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Properties of Heterocyclic Condensation Polymers

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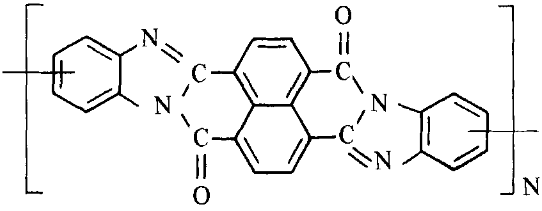
SUMMARY

Basic questions concerning heterocyclic polymers are reviewed. Initial investigations on the heterocyclic polymer BBB prepared from napthalene-1,4,5,8 tetracarboxylic acid and 3,3′-diaminobenzidine are described. These include infrared absorption studies of the structure of the polymer, fractionation of the polymer by exclusion chromatography on a porous substrate, and light scattering and dilute solution viscometry on fractions of the polymer dissolved in a strong acid. These data are interpreted to conclude that: (1) in dilute solutions BBB behaves as a "flexible coil" macromolecule, with perhaps relatively free rotation about the single bond connecting the long, inflexible, nearly planar repeat units; (2) a sufficient amount of interchain complex formation occurs in the solid state to give the linear, noncrystalline polymer some of the physical properties of a highly cross-linked network polymer.

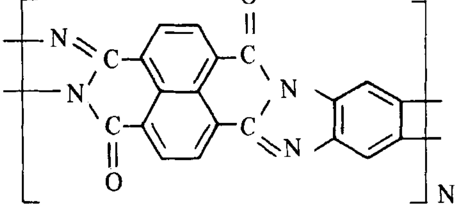
One of the recent noteworthy developments in polymer science has been the synthesis of a new generation of polymers capable of withstanding temperatures in excess of 500°C. In many ways, these materials are significantly different from the more familiar condensation or vinyl polymers that have been studied extensively in the past. It is timely to consider some of the special properties of these polymers related to structure, synthesis, and application. The purpose here is to pose some of the questions which seem to us to be central to increasing our understanding of these new materials. In part, these questions reflect a point of view on the nature of these new polymers. Some of the questions may have an obvious answer in connection with a specific polymer and the list may be incomplete, but it is our intent to bring some of the important questions on the nature of the new polymer in focus to stimulate further discussion.

A description of some experimental studies on a particular heterocyclic polymer follows the general discussion and is intended, in part, to consider some of the answers to the question posed, at least for the polymer studied.

The polymers of interest here are typically prepared by condensation reactions involving polyfunctional reactants. They are often comprised of large, relatively inflexible, repeating units. These units are sometimes linked by a single bond about which rotational isomerization is possible in principle, and are sometimes linked by multiple bonds so that no rotational isomerization can be imagined. Examples of these two structural alternatives can be seen with the polymers labeled BBB and BBL [1, 2]:



BBB



BBL

The problems that we will consider have their origins in the nature of the polymerization process and in the distinctive structure of typical repeat units. The polymerization of heterocyclic polymers often (but not always [3]) involves reactants of greater than difunctionality, and relies on intrachain ring closure to produce the final extensively cyclized repeat unit in the linear polymer. This suggests the following questions.

Chain Structure and Thermal Stability

1. Can the effects of stoichiometry of reactants, extent of reaction, impurities, and reaction conditions in the molecular weight and molecular weight distribution be understood by a simple application of the principles of condensation polymerization as, for example, put forth in Ref. [4]?
2. To what extent are the polymers branched, and how is this related to polymerization variables?
3. What methods can be used to determine the extent of the intramolecular cyclization that is postulated for those heterocyclic chains?
4. What methods can be used to determine the distribution of geometrical isomers of the repeat units when the possibility for such isomers exists?
5. Is the thermal stability of heterocyclic polymers more strongly dependent on substituting aromatic for aliphatic structure than in the presence per se of double-stranded groups in the polymer repeat unit?
6. How sensitive is the thermal stability of a heterocyclic aromatic polymer to small amounts of incompletely formed (e.g., chemically imperfect) repeating units?
7. Can specific groups be eliminated from linear heterocyclic chains by thermal degradation with concurrent bond formation leading to more stable linear polymers?

The new polymers often have bulky repeating units that have suggested to some that the polymers are in some sense "stiff." The fact that the polymers are often only soluble in a few select solvents, or even insoluble in any known solvent, has led to speculation that they are crystalline or cross-linked. These characteristics, which may have primarily to do with the intrachain structure of the polymer, lead to several questions on:

Chain Flexibility and the Properties of Concentrated and Dilute Solutions

1. Should the conformation of a (given) heterocyclic polymer in dilute solution be described as a flexible coil, or as a semiflexible or inflexible

coil, a rod, or some other structure altogether? What parameters should be investigated to determine the conformation?

2. Can some measure of chain "rigidity or stiffness" be determined from dilute solution properties?

3. Are problems of phase separation and low solubility inherent in the nature of an inflexible coil or of a rod-like polymer?

4. Can homogeneous concentrated solutions be formed, and will these show a dependence of the zero-shear rate viscosity on M characteristic of flexible chain polymers [5]? (e.g., $\eta \alpha M$ for $M < M_C$ and $\eta \alpha M$ [3, 4] for $M > M_C$, where M_C is a critical value of M characteristic of the polymer.)

5. Is the dependence of viscosity of concentrated solutions on shear rate $\dot{\gamma}$ typical of that observed for flexible coil chains? This is of special interest since chain "stiffness" may be expected to influence the function $\eta(\dot{\gamma})$.

6. Do concentrated solutions of the heterocyclic polymers exhibit viscoelastic properties with the same features as those familiar from studies on flexible coil polymers?

The preceding six questions are essentially concerned with the possibility of intrachain "stiffness" as it might affect observable properties. There is a second concept of stiffness that is useful to recognize, however. This is concerned with interchain interactions owing to the peculiar nature of the repeat units, or to the absence of rotational isomerization owing to the lack of single bonds in the polymer backbone. Thus, the final set of questions we pose concerns:

The Properties and Morphology of Bulk Polymer

1. If the polymer exhibits a high modulus, as is usual, is it in the glassy state as this is usually understood, and does it exhibit the normal glass-rubber transition and other characteristics of the glassy state such as necking, cold flow, etc.? Why is the apparent glass temperature so high for many of these systems?

2. Could the apparently high glass temperature and the high, temperature-insensitive modulus be associated with problems of interchain packing, or specific interaction leading to order short of complete crystallinity?

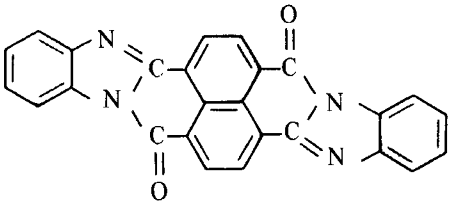
3. Are there special interchain packing considerations because of the distinctive character of the repeat units (setting aside special interchain interactions such as hydrogen bonding, π bonding, etc.) or the lack of single bonds in the polymer backbone?

4. How are any special features of these materials dependent on molecular structure reflected in processing variables?

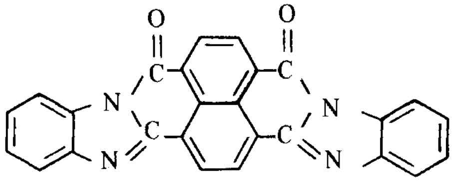
We now turn to a discussion of some experimental studies on the heterocyclic-polymer BBB that have been reported in more detail elsewhere [6]. Of course, the choice of experiments was motivated in large part by the questions given above, and these initial results are meant to be partial answers to these questions for at least one polymer system.

SOLUBILITY OF BBB AND FRACTIONATION OF THE POLYMER

So far as is now known, BBB is soluble only in strong acids such as concentrated sulfuric acid, benzene sulfonic acid, methane sulfonic acid, and concentrated phosphoric acid, and in certain aqueous reagents discussed below, in which a chemical reaction modifies the polymer. The vat dyestuffs are useful model compounds of the cis and trans repeating units of BBB. It is useful to keep in mind the similarity of BBB (and other heterocyclic polymers) to the more familiar dyestuffs since it can be anticipated that some of the chemical and physical properties of the latter, which have been



Vat Orange 7
CI 71105



Vat Red 15
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fairly well studied [7], will also apply to the polymer. Both the cis and trans compounds exhibit nearly as poor solubility as BBB, although they do have limited solubility in o-chlorophenol, pyridine, xylene, and a few other organic solvents. Examination of the electronic absorption spectra of the model compounds and of BBB in bulk and various solvents leads to the conclusion that these compounds act as a weak multifunctional base in strong acid, as do many similar compounds [8-10], leading to protonation and solubility in strong acids. The pyridine nitrogens and the carbonyl groups appear to be likely sites for the protonation [6].

A method of fractionating BBB and similar polymers is desirable both from the point of obtaining well-defined polymers for dilute solution studies and other physical measurements, and for the purpose of elucidating the polymerization process giving the polymer. The well-established methods of fractionation that rely on the dependence of the solubility of the polymer on its chain length are of little use in the fractionation of BBB. Attempts to fractionate BBB from solution in methane sulfonic acid by the addition of methanol, or from solution in sulfuric acid by the addition of water, confirm this conclusion. In both systems, the addition of the nonsolvent did not cause immediate precipitation of the polymer, but instead the solution became increasingly turbid over a period of several hours. Once precipitated, the polymer could not be redissolved simply by an increase in temperature, and it was difficult to avoid almost complete precipitation and effect fractional precipitation. Finally, analysis of the "fractions" that were recovered revealed that essentially no fractionation according to molecular weight had taken place.

Fortunately, it has been shown that chromatography on substrates with suitable-size pores can achieve a separation based on the molecular size of macromolecules in solution [11]. Consequently, a large-scale preparative column and a set of five analytical columns were constructed from the commercially available porous silica Porasil (Fig. 1) (see Ref. [6] for details of construction). The use of Porasil as a support for exclusion chromatography has been discussed recently by LePage et al. [12]. The substrate in the preparative scale was selected to fractionate a BBB polymer with $[\eta] = 2.6$ dl/g; the analytical column was designed to achieve separation over a wider range of species. Figure 2 illustrates the calibration of the analytical column with anionic polystyrene samples dissolved in butanone and tetrahydrofuran. The abscissa is given as the ratio V_e/V_T of the maximum elution volume V_e to the total void volume V_T in the column. It is noteworthy that the product $[\eta]M$ is independent of the solvent even though butanone is a relatively poor solvent for

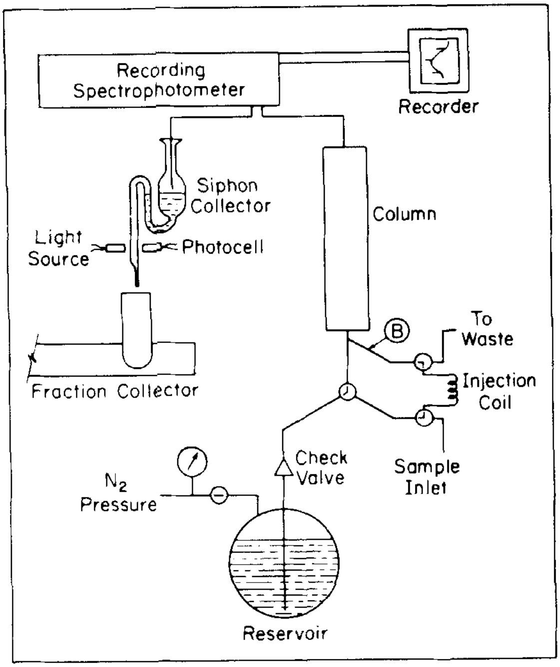


Fig. 1. Schematic flow diagram of the preparative scale chromatography column.

polystyrene, and tetrahydrofuran is a good solvent. This is to be expected if the separation is effected according to molecular size, as generally supposed [13, 14].

Figure 3, illustrating some data from the analytical column, shows chromatograms of two 0.5% solutions of unfractionated BBB samples with $[\eta]$ = 2.6 and 0.2 dl/g; Fig. 4 shows chromatograms of three of the fractions of the unfractionated sample with $[\eta]$= 2.6 that were obtained from the preparative column. The product $[\eta]M$ for these three fractions correlates satisfactorily with the function relating $[\eta]M$ with V_e/V_T found for the polystyrene fractions.

MISCELLANEOUS SOLVENT SYSTEMS FOR BBB AND BBL

The similarity of BBB and BBL to the vat dyestuffs suggests some

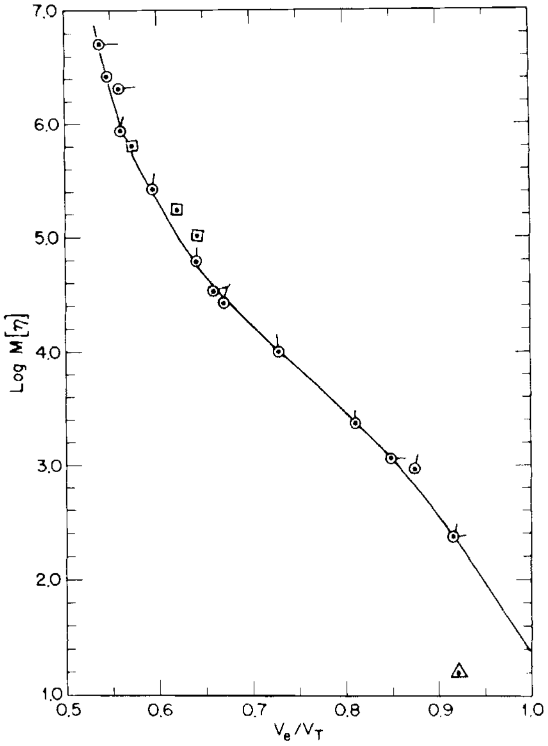


Fig. 2. Log M[η] versus the fractional elution volume V_e/V_T for anionic polystyrenes dissolved in toluene, ⊙—; and in butanone, ⦽; and for BBB fractions dissolved in sulfuric acid, ⊡.

alternate methods of forming solutions of these polymers by chemical modifications already well studied on the dyes. Both polymers can be converted to a soluble form in aqueous solution containing 4 g/liter sodium hydrosulfite, 10 g/liter sodium hydroxide, and one-third pyridine by volume. The polymers are easily recovered by oxidation in air. It is assumed that the carbonyl oxygen is reduced by the sodium hydrosulfite, which is a commonly used reagent to effect reduction in vat dyestuffs [7]. Both model compounds and the BBB and BBL polymers can be rendered soluble with this reagent. The intrinsic viscosity of a BBB sample with nearly the idealized structure (cf. below) shown above does not change after treatment with the reducing agent. This system has been found to be useful as a solvent for sedimentation velocity experiments in the ultracentrifuge, which cannot be carried out in sulfuric acid.

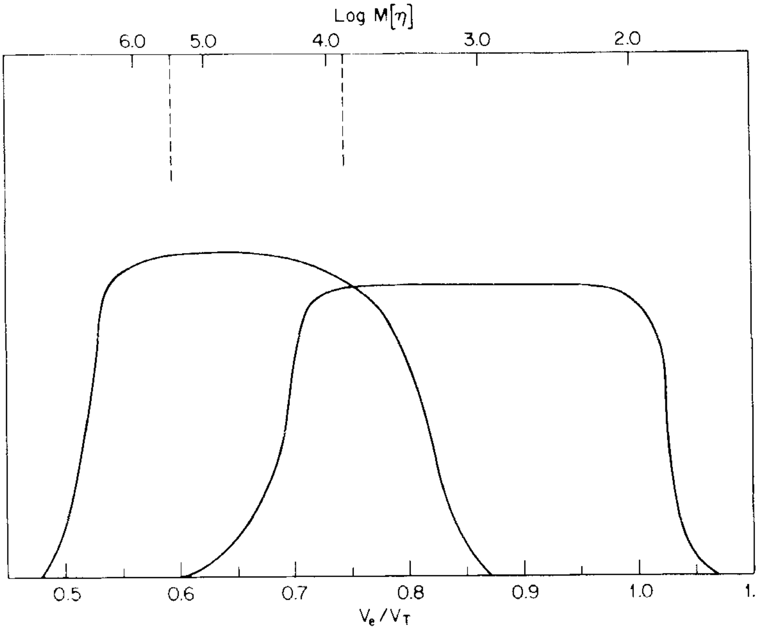


Fig. 3. Optical density versus the fractional elution volume V_e/V_T and log M[η] for two unfractionated samples of BBB. The dashed lines indicate the values of M[η] for the two samples.

Treatment with fuming sulfuric acid produces an irreversible change in BBB but has no effect on BBL if the polymer is completely cyclized to give the structure indicated above. Further condensation may occur in solution in fuming sulfuric acid if the BBL is not completely formed before dissolution. Infrared analysis of the acid-treated BBB after precipitation in water shows the presence of sulfone and sulfonate groups, and a gravimetric analysis shows that the polymer contains one sulfur atom per repeating unit of the polymer. The acid-treated BBB is soluble in 0.1 N sodium hydroxide.

INFRARED ABSORPTION STUDIES ON BBB

It is important to know to what extent the real polymer has the idealized structure that would result from polymerization without side reactions and

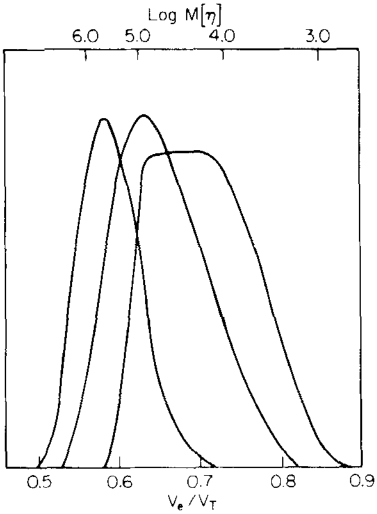
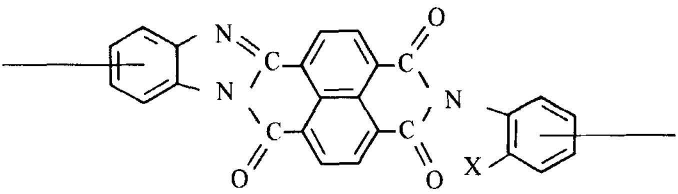


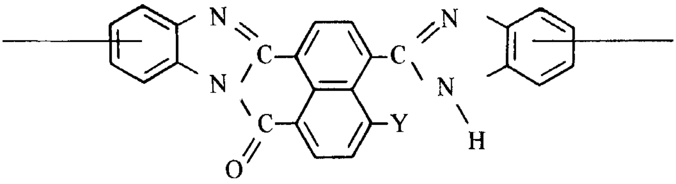
Fig. 4. Optical density versus the fractional elution volume V_e/V_T and log M[η] for the fractions of BBB.

completion of all desirable ring-forming reactions. Structural imperfections could include (a) branching, leading to complete insolubility if present in substantial amount, and/or (b) incomplete fusion of the ring structure of the heterocyclic repeat unit. Although side reactions that would lead to branching in a polymerization have been observed in condensation reactions involving pyromellitic dianhydride [15], these appear to be less likely with naphthalene 1,4,5,8-tetracarboxylic acid [16]. Incomplete ring formation is of more concern here since the physical properties of the polymer may be sensitive to the presence of a few imperfect repeat units. The imperfect repeat units could contain either of the groups



(I)

or



(II)

where X and Y can be amino and carboxy groups, respectively, or either can represent impurities in the monomers. The imide structure (**I**) can be detected in BBB through the characteristic strong absorption at 1650-1660 cm^{-1} that is evident in the spectra for the model compounds studied by Van Deusen et al. [2]. This band is absent in the spectra of both the cis and trans model compounds of the repeat unit of BBB.

Spectra of KBr pellets of BBB usually do not have sufficient resolution to allow this band to be unambiguously identified, and indicate that the imide content in the polymer is low. However, thin films of BBB can be rolled and examined in a cell in which the film can be evacuated and heated in situ. Figure 5 shows the results of a series of heat treatments in vacuo. Treatment at 110°C results in considerable sharpening of the band at 1660 cm^{-1}. Exposure to water vapor causes the band to assume its original diffuse shape. Therefore, the presence of adsorbed moisture is the cause of the poor resolution in the original film. The intensity of the band after heating at 110°C is a measure of the imide content in the polymer. The imide content of the polymer investigated in Fig. 5 is evidently low, less than 5%.

Further heat treatment at temperatures below 250°C causes a reduction in the imide content as measured by the absorption band at 1660 cm^{-1} and indicates completion of the remaining ring fusion. Continued heat treatment of the BBB film at temperatures in excess of 600°C results in a drastic alteration in the spectrum. Separate studies on an Associated Electric Industries MS-9 mass spectrometer reveal that CO is evolved from BBB at temperatures in excess of 600°C; a concomitant weight loss accounted for by the loss of CO is observed for polymer samples heated in vacuo. Consistent with these results is a gradual diminution of the absorption band at 1715 cm^{-1}, together with its overtone at 3400 cm^{-1}

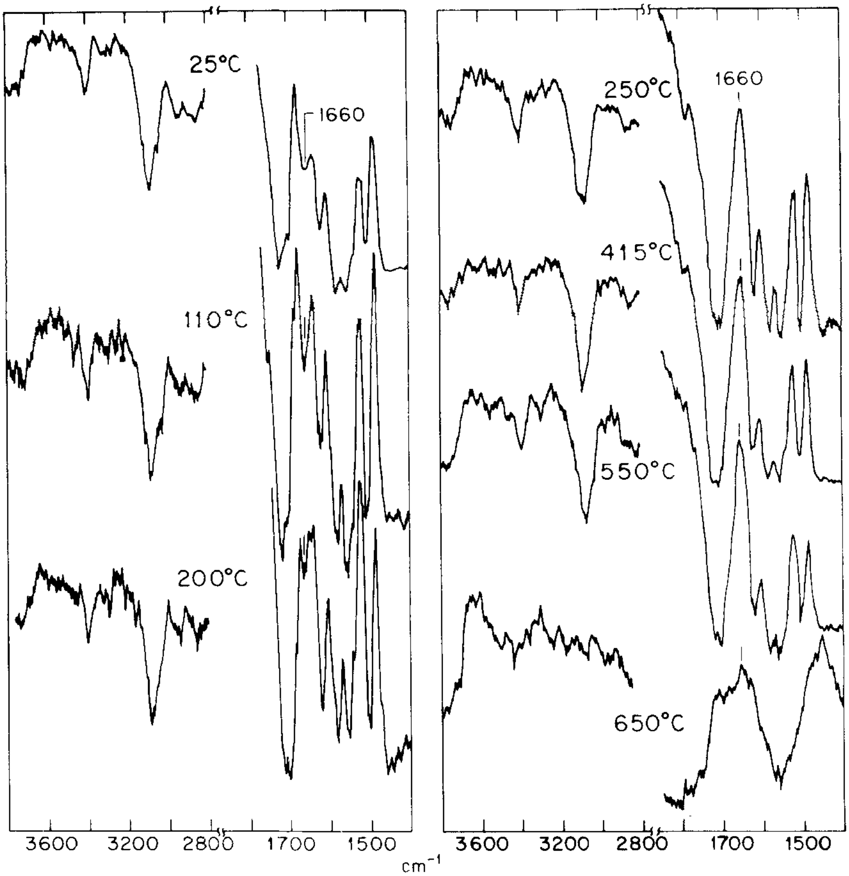


Fig. 5. Infrared spectra for a BBB film heat-treated in vacuo.

when the film is held at 600°C. These bands are characteristic of the carbonyl group.

PHYSICAL PROPERTIES OF BBB

The dilute solution properties of BBB in strong acids can provide information on the chain conformation of the polymer. Light-scattering studies cannot be carried out with the usual mercury vapor lamp with emissions of 4358 Å and 5461 Å because of the strong absorption by

BBB at these wavelengths. It is possible, however, to carry out measurements with a laser source of 6328 Å, although the scattered intensity still must be corrected for attenuation since the extinction coefficient is 1.25×10^3 cc g^{-1} cm^{-1} for BBB in methane sulfonic acid at this wavelength. Measurements were carried out with light-scattering apparatus described elsewhere [17], modified by introduction of a laser source. Small light-scattering cells in which the solution could be centrifuged in situ were utilized [18] (see Ref. [6] for details). The light-scattering data were analyzed according to the usual relations

$$Kc/R(u,c) = [1/MP(u)] + 2A_2c + 0(c^2)$$

$$P^{-1}(u) = 1 + \frac{1}{3}u + 0(u^2)$$

where $u = [\langle s^2 \rangle (4\pi n/\lambda)^2] \sin^2 \theta/2$, with $\langle s^2 \rangle$ the mean square radius of gyration, n the refractive index, θ the scattering angle, λ the wavelength, and K the optical constant proportional to $(dn/dc)^2$. It was not possible to extract the second virial coefficient A_2 from the data because, at the very low concentrations employed, c/R(u,c) is independent of c within experimental error. Values of M and, where possible, $\langle s^2 \rangle$ determined from the data are given in Table 1. The uncertainty in the value of $\langle s^2 \rangle$ increases with decreasing M, and $\langle s^2 \rangle$ becomes difficult to determine with reasonable accuracy with the 6328 Å light when $\langle s^2 \rangle = 10^{-12}$ cm^2.

Table 1. Dilute Solution Parameters of BBB Polymer in Methane Sulfonic Acid

Sample	$10^{-4}M_W$	$10^{12}\langle s^2 \rangle$, cm^2	$[\eta]$, dl/g
I-3	$16._7$	6.3_6	5.48
I-5	$13._1$	3.5_4	4.05
I-11	9.8	3.2_7	2.87
I-18	8.1	1.9_7	2.02
Whole I	9.7_3	2.6_4	2.66

Intrinsic viscosities of BBB in methane sulfonic acid were determined with a suspended level Ubbelohde viscometer by extrapolation of data for at least four concentrations to infinite dilution according to the simultaneous extrapolations:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c + 0(c^2)$$

$$\ln \eta_{rel}/c = [\eta] - \left(\frac{1}{2} - k'\right)[\eta]^2 c + 0(c^2)$$

The results are given in Table 1. Values of k′ vary from 0.3 to 0.5; these are typical for flexible coil polymers. It should be mentioned that [η] for the high-molecular-weight fractions could not be determined in 96% sulfuric acid owing apparently to considerable intermolecular aggregation as evidenced by a value of k′ well in excess of unity and very poor reproducibility of results. This suggests there may be aggregation effects in the fractionation of BBB in the porous silica permeation column as well, although such effects should be minimal since the concentrations on the column are well below those necessary in the viscometric measurement. The value of [η] could be determined in concentrated sulfuric acid for the unfractionated polymer with [η] = 2.6 dl/g in methane sulfonic acid. Interestingly, a salting out effect is suggested in the slightly aqueous acid by an increase in [η] from 1.8 dl/g in 96% sulfuric acid to 2.7 dl/g in 100% sulfuric acid.

The values of M_w recorded in Table 1 have been used to plot M[η] versus V_e/V_T on Fig. 5 for the fractions of BBB studied. The results are in reasonable agreement with the empirical relation between [η]M and V_e/V_T found with the polystyrene fractions.

The striking feature of the data given in Table 1 is that the exponent ν in the Mark-Houwink relation

$$[\eta] = KM^{\nu}$$

exceeds unity even though the span in M covered is admittedly small. Four distinct and entirely independent reasons can be postulated for this behavior:

1. An enormous excluded volume effect exists in methane sulfonic acid so that according to the relation

$$[\eta] = \Phi_0 \frac{\langle s^2 \rangle_0^{3/2}}{M} \alpha^3$$

we have

$$\nu = \frac{d \ln [\eta]}{d \ln M} = \frac{d \ln \Phi_0}{d \ln M} + \frac{d \ln(\langle s^2 \rangle_0/M)^{3/2}}{d \ln M} + \frac{1}{2} + \frac{d \ln \alpha^3}{d \ln M}$$

with d ln α^3/d ln M exceptionally large. The expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0$ is a measure of the increase of the molecular radius relative to the unperturbed value $\langle s^2\rangle_0$.

2. The excluded volume effect is not exceptionally large, but for the molecular weights of interest the unperturbed dimension $\langle s^2\rangle_0/M$ has not yet reached its asymptotic level for large M, and is still increasing with M.

3. The BBB coil is so highly expanded that it behaves as a partially draining or free-draining coil, in which case d ln Φ_0/d ln M is very large. For a free-draining coil we should put

$$[\eta] = \frac{N_A}{600}\,\frac{\langle s^2\rangle_0}{M}\,\frac{M}{m_a}\,D_s$$

where N_A is Avogadro's number and D_s is the equivalent Stokes diameter of a hydrodynamic segment with molecular weight m_a. Thus $[\eta]$ is proportional to M (excluded volume effects being neglected).

4. The fractionation achieved on the porous silica substrate actually separates according to molecular size and not according to molecular weight. In fact, BBB cannot be considered as a homopolymer in this kind of separation, but must act as a "hexapolymer" comprised of the six repeat units illustrated schematically in Fig. 6. In this case, $\langle s^2\rangle_0/M$ varies among the fractions not because of an inherent variation of $\langle s^2\rangle_0/M$ with M, but because the distribution of the repeat units is not the same for all fractions. In addition, and perhaps even more important, structural imperfections in the repeat units would greatly enhance this effect.

Of course, it is possible that the observed behavior is the result of some combination of these effects. The first possibility given above cannot be expected to explain the observed effect alone unless the BBB chain behaves in a far different way from other linear polymers [19, 20]. Calculation of the Stokes diameter D_s from the data for $[\eta]$, $\langle s^2\rangle$, and M in Table 1 yields values of the order 5 Å, which seems too low to be meaningful. Calculation of Φ from the Fox-Flory relation [21] together

$$\Phi = [\eta]M/\langle s^2\rangle^{3/2}$$

with the data in Table 1 yields values of $\Phi \times 10^{-21}$ ranging from 45 to 80, compared with 40 found experimentally for polystyrene [20] and 39.4 calculated theoretically [22]. Thus, taking into account the uncertainty in the determination of $\langle s^2\rangle$, it appears that BBB behaves essentially as a nondraining coil in methane sulfonic acid, despite the large value of ν.

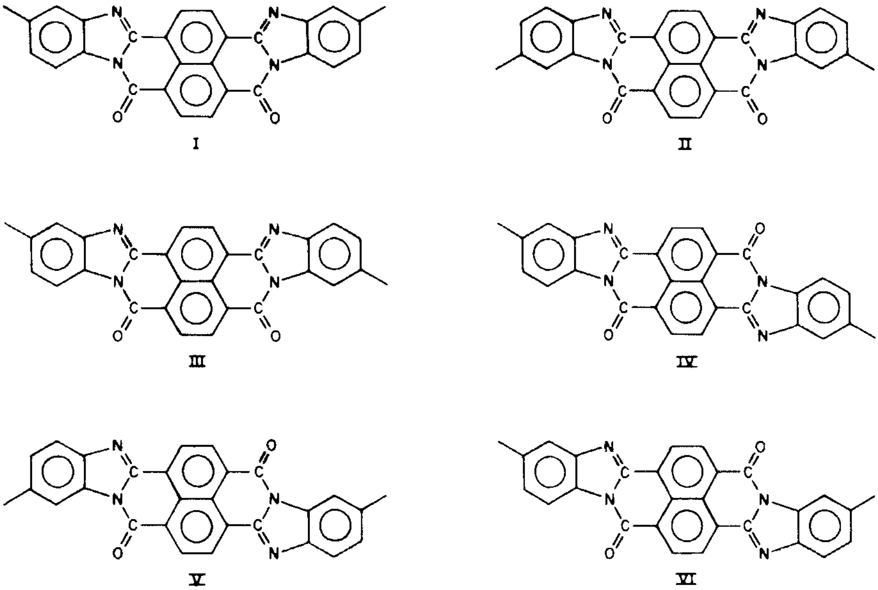


Fig. 6. Schematic representation of BBB isomers.

Although additional data are needed, it seems probable that the extreme variation of $\langle s^2 \rangle/M$ among the fractions implied by this conclusion can be accounted for by the effects of fractionation.

Calculation of the dimension $\langle s^2 \rangle_{FR}/N$ of a chain with N segments with free rotation about valence bonds has not yet been carried out because of uncertainties in the dimensions of the six isomers of the repeat unit. The measures values of $\langle s^2 \rangle$ correspond to $\langle s^2 \rangle/N$ on the order of 100 A^2, where a repeat unit is equated to a segment. It is anticipated that the freely rotating chain with fixed valence bonds will be a good model for BBB owing to the inappreciable steric interference to rotation about the single bonds connecting the repeat units. Such behavior has been inferred from data on $[\eta]$ versus M for other polymers containing groups in their backbone that tend to reduce hindrance to rotation about intrachain bonds [23, 24]. If we naively use the simple relation

$$\frac{\langle s^2 \rangle}{N} = \frac{b^2}{6} \, \frac{1 + \cos \alpha}{1 - \cos \alpha}$$

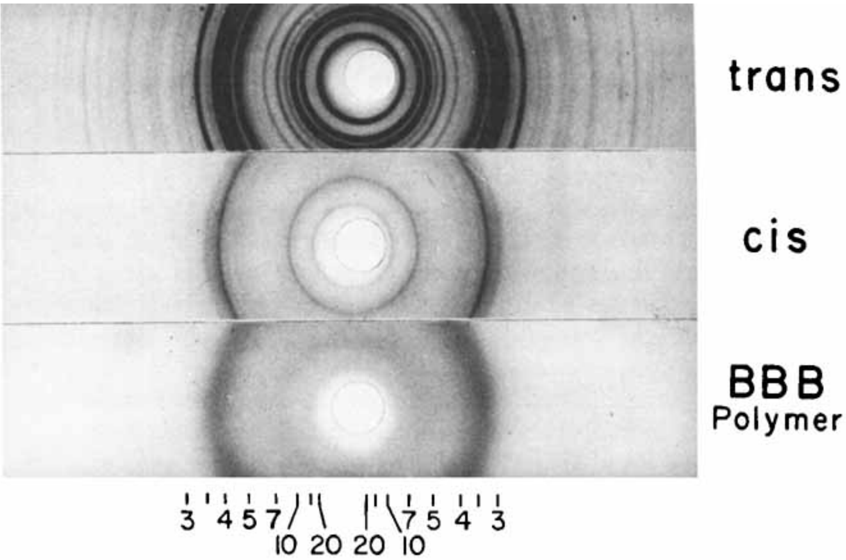


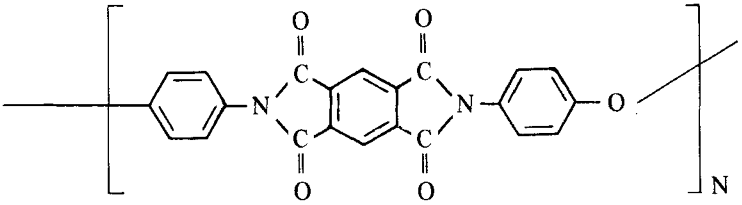
Fig. 7. X-ray powder-scattering patterns for the trans and cis model compounds of the BBB repeat unit and for BBB. The scale indicates Bragg spacings in Angstroms.

applicable for a chain with free rotation about fixed valence bonds of length b which make an angle of π-α with each other, then we obtain $(1 + \cos\alpha)/(1 - \cos\alpha) \simeq 2$ if $b = 18$ Å. Even though these correspond to a reasonable value of b and $\cos\alpha = 1/3$, the model is very crude since neither b nor α can be considered as constant along the chain.

The possibility of intermolecular aggregation must be considered in a discussion of the properties of BBB. For example, the electronic absorption spectra of solutions of BBB in sulfuric acid change markedly when the H_2SO_4 content of the acid is decreased below ca. 92%. This behavior is accompanied by a marked increase in the dependence of the viscosity of dilute solutions on the polymer concentration, resulting in values of the Huggins k' constant greater than unity. In addition, the angular distribution of the scattered light reveals the presence of aggregated species by high intensity in the forward direction and a rapid decrease as the scattering angle is increased. The X-ray diffraction patterns shown in Fig. 7 suggest that aggregation of BBB is also an important factor in the solid state. Thus, the diffraction patterns for the model compounds show them to be crystalline. In particular, the patterns for both model compounds reveal Bragg spacings in the neighborhood of 3.5 Å, which is characteristic of the interplanar separation of aromatic molecules with planar, or nearly planar, symmetry [25, 26]. The polymer is apparently not crystalline, but the diffraction pattern in Fig. 7c shows a diffuse band centered at a Bragg spacing of 3.5-3.6 Å.

It is not surprising that BBB is not crystalline in view of the six structural isomers possible for the repeat unit of the polymer. This spacing is interpreted as evidence for extensive short-range stackings of the repeat units of neighboring BBB chains giving the polymer some of the characteristics of a cross-linked network polymer. This interpretation is similar to that offered in explanation of the diffuse diffraction pattern observed for mixtures of polycyclic aromatic ketones. Thus, it has been shown that some planar polycyclic aromatic ketones that can easily be crystallized alone will not crystallize when mixed, even though they have similar overall size and shape [27]. It can be anticipated that the extra constraints imposed by the bonds connecting the repeat units in the polymer would still further inhibit crystallization. It can be argued that an intermolecular spacing of about 3.5 Å is bound to occur in substances such as BBB simply because of considerations of packing the (nearly) planar repeat units into a dense solid, and that no specific intermolecular bonding need be postulated. The mobility of such a molecular arrangement would still be low because of the interlocking of the repeat units and their relatively large size. It should be noted, however, that neither the trans or cis isomers of the model compounds can be melted to form liquids at atmospheric pressure. Thus, $\Delta H_f/\Delta S_f$ is large, so that the enthalpy of fusion ΔH_f is relatively large or the entropy of fusion ΔS_f is very small (or both). The entropy of fusion may be small because of the tendency of extended molecules to order simply on the basis of geometric arguments [28], but an appreciable value for ΔH_f would not be unexpected for aromatic molecules of this type that can engage in an intermolecular electron-transfer complex [29, 30]. The fact that films can be formed from BBB by rolling, although the polymer will not flow under moderate shear stresses, supports the postulate of extensive interchain coupling; it is presumed that intermolecular bonds are broken and reformed under the influence of the high stresses encountered in rolling.

A similar kind of association may be responsible for the mechanical properties of the polyimide with the (idealized) structure:



Previous studies have suggested that in solution in sulfuric acid [31] this polymer behaves as a chain with nearly free rotation about its valence bonds, but in bulk it exhibits a dynamic modulus that lacks the transition temperatures usually observed for linear flexible chain polymers [32]. Thus, the "10-second modulus" shows only a gradual decrease over the temperature interval 30-450°C, rather than an abrupt decrease over a small temperature span [32], as is usually observed for linear amorphous polymers at temperatures in the vicinity of the glass transition. It was suggested that a small amount of crystallinity was responsible for this behavior, which is similar to the explanation advanced for the properties of BBB. Despite this indication of limited molecular mobility, the polymide is reported to be ductile in elongation, and thus again similar to BBB. In conclusion, it appears that:

1. In dilute solution BBB behaves as a "flexible coil" macromolecule, perhaps with relatively free rotation about the single bond connecting the ling, inflexible, nearly planar, repeat units.
2. A sufficient amount of strong interchain complex formation occurs in the solid state to give the linear, noncrystalline polymer some of the physical properties of a highly cross-linked network polymer.

The model of the solid state of BBB discussed above is different from some others proposed for heterocyclic condensation polymers. For example, the concepts of a material in a glassy state in which molecular mobility is hindered by considerations of volume do not apply, and marked changes in the mechanical properties with variation in temperature are not to be expected. Moreover, the properties of the solid state are not controlled by an inherent long-range chain stiffness according to this model for BBB, but rather by the inflexible planar character of short segments of the chain. It is anticipated that further studies including low-angle X-ray scattering and investigation of the viscoelastic properties of concentrated solutions of BBB will further elucidate the model proposed for BBB.

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Discussion of Paper by G. C. Berry and T. G Fox

Properties of Heterocyclic Condensation Polymers

R. Landel: Dr. Berry, this is certainly a well-organized attack on the problem of relating the behavior of these materials to those of more familiar polymers and you and Dr. Fox are to be commended for your approaches. I have two specific questions: 1) Do you have any indication of the value of the average monomeric friction coefficient for BBB? 2) Have you had a chance to study the viscosity-concentration behavior?

G. C. Berry: Work along these lines is currently underway. Data in hand suggest that η is proportional to $M^{3.4}$ for concentrated solutions. A value for the monomeric friction coefficient will be calculated eventually from such data.

Mitchel Shen: Do you consider these polymer coils as random or helix-type coils? If they are random, do you have an estimate of what the statistically equivalent random link is?

G. C. Berry: We believe that BBB adopts a random coil conformation in dilute solution and that there is probably nearly free rotation about the single bond connecting the inflexible repeat units, which have a length of approximately 17 Å.

J. H. Hodgkin: How do you know that the infrared band at 1660 cm^{-1} is an imide band rather than due to some other structure? Most imide bands in the infrared spectrum are at considerably higher wave numbers.

G. C. Berry: The evidence that the 1660 cm^{-1} band is due to the imide structure is based on the model compound studies of Van Deusen cited in the text.