# Network Structure in Bisphthalonitrile Polymers

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## Synopsis

Bisphthalonitrile monomers were cured neat, with nucleophilic and redox coreactants, or in combination with a monofunctional model compound. Dynamic mechanical measurements on the resulting polymers from $-150°$ C to $+300°$C turn up several differences attributable to differences in network structure. Rheovibron results were supplemented with solvent extraction, DSC, vapor pressure osmometry, and infrared spectroscopy to characterize the state of cure.

## INTRODUCTION

As organic resins find wider use in structural applications, greater demands are being placed on polymeric materials. Thermoplastics that can meet the requirement for rigidity at high temperatures tend to be extremely difficult to process, so it is natural to seek materials which have reasonable viscosities at moderate temperatures, but which set up into solids by a curing (usually crosslinking) reaction.

This study focuses on resins prepared by thermal polymerization of bisphthalonitriles, a class of materials which show promise as matrix resins for advanced composites.[1] Heating the crystalline monomer produces a green soluble "B-stage" polymer which is stable indefinitely on room temperature storage, but which can be further polymerized by extended heating. A variety of monomers has been synthesized,[2] leading to products with high thermal stability, low moisture pickup, and good mechanical properties.[3]
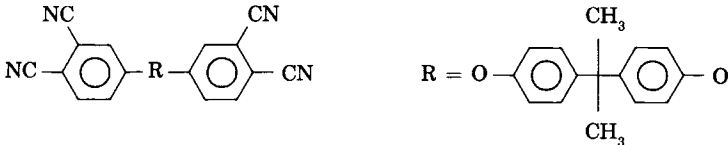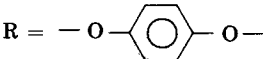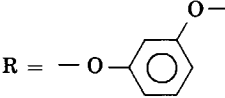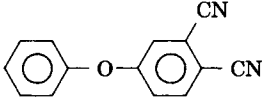
Dynamic mechanical and dielectric characterization of these materials is essential because the curing monomer mixture quickly becomes insoluble and because most of the interesting properties of these resins develop during the later stages of the reaction, when few other characterization techniques are applicable. In addition to this practical consideration, there is the interesting scientific question of what sorts of molecular motions occur in such a densely crosslinked system.

To help clarify the latter point, a series of bisphthalonitrile monomers was available, incorporating various aromatic structures between the functional groups. Table I lists the monomers used in this work.

## EXPERIMENTAL

Bisphthalonitriles were synthesized in this laboratory by Mr. T. R. Price. Polymerization was carried out in open aluminum molds (1.2 cm $\times$ 6 cm). In the experiments which used the monofunctional phthalonitrile, the aluminum foil mold was placed in a closed steel ointment can. This was necessary to prevent evaporative loss of the more volatile monophthalonitrile.

TABLE I
Monomer Structures

| Monomer designation | Structure |
| --- | --- |

I     NC—⟨○⟩—R—⟨○⟩—CN (with NC and CN substituents)     R = O—⟨○⟩—C(CH₃)₂—⟨○⟩—O

II     R = —O—⟨○⟩—O—

III     R = —O—⟨○⟩ (with O— substituent)

IV     ⟨○⟩—O—⟨○⟩—CN (with CN substituent)

Except as otherwise noted, the resins studied were cured in an air-circulating oven at 280°C for 6 days. Bulk samples were sectioned with a diamond saw to provide samples for the Rheovibron DDV II Viscoelastometer operated at 11 Hz. In some cases it was possible to cut a sample from a partially cured film formed between aluminum plates. The film was heated to the rubbery state, cut into strips while hot, and then returned to the oven to complete the cure.

Dielectric data came from a Tetrahedron dielectrometer.

DSC scans were performed at 20°C/min after a rapid quench from above the sample glass transition temperature.

Number-average molecular weight was measured in 1,2-dichloroethane at 40°C using a Wescan Model 232A Vapor Pressure osmometer.

Solvent extraction was done by placing small pieces of cured polymer in vials of chloroform which were shaken daily. After 1 week, the chloroform was poured off and replaced with fresh solvent. After another week, the extract was combined with the first and dried to yield the weight of sol.

For the infrared measurements of extent of cure, the monomer mixture was melted onto a salt plate, then cured in a closed can under conditions identical to those used for the mixtures in the sol/gel experiments. The plate was removed from the oven periodically and disappearance of the CN function was recorded on Perkin-Elmer Model 267 Spectrometer.[4]

## RESULTS

### Temperature of Cure and Catalysts

Figures 1(a) and 1(b) illustrate the effect of cure temperature for monomer I. The standard cure cycle adopted during the development of these resins was 7 days at 280°C [Fig. 1(a)]. This leads to a stable, reasonably tough resin
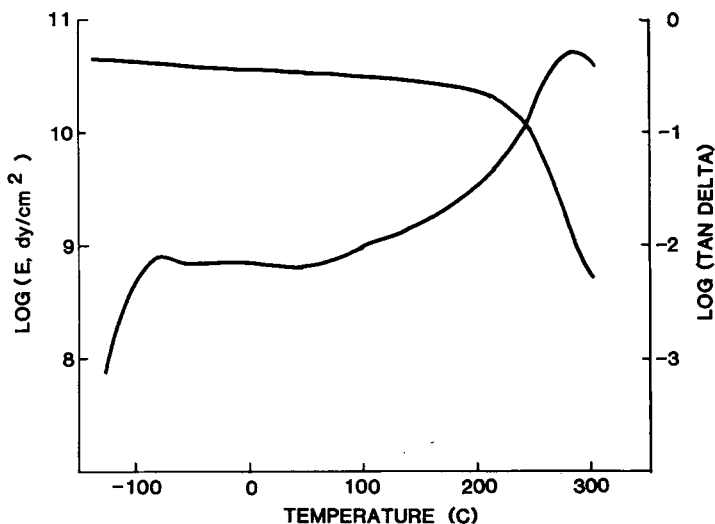
Fig. 1(a). Temperature dependence of dynamic modulus and loss tangent (11 Hz) of monomer I cured for 7 days at 280°C.

with a glass transition temperature $T_g$ of 280°C, as determined from the peak in the loss tangent at 11 Hz.

It was later observed[3] that extremely pure monomer does not polymerize; traces of water, methanol, or phenols accelerate the polymerization.[5] For example, the sample which gave the data in Figure 1(b) was cured for 2 days at 210°C and 2 days at 250°C in the presence of 10 mol % bisphenol A. Except for the lower $T_g$, it looks very similar to material given the standard cure.

In Figure 2 are the Rheovibron results for a sample of monomer I cured at 250°C with 30 wt% hydroquinone. Marullo and Snow[4] have shown that in addition to accelerating the reactions leading to high-molecular weight
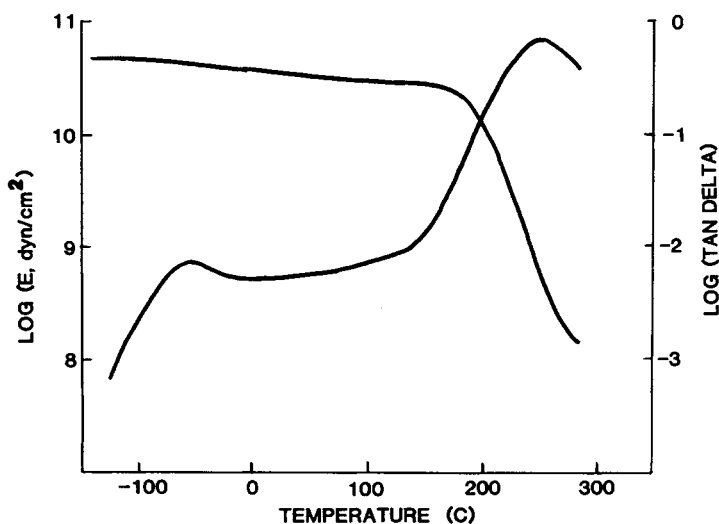


Fig. 1(b). Dynamic mechanical properties (11 Hz) of monomer I cured with 10 mol % bisphenol A at 250°C.
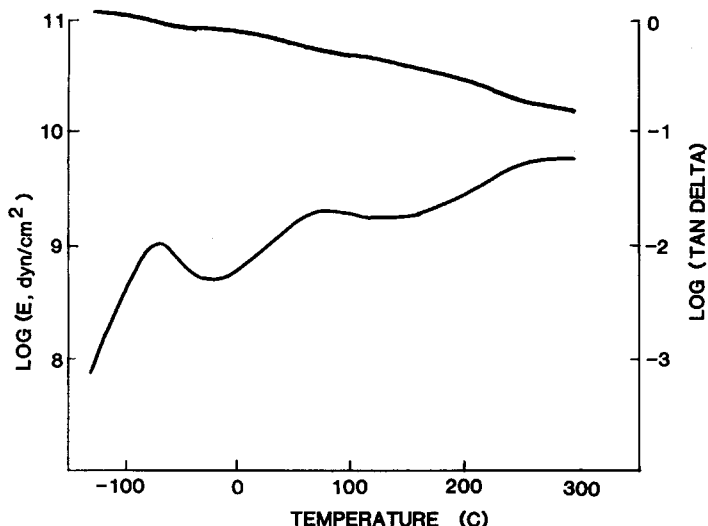
Fig. 2.　Dynamic mechanical properties of monomer I cured with stoichiometric excess of hydroquinone.

polymer, hydroquinone provides a redox pathway for phthalocyanine formation. Thus Figure 2 represents a significantly different network structure from those in Figure 1. This is evidenced by the very small change in modulus in the 200–300°C range. The peak in tan centered at 75°C is noteworthy. A similar, though smaller, peak is sometimes seen for samples prepared without added catalyst.

## Monomer Structure

It is of interest to learn how modifications in the spacer between the monomer functional groups might be used to vary polymer properties. Figure 3 shows Rheovibron curves for thin films of three different polymers
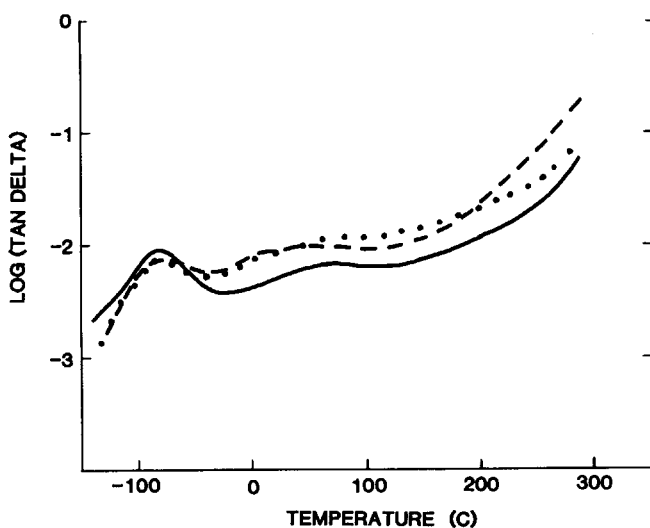


Fig. 3.　Mechanical damping of thin films cured at 280°C: (—) monomer I; (– – –) monomer II; (· · ·) monomer III.

cured at 280°C for 7 days. They are all very similar, which suggests that the use of coreactants and changes in the cure schedule may lead to more useful variations in bulk properties than do minor changes in monomer chemistry. In particular, both the glass transition temperature and the position and magnitude of the low temperature (−80°C, 11 Hz) damping peak are insensitive to the monomer structure.

## Sol/Gel Analysis

During polymerization of difunctional monomers such as the bisphthalonitriles, gelation occurs at a very early stage of the reaction making further analysis difficult. If, however, a "reactive diluent"—a monophthalonitrile —is added, a portion of the reaction mixture may remain soluble even after 100% consumption of functional groups. Table II gives gel fractions for mixtures of I + IV cured with methylene dianiline as an aromatic amine coreactant.[5] As expected, crosslinking is suppressed by the addition of monofunctional reactant. When the weight fraction of the monofunctional compound exceeds 0.8, gelation is not observed.

## DISCUSSION

### Cure Conditions

The data in Figures 1 are consistent with the frequently made observation that the glass transition temperature (and therefore the upper limit of use temperatures) depends on the cure temperature. As the crosslinking reaction proceeds during an isothermal cure, the sample $T_g$ increases until it reaches the cure temperature and the sample vitrifies. Since the reaction rate is virtually zero in the glassy state, no further cure takes place, and the $T_g$ remains constant at the cure temperature. Therefore, a suitable postcure at a temperature above the intended use temperature must be devised.

### Network Structure

The reactions leading to gelation of heated bisphthalonitrile monomers are not yet fully understood, although triazine and phthalocyanine rings have been identified spectroscopically in the polymer.[4] The product ratio seems to depend on reaction conditions (temperature, presence of water, or

TABLE II
Sol/Gel Analysis of Cured Monofunctional (IV)/Difunctional (1) Mixtures

| Weight fraction IV | Gel fraction |
| --- | --- |
| 0.0 | 1.0 |
| 0.1 | 1.0 |
| 0.5 | 1.0 |
| 0.65 | 0.90 |
| 0.74 | 0.81 |
| 0.77 | 0.84 |
| 0.80 | 0.0 |
| 1.00 | 0.0 |

other nucleophiles, air). The present results on mono/difunctional mixtures point the way toward increased understanding of the networks cured with amine.

It should be noted first of all that the pure model compound IV, when reacted with 10 wt% methylene dianiline for 7 days at 280°C, polymerizes to give a green product with a number-average degree of polymerization (DP) of 6.7. This result cannot be accounted for by triazine or phthalocyanine ring formation alone, since these would imply a maximum DP of 3 or 4, respectively.

Keller and Price[5] have proposed that the curing reaction may be a step-growth polymerization through isoindoline repeat structures. According to this model, the monofunctional compound could react to give a linear polymer with a molecular weight determined by (a) the amount of amine used, (b) the extent of reaction (fraction of nitrile groups consumed), and (c) the probability of chain termination. Similarly, the mixed monofunctional/difunctional systems would give branched or crosslinked structures, where each difunctional molecule incorporated into the network would result in one potential crosslink. Figure 4 demonstrates the expected linear relationship between $T_g$ and concentration of potential crosslinks.[6]

If we assume that a dangling unreacted functionality on a bisphthalonitrile molecule would affect $T_g$ in the same way as does a molecule of the model compound IV, then the extrapolation in Figure 4 implies that a typical bisphthalonitrile cured to a $T_g$ of 280°C has a relative crosslink density of 0.5, or about 70% reaction of nitrile groups. Recall that the mixtures used to generate Figure 4 did not vitrify during cure; IR showed 85% consumption of the —CN function. If the extent of reaction could be driven as high as 85% in the difunctional case, significantly higher $T_g$'s (at least 350°C) might be obtained.
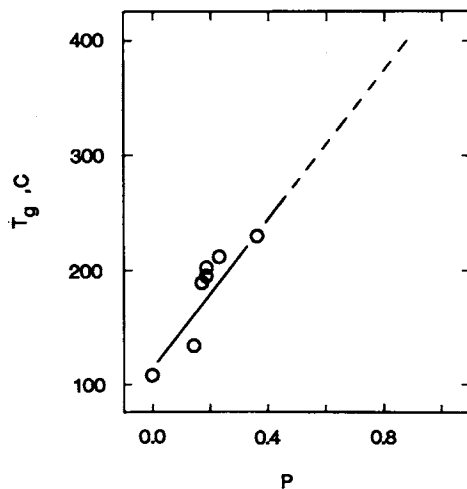


Fig. 4.   Glass transition temperatures of mixtures vs. relative crosslink density. $P$ is calculated as the probability that a randomly chosen monomer unit is reacted at both ends, assuming 85% consumption of functional groups.

## Dynamic Mechanical Properties

In the Rheovibron plots, three distinct relaxations can be identified. The peak in loss tangent at −65°C appears in all the samples studied. Like similar peaks in aromatic polysulfones and polycarbonates,[7,8] it may be assigned to local backbone motion of monomer sized units.[9] As is the case with the thermoplastics, the motion is dielectrically active, albeit weakly (peak dissipation $5 \times 10^{-2}$). From an Arrhenius representation of the shift with frequency of the temperature of maximum dielectric dissipation, an activation energy of 10.6 kcal is obtained, which again is of the same order as that obtained for the polysulfones.

The magnitude of this peak, however, is in all cases two to three times smaller than the corresponding peak in polysulfone. The reasons for this are as follows: It is safe to assume that the motion of units participating in crosslinks is severely limited. If, as pointed out in the last section, the reaction is 70% complete, about half the bisphthalonitrile units in a typical preparation will be reacted at both ends, and hence inactive at −80°C. Beyond this, an additional reduction in relaxation strength occurs because the motion has an intermolecular component,[9] which tends to be suppressed by crosslinking.

In line with the idea that increasing temperatures activate motions of larger and larger chain segments, the relaxation at +50°C (11 Hz; $\Delta E^{act} =$ 24 kcal) is tentatively attributed to bulky structures associated with cross-links in samples where the cure is well advanced. This relaxation is more pronounced when the sample is wet, and is very prominent in dielectic measurements, suggesting that water tends to be associated with these structures. When mono- and difunctional monomers are combined, a looser network structure results, and this peak narrows and shifts to lower temperatures (Fig. 5). Thus its location on the temperature scale reflects the overall network structure. In the related C-10 polyphthalocyanines, where
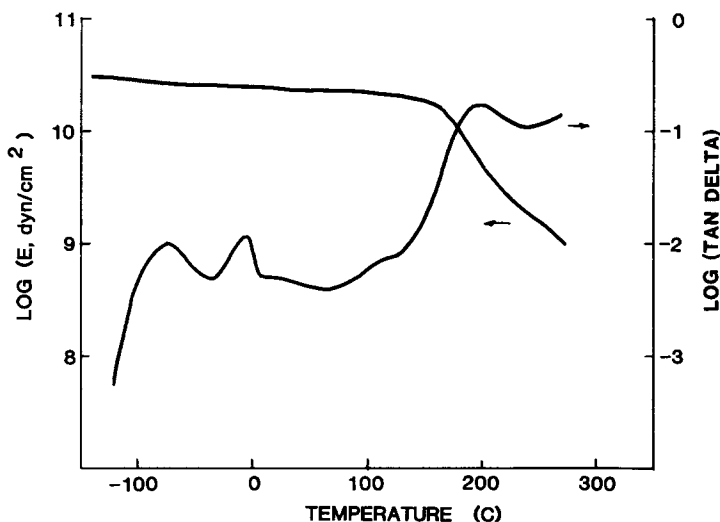


Fig. 5. Dynamic mechanical response of resin prepared from 3.3:1 mixture of monofunctional and difunctional phthalonitriles IV and I with diamine as coreactant.

the spacer between crosslink sites is a flexible aliphatic chain, a corresponding peak appears near 0°C.[10]

Consider finally the high temperature relaxation (280°C, 11 Hz) in Figure 1(a). This is assigned to the glass rubber transition and corresponds to a drop of a factor of 100 in the Young's modulus $E$. The temperature of the peak in the loss tangent matches exactly the midpoint of the transition observed in a differential scanning calorimeter. The transition is broad, reflecting the heterogeneity of molecular environments in this rather complex chemical system.

At the highest temperatures attainable in the Rheovibron, $E$ tends toward a value of ca. $10^8$ dyn/cm², which for comparison is similar to what is seen in tetrafunctional epoxies.[11] A theoretical value of the concentration of elastically active chains is available from the statistical treatment of gelation.[12] Using the estimate of 70% reaction obtained in the last section, one calculates as an average molecular weight of a network strand $M_c = 0.8 \times 10^3$.

The observed rubbery modulus, on the other hand, yields, via the relation

$$M_c = 3pRT/E \qquad (1)$$

from rubber elasticity theory, $M_c = 1.6 \times 10^3$ for $E = 10^8$. (In this equation, $p$ is the polymer density, $T$ is the absolute temperature, and $R$ is the gas constant). Actually, eq. (2), which was derived for flexible chains, probably underestimates $M_c$ in a highly-crosslinked system.[13]

Thus the typical bisphthalonitrile polymer in the rubbery state behaves as if it is less densely crosslinked than might have been expected. Evidently a sizeable proportion of the crosslinkages do not produce elastically active chains; rather, they are "wasted" in short chains, rings, and ladder structures. In contrast to this is the behavior evidenced by the hydroquinone-cured material in Figure 2, where there is only a slight drop in modulus in the 200–300°C range. As was mentioned earlier, this network may be linked by phthalocyanine structures. It may be inferred that the isoindoline repeat units and unreacted functionality hypothesized to exist in the usual base-catalyzed polymers play important roles in conferring high-temperature flexibility. Their dominance may also be in large measure responsible for the similarity of the curves in Figure 3.

Dynamic mechanical measurements through $T_g$ may provide useful screening for variations in cure, especially since the elasticity of the network is very likely related to such important properties as fracture toughness and elongation-to-break.

## CONCLUSIONS

1. The usual base-catalyzed polymerization of bisphthalonitriles does not go to completion. A model that assumes that the primary reaction is polymerization to isoindoline structures accounts for much of the data.

2. Dynamic mechanical measurements permit the characterization of the glass transition and two secondary damping peaks. The low temperature peak appears in all samples studied and is assigned to motions of monomer-

sized backbone units. Intermediate between this peak and the glass transition is a relaxation which depends on cure state and flexibility of the network structure.

3. Variations in monomer structure produce only minor changes in the dynamic mechanical response of these polymers. Optimization of curing is more likely to lead to useful improvements in mechanical properties than slight changes in monomer structure can produce.

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