

## Viscoelastic Properties and Stability of BBL Ladder Polymers

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### Synopsis

Viscoelastic properties of the BBL ladder polymer were determined by a dynamic mechanical technique for the temperature range  $-150^{\circ}\text{C}$  to  $250^{\circ}\text{C}$  and at frequencies of 3.5, 11, and 110 Hz. A secondary loss dispersion centered at  $-50^{\circ}\text{C}$  (at 110 Hz) was discovered which probably arises from an in-chain relaxation mechanism. The loss dispersion resembles  $\beta$ -transitions found in more conventional polymers in intensity (maximum  $\tan \delta = 0.035$ ), activation energy ( $E = 19,000$  cal/mole), and in its close relation to the high-temperature mechanical properties of the polymers. Only slight changes in the low-temperature loss peak cause significant increases in brittleness. It is proposed that such changes, produced by a variety of environments, result from random chain scission at imperfection points in the ladder structure. For this reason we conclude that improving the environmental stability of BBL is of prime importance in its further development for specific applications.

### INTRODUCTION

The search for polymers with greater thermal stability has led to the synthesis of many materials with exotic structures. These new generation substances are generally capable of withstanding temperatures in excess of  $500^{\circ}\text{C}$  for extended intervals. Among the newer experimental polymers described in the literature are the heterocyclic BB polymers, BBB and BBL.<sup>1,2,3</sup> These are formed by polycondensations of 1,4,5,8-naphthalene-tetracarboxylic acid with 3,3'-diaminobenzidine and 1,2,4,5-tetraaminobenzene, respectively.<sup>1,2</sup> Their repeat units, diagrammed in Figure 1a, are considered to be benzimidazobenzophenanthroline types, Figure 1b, or, in abbreviated form, BB. Beyond the basic BB structure, BBB has an additional phenyl (or benzene) group while BBL is a ladder polymer. The reader may refer to Van Deusen *et al.*<sup>1</sup> for a more detailed description of the organic nomenclature suggested here.

Because of their unusual structures and large, relatively inflexible repeat units, these polymers are quite different from more conventional condensation polymers. For example, in addition to their great thermal stability they are only soluble in strong acids,<sup>1,2</sup> will change shape only under high stresses,<sup>3</sup> and will form films by precipitation onto a substrate.<sup>4</sup>

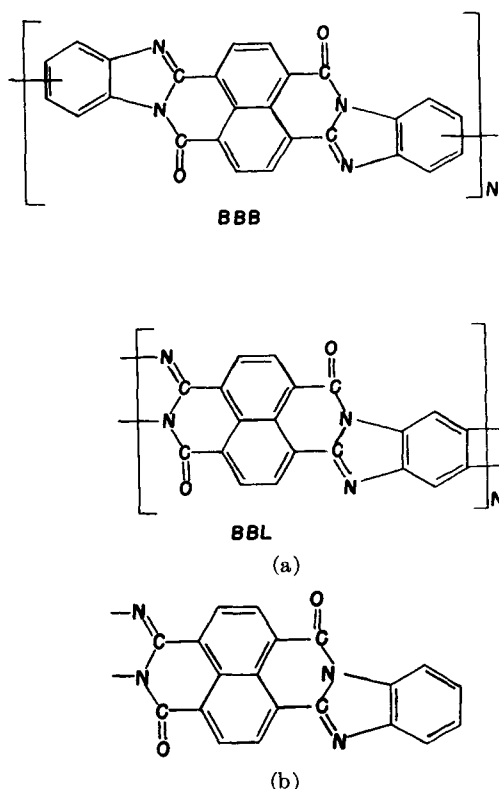


Fig. 1. (a) Structural repeat units of BBB and BBL; (b) benzimidazo-benzophenanthroline structure.

These factors suggest some obvious difficulties in studying the properties of the BB family. Nevertheless, some progress has been made in determining the physical and mechanical properties of BBB. Arnold and Van Deusen<sup>2</sup> have considered thermal stability by measuring weight loss. Barry and Yen<sup>5</sup> measured some dilute solution parameters of a BBB sample in methanesulfonic acid. The same sample was found to have a weight-average weight of 97,000 as determined by light scattering.<sup>5</sup> Barry and Fox<sup>3</sup> have published further comments on the solution properties of BBB and have also related x-ray diffraction patterns of BBB to those of model compounds of the BBB repeat unit. Gillham<sup>6</sup> has recently completed studies of the dynamic mechanical properties of BBB over an extensive temperature range by torsional braid analysis.

In summary, the data presented by these researchers show that BBB is a linear polymer of high molecular weight.<sup>3,5</sup> It undergoes little weight loss in air under transient conditions until 500°C is exceeded. Under static conditions, weight loss in air at 370°C is minimal up to 200 hr.<sup>2</sup> No glass transition has been observed in the temperature range studied (up to 500°C), but a mechanical loss peak is found at approximately -120°C in

torsional shear at 1 Hz.<sup>6</sup> It is noncrystalline but appears to possess a sufficient amount of strong interchain complex formation in the solid state to give it some of the physical properties of a highly crosslinked network polymer.<sup>3</sup>

While BBL seems to have properties similar to those of BBB, much less definite information concerning these properties is available. The fact that its thermal stability is superior to that of BBB<sup>2</sup> provides added incentives for finding out more specific information about BBL. This paper is a report on a study of the dynamic mechanical behavior of BBL and how its response characteristics are affected when the polymer is exposed to various environments.<sup>7</sup>

### EXPERIMENTAL

The dynamic mechanical properties reported here for BBL films 1 mil in thickness were determined using a Rheovibron viscoelastometer operating at frequencies of 3.5, 11, and 110 Hz and covering the temperature range of  $-150^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ . The samples examined were pieces cut from films supplied by the Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio. These were prepared by two methods: casting from methanesulfonic acid using a vacuum sublimator and precipitation from solution onto a fritted glass filter. The latter technique is described in detail by Arnold.<sup>4</sup>

Dynamic tests were performed on specimens aged for many hours in air and nitrogen at  $260^{\circ}\text{C}$  and boiling water. The material was also refluxed in 1*N* sodium hydroxide but could not be tested subsequently because of excessive brittleness. Additional tests were made using untreated samples of both BBL and BBB to serve as standards for comparison.

In addition to dynamic mechanical data, further information was obtained on solution viscosities, elemental sulfur, infrared spectra, and thermal analysis characteristics of the samples tested. These also will be discussed subsequently.

### RESULTS

Examples of the data obtained are shown in Figures 2 to 4; these are plots of storage moduli and loss tangents for several cast films. We find the same low-temperature loss maximum for BBB which Gillham had found previously.<sup>6</sup> A similar loss peak is noted in Figure 2 for BBL but is lower in intensity and centers at a higher temperature,  $-50^{\circ}\text{C}$ . On aging BBL in air at  $260^{\circ}\text{C}$  for only a few hours, we find a noticeable decrease in intensity of the loss peak and an increase in  $E'$  at temperatures above the loss maximum as shown in Figure 3. Qualitatively, we also observe a noteworthy increase in brittleness on flexing the aged samples. These trends are also obtained for BBL aged in nitrogen at  $260^{\circ}\text{C}$ .

Treatment in boiling water yields more marked changes in mechanical spectra as shown in Figure 4. The increase in brittleness in this case is

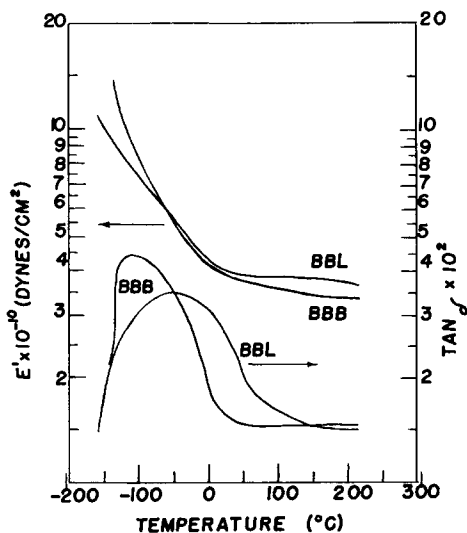


Fig. 2. Storage modulus  $E'$  and loss tangent for cast films BBB and BBL—sample A; frequency 110 Hz.

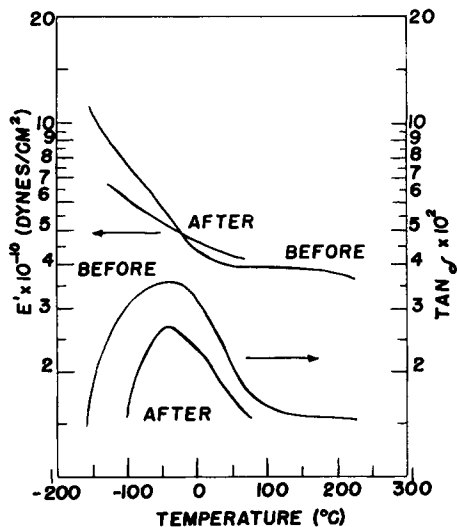


Fig. 3. Change in storage modulus  $E'$  and loss tangent on heating in air at 260°C for 42 hr; frequency 110 Hz.

even more noticeable than in the previous case. Samples heated in 1*N* sodium hydroxide at 80°C become too brittle to test after only a few minutes of refluxing. After 15 hr in NaOH, the material becomes too brittle to handle. Care was taken to thoroughly dry all samples treated in aqueous media before testing.

Inherent viscosities of representative samples dissolved in methanesulfonic acid are listed in Table I. Whenever the polymer is exposed to

TABLE I  
Changes in Inherent Viscosity on Aging of BBL

Sample treatment	$\eta_{inh}$ , dl/g <sup>a</sup>
Original untreated	3.67
Heated in air at 260°C 45 hr.	2.96
Boiled in H <sub>2</sub> O 42 hr.	2.32
Refluxed in 1N NaOH 15 hr.	1.71

<sup>a</sup> Inherent viscosity,  $\eta_{inh}$ , determined in methanesulfonic acid, concentration 0.0625 g/dl, temperature 25°C.

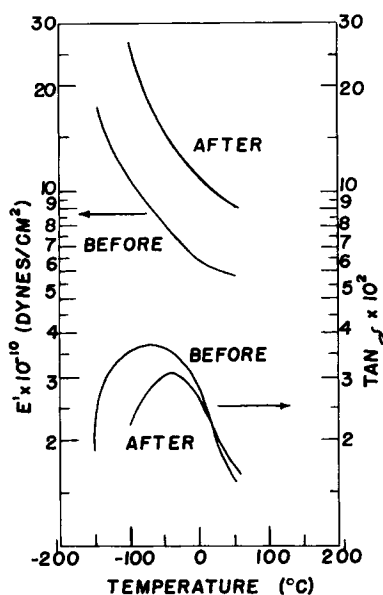


Fig. 4. Change in storage modulus  $E'$  and loss tangent on boiling in water for 20 hr; frequency 110 Hz.

any of the media considered, its inherent viscosity decreases. This indicates a decrease in molecular weight which is reflected in the dynamic mechanical characteristics. Obviously, then, dynamic testing is a rather sensitive test for chemical changes in the BBL system.

Further evidence of chemical reaction within the polymer includes slight alterations in infrared spectra in the 6- to 8- $\mu$  region. Bands at 6.3, 6.6 and 8.1  $\mu$  are altered as shown in Table II. Similar effects were reported previously by Van Deusen and co-workers.<sup>1</sup> Moreover, elemental sulfur analyses on various samples differ according to treatment as shown in Table III. Additional data reported by Powell<sup>7</sup> indicate that DSC thermograms are also different for each of the samples tested. In the temperature range investigated, Powell, using rough measurements, observed no weight

TABLE II  
Intensity of Selected Infrared Absorptions in BBL with Respect to Band at 10.8  $\mu$

Sample	Band location				
	6.3 $\mu$	6.6 $\mu$	8.1 $\mu$	10.8 $\mu$	13.2 $\mu$
BBL untreated	0.986	1.144	1.159	1.00	0.688
BBL refluxed in H <sub>2</sub> O					
41 hr	0.903	1.063	1.175	1.00	0.890
BBL untreated	1.26	0.910	0.723	1.00	0.722
BBL aged in air 260°C					
24 hr	1.12	0.869	0.772	1.00	0.804
BBL untreated	1.025	0.942	1.088	1.00	0.975
BBL aged in N <sub>2</sub> 260°C					
24 hr	0.904	0.894	1.012	1.00	0.955

TABLE III  
Residual Sulfur Analysis

Sample	Per cent sulfur <sup>a</sup>
BBL original untreated	0.64 $\pm$ 10%
BBL heated in air at 260°C 24 hr	0.33 $\pm$ 10%
BBL heated in N <sub>2</sub> at 260°C 24 hr	0.70 $\pm$ 10%

<sup>a</sup> Determined gravimetrically.

loss, a result also obtained by Arnold and Van Deusen<sup>2</sup> by a thorough TGA analysis.

The same trends are found when precipitated films are treated instead of cast films. In this case, breakdown processes occur more quickly because of the high porosity of the films.<sup>4</sup>

Analyses for the inherent viscosity of BBL aged in N<sub>2</sub> at 260°C and sulfur per cent after boiling water treatment were not made because of a scarcity of polymer. While such data would be desirable, the other data available for samples aged in these environments provide ample evidence that chemical reaction does occur.

## DISCUSSION

The data presented here indicate that BBL has a distinct low-temperature relaxation process which is very sensitive to aging in a variety of environments. Only slight alterations in the relaxation behavior of the polymer seem to have a significant effect on high-temperature mechanical properties. This relationship presently is being studied in more detail. It is apparent at this point that improving environmental stability is of prime importance in the further development of BBL for specific applications.

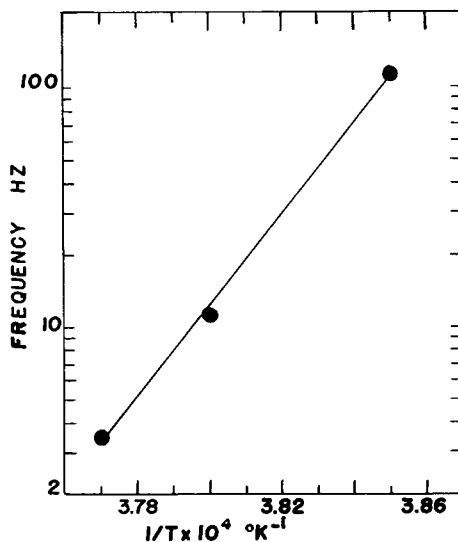
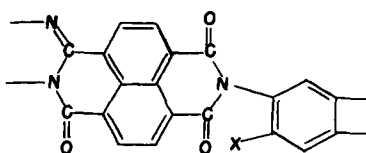
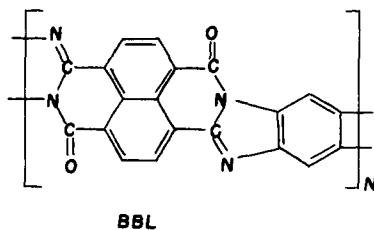


Fig. 5. Position of loss maximum for BBL.

The loss dispersion reported here for BBL resembles the  $\beta$ -transition in more conventional polymers<sup>8</sup> both in intensity and in thermal characteristics. The temperature dependence of the loss maximum follows an Arrhenius expression with an activation energy of 19,000 cal/g mole, as shown in Figure 5. The intensity of  $\tan \delta$  maximum is approximately 0.035. Mechanistically, this suggests that some type of in-chain molecular motion may be associated with this loss dispersion.

The possibility of an in-chain relaxation process occurring in BBL is easier to visualize if one notes that some single-bond linkages between structural units are thought to exist as imperfections.<sup>2,3</sup> A few of these "imide" linkages, shown in Figure 6, may exist per molecule. Their existence is consistent with the difference in loss dispersion between BBB and BBL. In BBL, where there are likely fewer single bonds, molecular mobility must be more restricted. Thus, the loss peak occurs at a higher temperature and is less intense than in BBB, which has the more completely single-bonded structure.

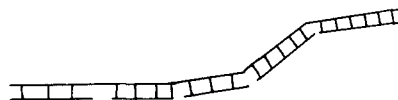
If molecular cleavage at single-bond imperfections is the dominant breakdown process which occurs in BBL, a more perfect ladder structure will result. Because very few cleavages of this type are possible per chain, high molecular weights should still prevail after cleavage.<sup>2,3</sup> The more rigid molecules remaining are expected to exhibit less relaxation in accord with the trends reported in this paper. Figure 7 illustrates the effect of such structural changes. Since a reduction in mechanical dispersion also results in undesirable brittleness characteristics, it is likely that a slightly imperfect ladder structure (with greater stability) is the most desirable from an applications viewpoint.



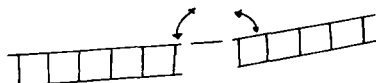
**IMIDE IMPERFECTION**

Figure 6.

**BROKEN LADDER SEQUENCE**



**MOTION POSSIBLE**



**DEGRADATION YIELDS MORE RIGID STRUCTURE**

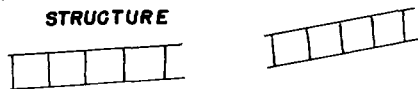


Figure 7.

According to the interpretation of infrared spectra forwarded by Arnold and Van Deusen,<sup>2</sup> our infrared data are indicative of the structural changes described above. It is possible, however, that chain scission occurs by different chemical mechanisms in the various environments studied. This is suggested by the dissimilar residual sulfur content in some of the samples examined. Sulfur in these samples, of course, originates from the solvent methanesulfonic acid, a nonvolatile substance, entrained in the polymer during processing. Additional studies need to be carried out to determine



its role in altering the polymer's structure. It is clear, however, that in spite of the possibility of various reaction routes, molecular cleavage always appears to occur with no weight loss.

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