Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Amine-Cured Bisphenol-Linked Phthalonitrile Resins

Teddy M. Keller[a]; Thomas R. Price[a]
[a] Polymeric Materials Branch Chemistry Division, Naval Research Laboratory, Washington, D.C.

To cite this Article Keller, Teddy M. and Price, Thomas R.(1982) 'Amine-Cured Bisphenol-Linked Phthalonitrile Resins', Journal of Macromolecular Science, Part A, 18: 6, 931 — 937
To link to this Article: DOI: 10.1080/00222338208077208
URL: http://dx.doi.org/10.1080/00222338208077208

J. MACROMOL. SCI.–CHEM., A18(6), pp. 931-937 (1982)

Amine-Cured Bisphenol-Linked Phthalonitrile Resins

TEDDY M. KELLER* and THOMAS R. PRICE

Polymeric Materials Branch
Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375

ABSTRACT

Neat polymerization of bisphenol-linked phthalonitrile monomers, which contain no active hydrogen atoms, is extremely difficult and requires several days of continuous heating at 260-290°C before a viscosity increase becomes evident. In the presence of a nucleophilic compound such as an organic amine, the cure time and temperature can be greatly reduced. The amine-cured polymers are more thermally stable than their neat cured counterparts. Preliminary results indicate that the amine causes no significant changes in the mechanical properties of the cured polymer. The bisphenol-linked phthalonitrile resins are particularly appealing as matrices for composite formulations due to the projected low material cost, the greatly improved processability, and the nonreactivity of the prepolymer at ambient temperature.

INTRODUCTION

High temperature resins that are low melting in the prepolymer stage and do not produce gaseous products when cured have received

---

*To whom correspondence should be addressed.

increased attention as candidate matrices for fiber-reinforced composites. To be useful, the prepolymer should melt at a temperature not much higher than 200°C, flow easily, and adhere to the reinforcing fiber. Advanced design concepts have created new demands and pushed the temperature requirements into even higher regions. The need for more thermally stable materials in the aerospace industry is well known. To meet this challenge, our research efforts are aimed at providing new polymeric materials serviceable in the 200-300°C range.

During the last 30 years, many novel polymer systems have been reported which retain satisfactory mechanical properties at elevated temperatures. However, only a small fraction of these new materials has been successfully marketed due to shortcomings not often spelled out in technical papers which tend to emphasize accomplishments rather than unsolved problems. Workers with chemical backgrounds tend to view high temperature polymers as being able to withstand thermal and oxidative degradation over long periods at high temperatures in air, whereas engineers are more interested in the utility, cost effectiveness, and processability of polymeric materials. Failure to recognize cost/performance constraints has also spelled commercial doom for innumerable technically successful programs.

To achieve our objective of developing polymeric materials that exhibit high thermal and oxidative stabilities with insensitivity to high humidity, several bisphenol-linked phthalonitrile monomers 1, which are potentially low-cost materials, were prepared and polymerized. Neat polymerization through the cyano functional groups under the influence of heat affords thermosetting polymeric materials that are void-free. The time and temperature necessary for the polymerization were markedly reduced by the addition of various organic amines as coreactants. The enhancement by amines of the polymerization of bisphenol-linked phthalonitrile monomers 1 are discussed in this paper.

EXPERIMENTAL

Pure bisphenol A phthalonitrile monomer 1A, which was mainly utilized in our studies, was obtained by recrystallization from acetonitrile. The amines were used without further purification as acquired from the suppliers.

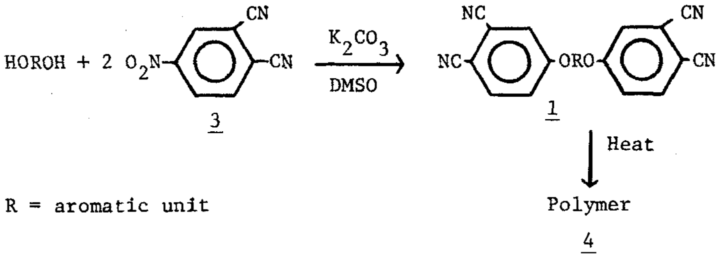
General Procedure for the Polymerization of Phthalonitrile Monomer 1 with an Organic Amine

The monomer 1 and amine (>1%) by weight) were melted, mixed, and heated in air at a temperature above the melting point of the mixture. After an initiation period (0-2 h) which is dependent on the concentration of reactants and on the reactivity of the amine, the color of the melt changed from clear to orange to dark green. At the dark green stage the viscosity of the sample increased rapidly, with gelation occurring shortly thereafter. After solidification, the temperature was increased to 280-310° C, and the sample was postcured at this temperature for a short time to enhance the toughness of the polymer.

RESULTS AND DISCUSSION

Highly aromatized phthalonitrile monomers 1 prepared from bisphenols are being emphasized since the corresponding polymers display, in general, high thermal and oxidative stability, low flammability, chemical resistance, and low water absorptivity [1]. The flexible ether linkage was selected as the connecting group due to the known thermal stability of diaryl ethers [2, 3] and to the general chemical resistance of the ether bond. The resins show excellent thermal stability when heated in air at 280° C for extended periods. Exposure to a high temperature flame has demonstrated that these resins are self-extinguishing. Polymers which contain no polar units on the linking structure show a low affinity for water (<1.5%). Consequently, these polymers show great potential as matrix materials for high performance composites.

The chemistry of bisphenol-linked phthalonitrile resin synthesis and polymerization has been reported previously [1]. Briefly, the monomers 1 are prepared from the reaction of the dialkaline salt of a bisphenol 2, e.g., bisphenol A, bisphenol S, hexafluoroacetone bisphenol A, 4,4'-dihydroxybiphenyl, and resorcinol, with 4-nitrophthalonitrile. These monomers, which do not contain active hydrogen atoms, are very difficult to polymerize even under extreme thermal conditions. Neat polymerization requires several days of continuous heating at 260-290° C before a viscosity increase is detected. The slow rate of polymerization could be attributable to the rigidity of the



linking structure which reduces the mobility of the reaction sites or more probably to the absence of initiating agents.

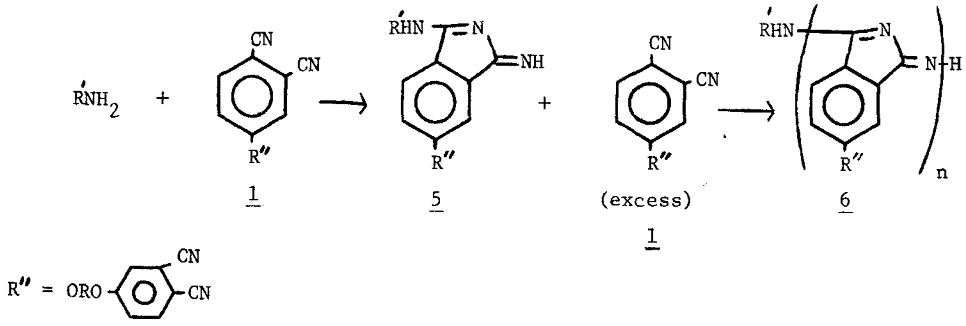
Primary consideration has been devoted to amine curing agents for the phthalonitrile components to reduce both the time and temperature for gelation. The amine and phthalonitrile 1 are blended together and then heated at elevated temperatures to affect the cure. To be suitable for this process, the curing agent should possess the following requirements: (a) It should generate a reactive intermediate that will react rapidly with excess phthalonitrile monomer. (b) The reaction should afford a thermally stable link. (c) The reaction should be initiated under convenient conditions where control of the reaction temperature is possible. (d) No volatiles can be generated. (e) The curing agent must not evolve from the sample during the curing process. (f) The curing agent must be compatible with the monomer so that it will be molecularly dispersed.

Several types of amines have been found to enhance the cure rate of 1. Aromatic diamine, e.g., m- and p-phenylenediamine, 4,4'-methylenedianiline, 4-aminophenyl ether, 4,4'-(p-phenylenedioxy) dianiline, and 4-aminophenyl sulfone were mainly used due to their commercial availability and to their thermal stability at the elevated temperature necessary for polymerization. Aliphatic amines are less desirable due to a sacrifice in the thermooxidative stability. Any amine (primary, secondary, or tertiary amine) will enhance the cure rate to a certain degree if it does not vaporize or decompose below the polymerization temperature.

The polymerization reaction is accomplished by mixing the amine and 1 at the melt stage and curing at elevated temperatures ($> 200°C$). After a short time which will be dependent on the reactivity of the amine, the melt starts to darken with a resulting viscosity increase. Quantities of 1-20% by weight of amine to 1 are generally preferred. However, for less reactive amines, 1:1 molar ratios of diamines to 1 have been used without any detrimental effects from void formation or escalating temperature changes. The preferred polymerization temperature is from 10°C above the melting point of 1 to 30°C below the decomposition temperature of the resin. Polymerization is usually performed in several steps over a series of temperatures.

Condensation of an amine with phthalonitrile 1 is expected to produce a complex structural mixture. The amine, when present in minute quantities, probably initially attacks the nitrile components of 1 to afford an N-substituted-3-iminoisoindoline unit 5, shown in a simplified mode involving only one of the phthalonitrile units of 1. Compound 5 then reacts with other nitrile substituents to form polymer 6. However, other cyano-additions involving macrocyclic and linear polymeric molecules may also be present, especially at higher concentrations of amine [4-6]. In essence, the overall physical properties should be dependent on the relative amount of amine to 1.

The rate of the amine-cured phthalonitrile reaction seemingly depends on the basicity of the primary amino groups. In particular,



R = aromatic unit

4,4'-(p-phenylenedioxy) dianiline and 4-aminophenyl ether reacted rapidly whereas the rate of reaction for 4,4'-methylene dianiline was somewhat slower. The rate of reaction of 1 with 4-aminophenyl sulfone was sufficiently slow that ample time would be available for component processing even at higher concentrations. In the case of 4,4'-methylene dianiline and m- and p-phenylenediamine, some void problems arose when present in amounts greater than 10 wt% and when the melting point of 1 or the initial cure temperature exceeded 230°C. This problem was attributed to the volatilization of the amine.

The thermal and oxidative stabilities of the amine-cured phthalonitrile resins were measured in nitrogen and in oxygen, respectively, using thermogravimetric analysis (TGA) equipment. A programmed constant heating rate of 10°/min was employed. Under these conditions it was difficult to determine precisely the temperature at which the polymers began to decompose. In order to assess the relative merits of these polymers, the temperature was determined at which a 10% weight loss occurred. The results for bisphenol A phthalonitrile 1A cured with various amines and postcured at a maximum temperature of 280°C are given in Table 1.

The thermal and oxidative stability of the amine-cured bisphenol A phthalonitrile resins were found to be dependent on both the reactivity and the quantity of amine present. For example, the polymers prepared from 4,4'-(p-phenylenedioxy) dianiline and 4,4'-methylene dianiline exhibited similarities in their thermal stabilities in an inert atmosphere whereas the former amine-cured polymer was less stable in air. The polymer formed from 4-aminophenyl ether appears to be more stable in air than in nitrogen. This phenomenon can be attributed to a higher molar ratio of amine to 1A which will probably afford a higher degree of polymerization and which would superficially appear to enhance the thermal stability of the polymer due to the initial absorption of oxygen preceding oxidative degradation. When a less

TABLE 1. Temperature at Which Polymers from Bisphenol A Phthalonitrile 1A and Diamines (R) Show a 10% Weight Loss

R	Weight percent of diamine	In air (°C)	In nitrogen (°C)
4-Aminophenyl sulfone	10	473	482
4-Aminophenyl sulfone	5	440	460
4,4'-(p-Phenylenedioxy) dianiline	3	455	485
4-Aminophenyl ether	3	490	478
4,-4'-Methylene dianiline	3	480	488
-	0	440	467

reactive amine such as 4-aminophenyl sulfone was used, higher concentrations of amine to monomer 1A were needed to obtain comparable thermal and oxidative results.

The amine-cured bisphenol A phthalonitrile resins exhibit a low affinity for water similar to the corresponding neat cured polymers [1]. For example, a polymeric sample containing 3% by weight of 4,4'-methylene dianiline showed a maximum water absorption of approximately 0.7% after 2 months immersion. A sample with 3% of 4-aminophenyl ether was more susceptible to water penetration (~ 1.5%) under the same conditions. Thus it appears that the degree of water absorptivity can be minimized by the proper selection of curing agent.

Polymerization can be performed under controlled conditions which is an attractive feature relative to epoxy resins. It is possible to terminate the polymerization reaction at the B-stage which is determined by an increase in viscosity. The B-staged prepolymer is a frangible solid which can be stored indefinitely without further reaction at ambient temperature. When needed, the prepolymer can either be remelted and heated until solidification occurs (C-stage) or can be pulverized and molded into any desired shape or form.

CONCLUSIONS

The amine-cured bisphenol A-linked phthalonitrile resin system provides a new matrix material with long-term operational capability in excess of 250°C with insensitivity to high humidity and with the ability to retain reinforcing fibers during or following exposure to a fire environment. The polymers are hard, amorphous materials with mechanical properties similar to Narmco 5208 and with a glass transition temperature greater than 300°C [7]. The ultimate cost of the polymers will be largely dependent on the cost of 4-nitrophthalonitrile because the other reagents used are relatively inexpensive. Possible applications for this material will be in areas, e.g., military, aircraft construction, and aerospace, where its special properties are required.

REFERENCES

[1] T. M. Keller and J. R. Griffith, "Resins for Aerospace," Am. Chem. Soc. Symp. Ser., 132, 25 (1980).
[2] F. E. Krosz and J. M. O'Reilly, J. Polym. Sci., Polym. Lett. Ed., 3, 561 (1965).
[3] C. L. Mahoney, E. R. Barnum, W. W. Kerlin, K. J. Sax, and W. S. Saari, J. Chem. Eng. Data, 5, 172 (1970).
[4] D. I. Packham, Br. Polym. J., 2, 280 (1970).
[5] D. I. Packham and F. A. Rackley, Polymer, 10, 559 (1969).
[6] J. A. Elvidge and R. P. Linstead, J. Chem. Soc., p. 5008 (1952).
[7] J. A. Hinkley and F. J. Campbell, Am. Chem. Soc. Polym. Prep., 22(2), 297 (1981).

Accepted by editor November 28, 1981
Received for publication December 12, 1981