optimum copolymer composition combining the cross-linkability of PTQ and the stability of PPQ was sought. In fact, no such composition exists for this system. Whereas a small percentage of PTQ leads to substantial loss in stability, it has virtually no effect on cross-linkability. For example, the half-life at 400 C in air for 10% PPQ has been reduced by 55% relative to PPQ while its cross-linkability is almost unchanged. Apparently, the cross-linking reaction is inefficient such that only high concentrations of the cross-linkable species leads to a useful enhancement of the thermal cross-linkability. Conversely, the thermal oxidation reaction appears to be quite efficient. It is concluded that this copolymer approach can be successful in eliminating thermoplasticity if a system can be found in which the relative efficiency of the competing reactions is reversed.

INTRODUCTION

In previous reports,[1,2] we have described the synthesis and thermal analysis of poly-p-tolylquinoxaline (PTQ). These studies demonstrate that PTQ is significantly more thermally cross-linkable than is polyphenylquinoxaline (PPQ) and thus offers a potential solution to the problem of high temperature thermoplasticity long associated with PPQ's.[3] However, it was also found that this enhanced cross-linkability was attained only with considerable loss in thermo-oxidative stability.[1] In an effort to incorporate the cross-linkability of PTQ and the thermo-oxidative stability of PPQ into one resin, a series of PPQ/PTQ copolymers was prepared and evaluated by means of thermal analysis. This report details these studies.

EXPERIMENTAL

Materials: 1,4-bis(Phenylglyoxaloyl)benzene (PGB) was purchased from Whittaker Corporation, San Diego, California, and recrystallized once from ethanol. 3,3'-Diaminobenzidine (DAB) was purchased from Whittaker Corporation and recrystallized once from water. 1,4-bis(p-Tolylglyoxaloyl)benzene (TGB) was prepared as described previously.[1] m-Cresol was vacuum distilled.

Polymer Synthesis: The following procedure is illustrative of that used for all polymers or copolymers prepared in this study. Only the quantities of bis-α-diketones were changed as per Table 1 to yield the desired copolymers. A solution of 0.2143 g (0.001 mole) of DAB in 10.0 ml m-cresol was poured into a 50 ml 1-neck flask equipped with a magnetic stirrer. To this stirred solution was added a solution of 0.3252 g (0.0008 mole) of PGB and 0.0185 g (0.0002 mole) of TGB in 10.0 ml m-cresol. The resulting reaction mixture was capped with an air condenser and warmed to 100 C over approximately 1 hour. This temperature was maintained for 23 hours. After cooling to ambient temperature, the reaction mixture was poured with stirring into 150 ml of methanol and stirred for 2 hours. The resulting precipitate was removed by filtration through a fine fritted glass funnel. After washing with several portions of hot methanol, the precipitate was air dried overnight and dried in vacuo at 85 C for 6 hours to yield 0.4663 g (92.6%) of 5% PTQ.

Characterization and Thermal Analysis: Viscometry was carried out in a Cannon-Ubbelohde dilution viscometer using m-cresol at 30 C as the solvent. Thermogravimetric analyses were performed with a DuPont Model 951 Thermogravimetric Analyzer using a heating rate of 10 C/minute in an atmosphere of static air. Isothermal aging studies were conducted with this equipment in a nitrogen or static air environment as appropriate.

Table 1. REACTANTS USED IN POLYMER SYNTHESES

Experiment	Polymer (% PTQ)	DAB (g)	PGB (g)	TGB (g)	m-Cresol (ml)
1001-57	0	0.2143	0.3424	-	24
-58	5	↓	.3252	0.0185	↓
-59	10		.3081	.0370	
-61	20		.2793	.0741	
-63	100		-	.3704	

1. WENTWORTH, S. E., and MULLIGAN, G. D. *Preparation and Preliminary Thermal Evaluation of Poly-p-tolylquinoxaline, A Crosslinkable Polyphenylquinoxaline.* Army Materials and Mechanics Research Center, AMMRC TR 74-12, May 1974.
2. AUGL, J. M., DUFFY, J. V., and WENTWORTH, S. E. *Isothermal Crosslinking Studies on Polyquinoxalines by Dynamic Mechanical Methods.* Journal of Polymer Science, Polymer Chemistry Edition, v. 12, 1974, p. 1023-1039.
3. SANTELLI, M. L. *Fabrication and Testing of Carbon Fiber/Phenylated Polyquinoxaline Resin Composites.* Naval Ordnance Laboratory, NOL TR 71-187, 18 November 1971.

Torsional braid analyses were performed with a Chemical Instruments Corporation Model 100-B1 Torsional Braid Analyzer. A controlled heating rate of 4.2 C/minute was provided by a Tetrahedron Associates Model ATC-200 Temperature Indicator Controller in conjunction with a Research Incorporated Model 5310 Data Trak Card Reader. All determinations were conducted in a nitrogen atmosphere with 8-inch multifilament quartz braids being used throughout.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The polymers synthesized for this study together with their intrinsic viscosities, decomposition temperatures, glass transition temperatures, and yields are given in Table 2. As can be seen, a high yield of high molecular weight polymer was obtained in all cases. The synthesis, as described in the experimental section, is straightforward with no complications other than a tendency of the finely divided polymer to clog the fritted glass funnel during isolation.

In all cases, the polymers were readily soluble in chloroform, thus facilitating the preparation of braids for torsional braid analysis and indicating the probability of facile processing into useful end-items. The glass transition temperature is apparently independent of polymer composition but seems to show a small dependence on molecular weight as indicated by the parallel between T_g and $[\eta]$. The polymer decomposition temperature decreases with increasing PTQ content as might be expected from the earlier report[1] that PTQ is less thermo-oxidatively stable than PPQ. Finally, it is presumed that the copolymers are random based on the method of synthesis, i.e., addition of a solution of both tetraketones to a solution of the tetraamine. The production of a nonrandom copolymer from such a procedure requires greatly different reactivities for the competing monomers. This is not expected to be the case in the present system.

Isothermal Aging

Since a major goal of the present study was to obtain a resin whose thermal stability was at least comparable to that of conventional PPQ, it was obviously necessary to determine the respective isothermal aging behavior of each of the polymers listed in Table 2. In view of our earlier observation[1] that 100% PTQ exhibited significantly enhanced isothermal aging performance when preconditioned at 400 C in an inert atmosphere (probably as a result of cross-linking), the following experiment was conducted on each of the polymers in the present study. Approximately 8 mg of the powdered polymer was placed in the balance pan of the thermogravimetric analyzer, the quartz furnace tube affixed and a slow flow of nitrogen established through the system. The sample was then inserted into the furnace which had equilibrated at 400 C. After 18 hours, the sample was removed from the furnace and allowed to come to ambient temperature. Virtually no

Table 2. VARIATION OF SELECTED POLYMER PROPERTIES WITH COMPOSITION

Experiment	Composition (% PTQ)	Yield (%)	Intrinsic Viscosity (dl/g)	PDT* (°C)	T_g† (°C)
1001-57	0	96.2	1.22	598	356
-58	5	92.6	1.02	605	355
-59	10	96.4	1.24	582	361
-61	20	98.8	1.53	569	364
-63	100	92.2	0.57	540	353

*In static air.
†Determined by torsional braid analysis.

weight loss was observed during this procedure. At this point, the nitrogen flow was interrupted, the furnace tube was removed and flushed with air and then replaced and the sample reinserted into the 400 C furnace. This point is taken as 0 hours in the isothermal aging in static air experiment. Figure 1 shows the results of this experiment for each of the polymers in Table 2. Each curve is the average of two runs. The half-lives reported in Table 3 are taken from Figure 1. They show very clearly the progressive loss of thermal oxidative stability with increasing PTQ content. At 20% PTQ, it has diminished by over 70%. Even the introduction of only 5% PTQ causes an almost 40% loss in thermo-oxidative stability. Thus, contrary to our initial postulate, it is obvious that any copolymer which contains significant PTQ character will have markedly reduced stability in air at elevated temperatures.

Thermal Cross-Linking

A PPQ possessing enhanced cross-linkability was the second major objective of this study. We have described a technique for the evaluation of thermal cross-linkability of PPQ's based on torsional braid analysis.[4] This method is based on the assumption that an increase in T_g is a valid indicator of increased cross-link density. The T_g of the unconditioned polymer (T_{g_0}) is compared to that of the polymer after conditioning for 2 hours under nitrogen at various temperatures (T_{g_T}). The results are reported as ΔT_g which is defined as $T_{g_T} - T_{g_0}$. It is emphasized that a fresh sample is used for each temperature and that a cumulative effect is not being observed. The results of this experiment are presented in Table 4 and graphically in Figure 2.

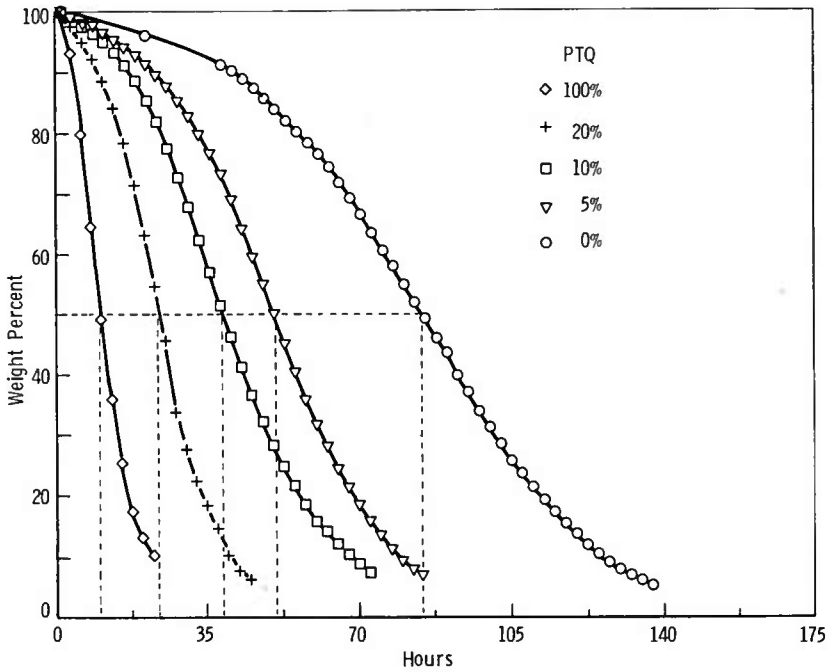

Figure 1. Weight loss with time at 400 C under static air.

Table 3. VARIATION OF HALF-LIFE AT 400 C IN STATIC AIR WITH COMPOSITION

Experiment	Composition (% PTQ)	Half-Life (Hr)
1001-57	0	84
-58	5	51
-59	10	38
-61	20	24
-63	100	10

As can be seen, the only material to exhibit a significant enhancement in cross-linkability is the 100% PTQ. In fact, almost to within experimental error, the curves for the three copolymers coincide with that of the 100% PPQ. This stands in marked contrast to the isothermal aging results where thermal stability varies systematically with PTQ content.

4. WENTWORTH, S. E., and MACAIONE, D. P. *Synthesis and Thermal Crosslinking of p,p'-Divinylbenzil End-Capped Phenylquinoxaline Oligomers.* Journal of Polymer Science, Polymer Chemistry Edition, v. 14, 1976, p. 1301-1307.

Table 4. EFFECT OF CONDITIONING TEMPERATURE ON T_g

Polymer		Conditioning Temperature (°C)											
		Ambient		250		300		350		400		450	
Experiment	% PTQ	T_g	ΔT_g	T_g	ΔT_g	T_g	ΔT_g	T_g	ΔT_g	T_g	ΔT_g	T_g	ΔT_g
1001-57	0	360	-	359	3	357	1	367	11	383	27	416	60
-58	5	355	-	352	-	354	-	365	10	382	27	427	72
-59	10	361	-	360	-	360	-	365	5	391	31	440	79
-61	20	364	-	362	-	363	-	369	5	390	26	440	76
-63	100	353	-	357	4	358	5	385	32	440	87	-	-

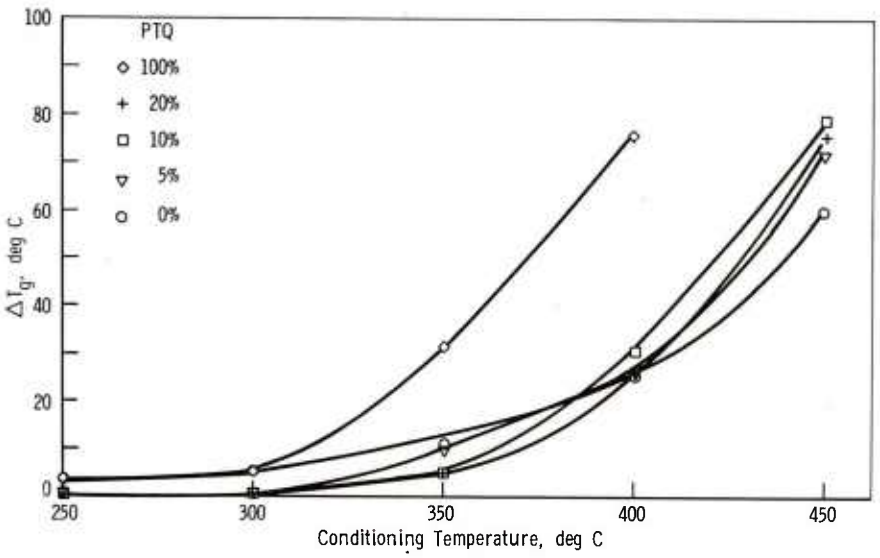

Figure 2. Variation of T_g with conditioning temperature, 2 hours under nitrogen.

CONCLUSIONS

It had been hoped to discover an optimum PPQ/PTQ copolymer composition in which enhancement of cross-linkability increased with increasing PTQ content at a greater rate than did decrease in thermo-oxidative stability. Unfortunately, just the opposite has been found to be the case. Apparently the cross-linking reaction is not very efficient such that only high concentrations of the cross-linkable species can lead to a significant elevation of T_g. Conversely, the thermal oxidation reaction appears to be quite efficient, very modest levels of PTQ character leading to serious loss in stability. Obviously then, it must be concluded that no optimum composition exists for this system. This does not invalidate the concept, however. To be successful, a system must be found in which the cross-linking reaction is more efficient than the thermal oxidation reaction. We are currently searching for such a system.

ACKNOWLEDGMENTS

The author gratefully acknowledges the many helpful discussions with Dr. G. Hagnauer and Mr. D. Macaione and the technical assistance of Miss S. Kalian and Mr. R. Cherill.

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AMCMS Code 612105.11.H8400

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