Unusual Film-Forming Properties of
Aromatic Heterocyclic Ladder Polymers

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Synopsis

A new method of obtaining films of aromatic heterocyclic ladder polymers has been found which circumvents casting from high-boiling acidic solvents. The BBL ladder polymer has been formed into tough, durable films by collecting suspensions of the polymer obtained from acid reprecipitations upon a fritted glass funnel. After drying, the polymer can be removed as film, with thickness dependent upon the amount of material used. Such a film has a tensile strength of 9,600 lb/in.^{2} as compared to a tensile strength of 16,000 lb/in.^{2} obtained from the same polymer when cast from methanesulfonic acid solution.

INTRODUCTION

The current literature reflects a growing interest in the synthesis and properties of aromatic heterocyclic ladder polymers.[1-4] Polymers possessing the complete double-strand structure are predicted[5,6] to be more resistant to degradation than analogously structured nonladder systems. If the advantage of such improvements can be realized, it is anticipated that ladder polymers will be the next generation of high-performance nonmetallic materials.

Although the aromatic heterocyclic ladder polymers are attractive for high-temperature applications, they are soluble only in strongly acidic solvents, which makes processing and/or fabrication difficult. This difficulty is often a major limiting factor in determining usefulness. For example, processing such a polymer by conventional techniques for coating metals would be impossible owing to the corrosive nature of the acidic solvents. This investigation was directed toward learning whether some means to circumvent such problems may be available.

Earlier work in this laboratory[7] on the synthesis of high molecular weight poly[(7-oxo-7,10H-benz[de]imidazo[4′,5′:5,6]benzimidazo[2,1-a]iso-quinoline-3,4:10,11-tetrayl)-10-carbonyl], referred to as BBL (I),
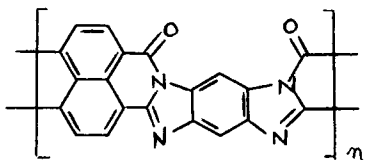
2035

has uncovered a very unusual phenomenon which could give rise to a means for fabricating aromatic heterocyclic ladder polymers more readily. In the case of the BBL ladder polymer, we found that it can be formed into reasonably strong films by filtration and drying after precipitation from acid solution. It was also found that a nonsolvent dispersion of BBL could be spray coated on a variety of substrates. By utilizing this unusual property displayed by the polymer, one is able to obtain films and coatings with relative ease and, very significantly, without residual acid impurities. This unusual film-forming property was also found to be exhibited in other ladder polymers. Our findings on aspects of this film formation comprise the subject of this report.

DISCUSSION

Various methods were used to obtain films of the BBL polymer by means other than casting from solution. The methods were all variations in the deposition of swollen polymer on a substrate and its subsequent removal from the substrate as a film.

The method giving the strongest films to date involves the precipitation and vacuum filtration on a glass frit. Upon drying, the precipitated solids have coalesced to form a tough, durable film having a gold-metallic luster. The film loosens from the glass frit when the suction is released.

Dilute methanesulfonic acid solutions (0.05–0.5%) of ladder polymer were used which gave finely dispersed solid precipitates when added to nonsolvents. The solutions were usually precipitated into methanol; however, other low-boiling nonsolvents such as benzene, ethanol, chloroform, ether, and water were also used. The precipitates were extensively washed with nonsolvent to remove all residual acid prior to film formation. The films which formed upon filtration provided excellent samples for obtaining the infrared spectra of the BBL polymer (Fig. 1).

It is important to note that precipitated BBL is neither isolated nor allowed to dry prior to its use in this type of film formation. It is always kept wet in the nonsolvent slurry before filtering. During filtration, the film being formed is never allowed to dry as it is being built up on the filter. If allowed to dry before all of the slurry is added, changes occur on the exposed surface such that subsequent addition of more slurried polymer does not adhere or coalesce to form a uniform film. Instead, definite layers form where intermittent drying occurs to give rise to permanent layers in the resulting film. When deposition is completed, these layers can be teased or peeled apart with very little difficulty even though cohesion within layers does not seem to be weakened.

Examination of the nature of wet precipitate (slurry) proved to be very interesting. When observed under magnifications up to 500×, we found that the BBL as precipitated is transparent and blue despite the fact that it appears very dark and opaque as normally viewed in the slurry. More unusual, the precipitation process appears to have produced solid polymer in the form of smooth, fragile sheets. These sheets are not rigid
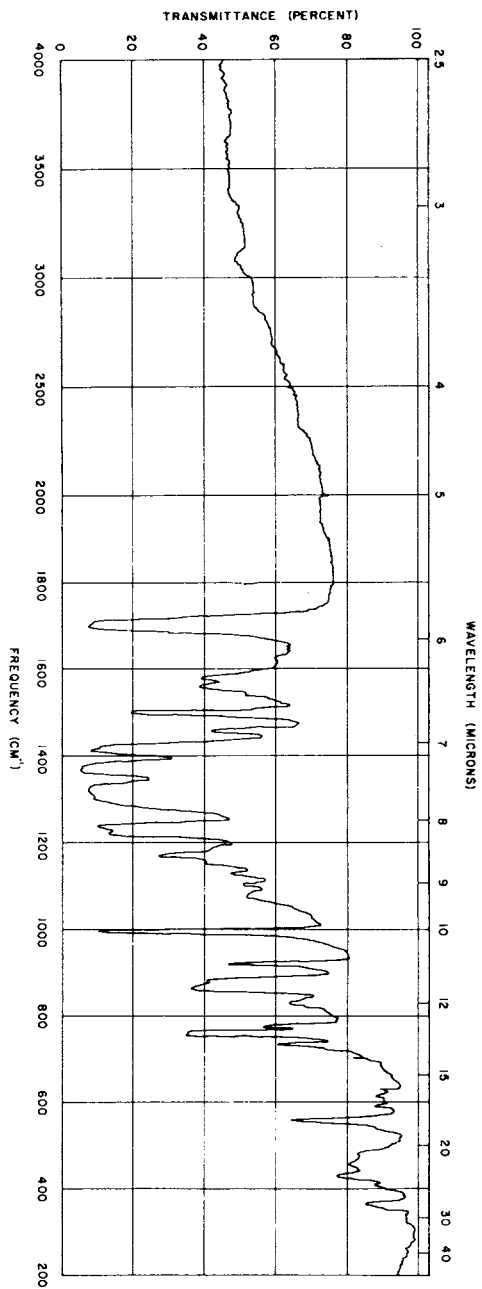
Fig. 1. Infrared spectrum of BBL polymer (film).

but readily undergo fragmentation during rinsing and stirring. Despite folding and wrinkling, the two-dimensional (sheet-like) character is clearly evident. There is a resemblance to torn pieces of tissue paper immersed in a liquid, except that edges of the polymer fragments do not appear ragged. Although they are irregular, they appear smooth as if cut or broken instead of being torn.

The sizes of fragments or sheet-like particles of polymer found in the slurry are dependent upon the initial concentration of polymer solution used in the precipitation and on the method of mixing a nonsolvent with the solution. When the acid solution is dilute (e.g., about 0.1%) and the method of stirring is with a magnetic stirring bar, the resulting sheet-like forms measure 50–150 microns across. Vigorous agitation, such as achieved with a blender, tends to break up the material into smaller pieces.

Deposition of BBL on substrates such as a metal surface was also accomplished. Film-like coatings were obtained by spraying swollen polymer precipitate dispersed in volatile nonsolvents. A simple apparatus of conventional makeup was put together to force the dispersion through a small orifice under pressure. A simple atomizer was used in some cases. With quick-drying nonsolvents such as ether or methanol, the thickness of polymer could be built up on a target substrate by alternately spraying and allowing the volatile nonsolvent to evaporate. Best results were obtained when complete drying was prevented, i.e., allowed to dry only enough to result in the laying down of solid to prevent running. In some cases, polymer dispersions were sprayed onto glass plates to a desired thickness and allowed to air dry. After drying, the coating appeared as a gold mirror when viewed through the back surface on the glass plate. These could be removed as films by immersing the plates into anhydrous methanol. Layers of polymer could be built up by heating the glass plates with a hot-air gun while spraying to promote intermittant drying. The dispersions used were obtained from dilute acid solutions (0.05%) in order to obtain particles that would not obstruct the atomizer when sprayed.

In general, the strength of the films varied according to the way in which they were prepared. The films formed by filtration were stronger than those formed by spraying. The greater strength of the films formed by filtration on the glass frits could be due to the compressive forces applied through suction. Unlike the sprayed films, the suction filtration exerted pressure on the film during both the final deposition and the drying cycles. This surely aided by compacting the solid and may have produced other desirable effects depending upon the mechanism of film formation.

Film strength was also a function of the intrinsic viscosity of the polymer sample used. Films produced from polymer having intrinsic viscosities below 1.5 were noticeably brittle. The limiting molecular weight in order to accomplish film formation for BBL was represented by a solution viscosity of about 0.5 dl/g in methanesulfonic acid. Films formed from lower polymers could not withstand ordinary creasing.

FILM COMPARISONS

Since films of BBL could also be cast from methanesulfonic acid, a comparison between properties of cast film and those prepared by filtration was made. The BBL used for the formation of both types of film had an intrinsic viscosity of 5.2 in methanesulfonic acid. The cast films were obtained from polymer dissolved in methanesulfonic acid where this acid solvent was removed in a sublimator at 60°C under a reduced pressure of 0.03 mm. The film obtained from filtration (Table I) was of lower density, strength, and initial modulus than the cast film. Nevertheless, the strength is higher than might be expected in view of the high porosity suggested by the low density value.

The surfaces of the two types of films are quite different when viewed through an electron microscope. Photomicrographs of both films were
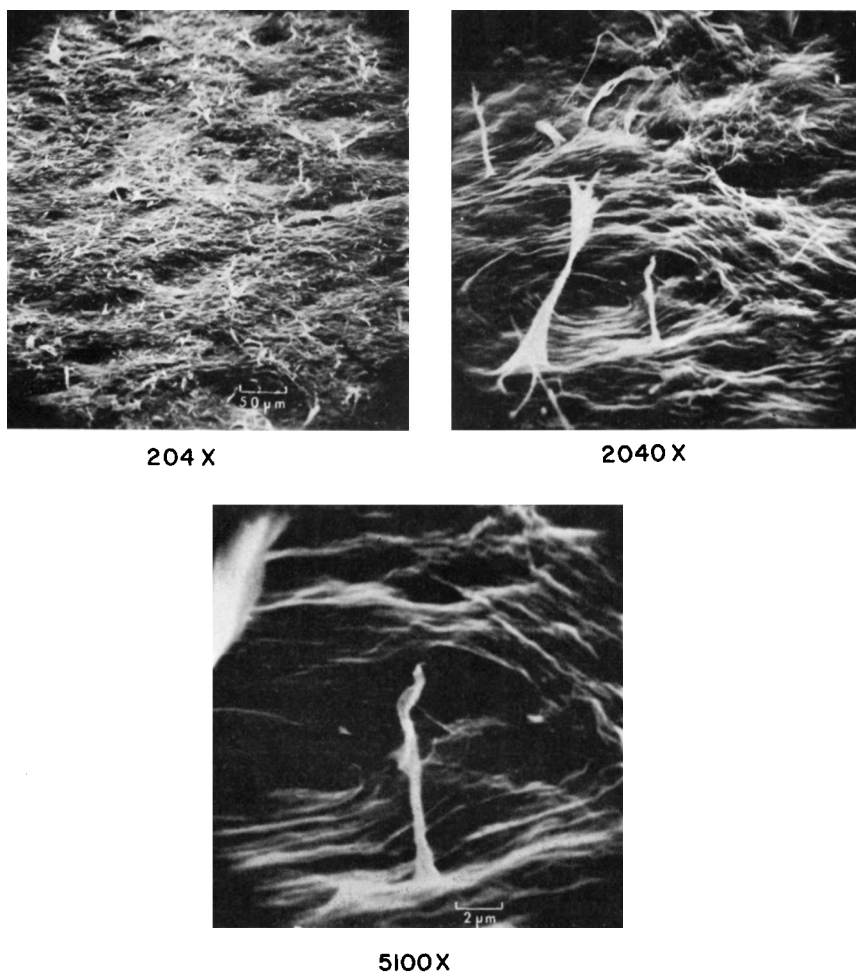

204 X

2040 X

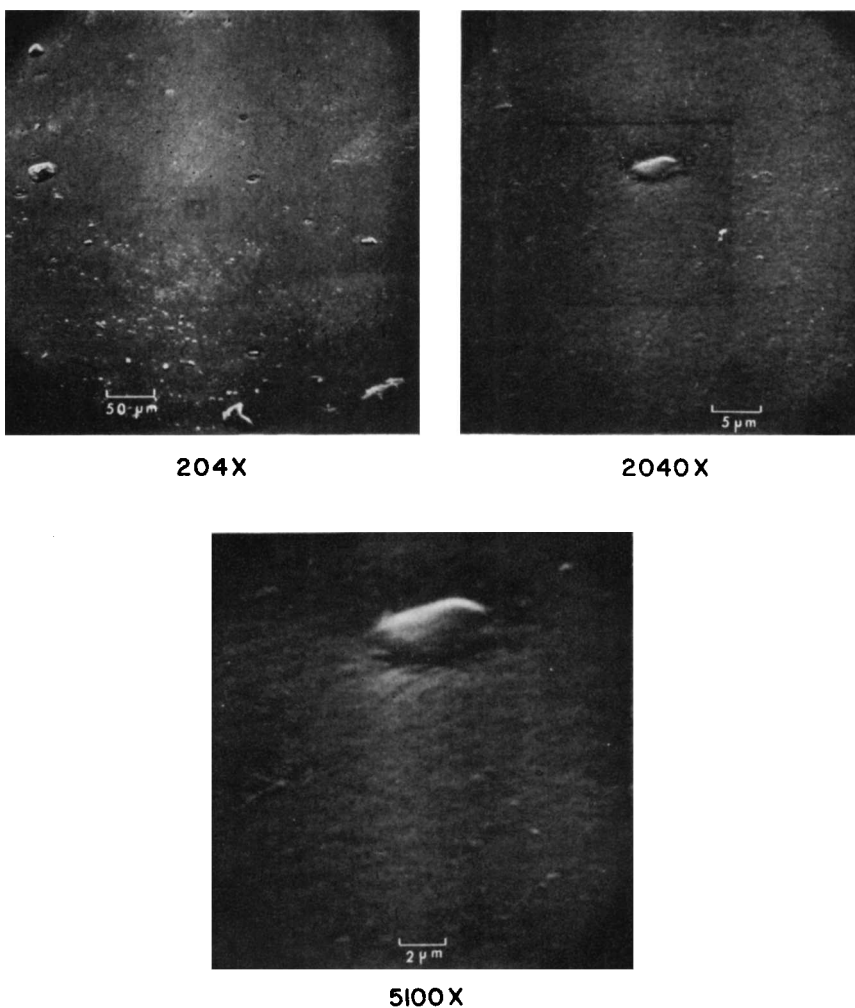5100 X

Fig. 2. Photomicrographs of filtration film at 204×, 2040×, and 5100×.

204X

2040X

5100X

Fig. 3. Photomicrographs of cast film at 204×, 2040×, and 5100×.

taken at 204×, 2040×, and 5100× magnification. The surface of the filtration film (Fig. 2) is rough, showing a great deal of irregularity as opposed to that of the cast film (Fig. 3), which is smooth and almost void of surface structure. The smoothness observed for the cast film is consistent with the high metallic sheen and reflection of light it exhibits.

As might be expected, the amount of surface structure or lack of smoothness was found to be dependent in part upon the smoothness of the surface on which the film was deposited. The size of the particles of dispersed solid used was also found to be a factor. Figures 4 and 5 show the photomicrographs of both sides of a film deposited by the spraying method. The side facing the glass plate substrate (Fig. 4) exhibited a bright, metallic sheen comparable to the high sheen of a cast film, and the appearance of its
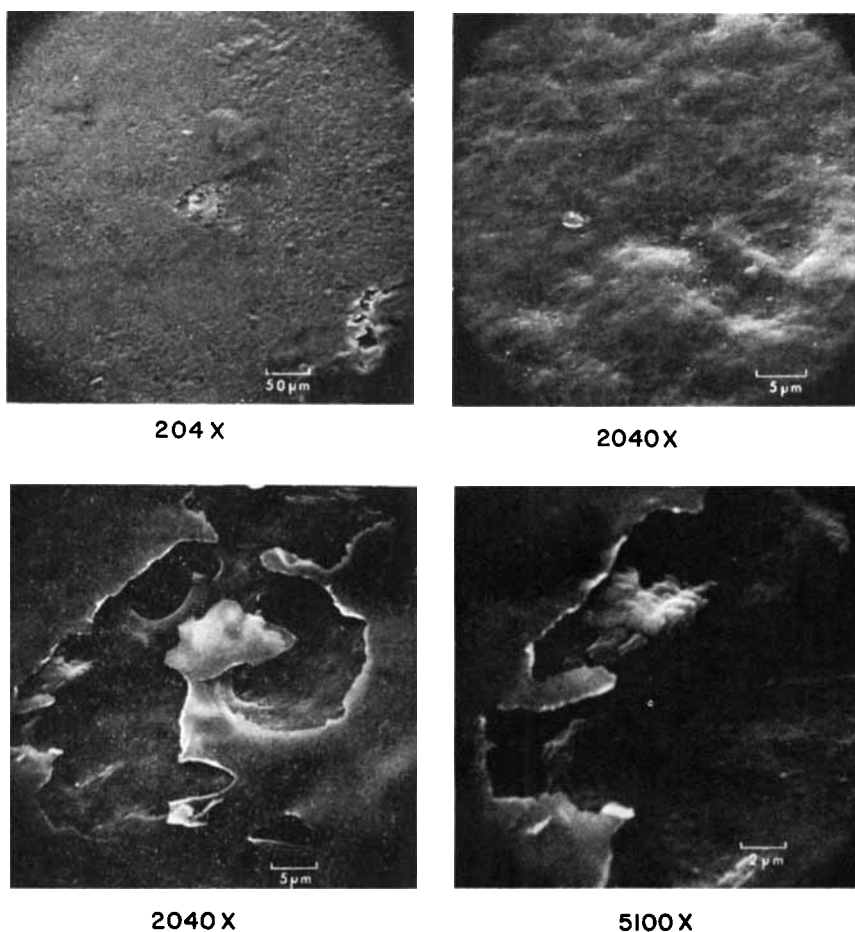
204 X

2040 X

2040 X

5100 X

Fig. 4. Photomicrographs of sprayed film (side facing glass) at 204×, 2040×, and 5100×.

surface in the photomicrograph was much like that of a cast film. The opposite side of the film (Fig. 5) proved to be dull by comparison and resembled the photomicrographs of the film formed on the glass frit. Nevertheless, there was less surface irregularity than in frit-formed films

TABLE I
Properties of Films[a]

Film type	Density, g/cm³	Tensile strength, lb/in.²	Rupture elongation, %	Initial modulus, lb/in.²
Cast from solutions	1.31	16,600	2.9	1.1×10^6
Filtered precipitate	0.94	9,600	2.8	0.53×10^6

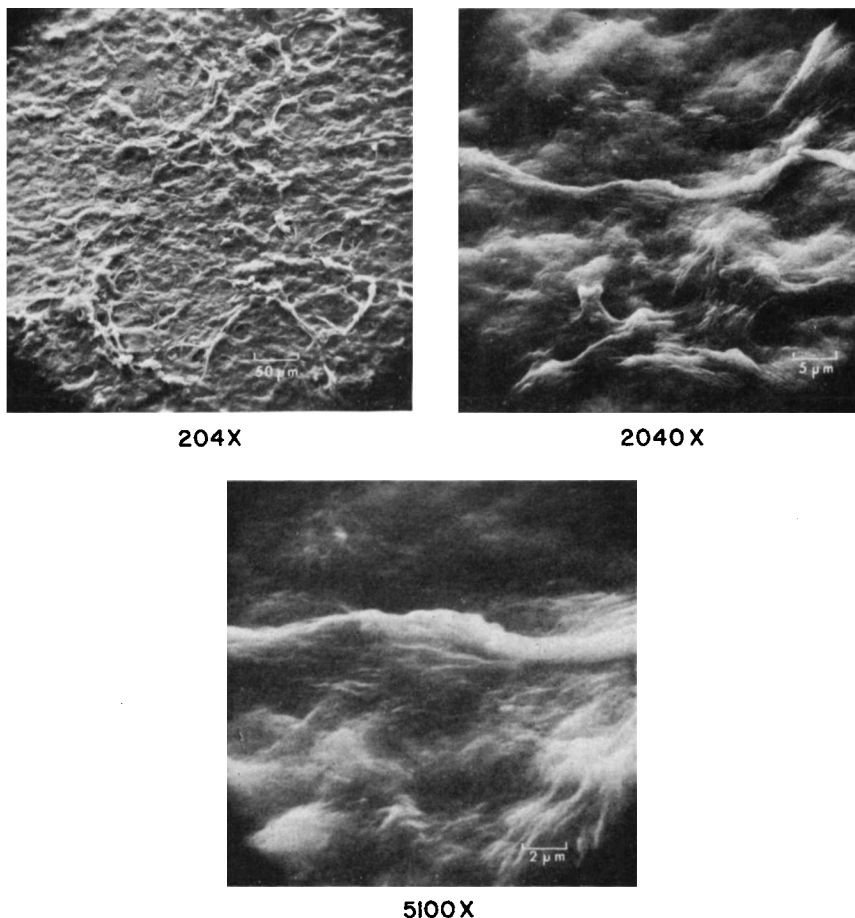[a] Film thickness was from 0.3 to 1 mil average; tensile data obtained on a Instron/ 1 in. G.L./0.2 in. per min.

204X

2040X

5100X

Fig. 5. Photomicrographs of sprayed film (side opposite glass) at 204×, 2040×, and 5100×.

since the sizes of the particles sprayed were smaller by intention. Noticeable differences in filter films were also observed when frits of varying porosities were used for deposition of the swollen polymer particles. The greater the porosity, the more evident was the surface structure. From the exposed cross-sectional area of the sprayed film (Fig. 4), one can see evidence that it is made up of multiple layers of polymer. This is the result of spraying and drying consecutive coatings.

X-Ray diffraction studies[8] on the BBL polymer have shown it to exhibit Bragg spacings at 3.45 and 7.5 Å. The scattering is the result of orientation derived from the high degree of ordered packing of the material. The spacings were present in both film samples, with the intensity of scattering an order of magnitude stronger for the film formed from polymer precipitate than for the film cast from methanesulfonic acid solution. It seems apparent that the precipitation process from which the slurry of two-

dimensional sheet-like solid material is obtained is associated with ordered packing of the polymer chains.   However, it is not as yet clear as to what role, if any, the collecting and compressing of the solid during filtration plays with regard to orientation of polymer molecules.   Conceivably, two different kinds of orientation or molecule arrangement could be involved, one manifested as a part of the precipitation from solution while the other could come into effect as a result of the filtration process.

RELATIONSHIP OF STRUCTURE TO FILM FORMATION

To better formulate some qualitative mechanism for the film formation, additional information was sought.   Other aromatic heterocyclic polymers were examined to permit comparisons from a structural point of view.

The nonladder poly(6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',2'-j]-benzo[1mn][3,8]phenanthroline-3, 12-diyl), referred to as BBB (II),
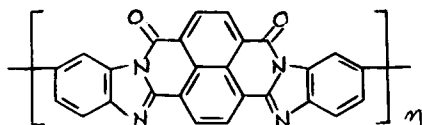
was an ideal polymer to examine since one could compare the behavior of BBL ladder structure to the very similar nonladder BBB structure. BBB is prepared[9] by methods analogous to those used for BBL, but instead of employing 1,2,4,5-tetraaminobenzene as the tetramine monomer, 3,3'-diaminobenzidine is used.

When dilute methanesulfonic acid solutions (0.05% to 0.3%) of BBB are precipitated in methanol, tiny globular particles of solid are formed. Washing and collecting this precipitate on a glass frit as described above for BBL produces a filter cake which cracks and crumbles as drying occurs. No film is obtained.   When concentrations of 0.4% or higher are precipitated, polymer solid in the form of red, transparent sheets is obtained. This material when collected on a frit does show tendencies for film formation.   The polymer does not crumble as a cake when it dries, but it does shrink away from the outer edges of the frit.   We noted also that when BBB was sprayed onto a glass plate, a metallic gold coating was formed; but when this was immersed in methanol to separate the coating as a film, it cracked into several tiny pieces.

By considering model forms of the BBL chain structures, one expects that this ladder polymer closely resembles a rigid rod.   There is very little opportunity for bending or twisting except where cyclization to completely fused ring structure has not been accomplished as previously discussed.[7]   On the other hand, the nonladder BBB backbone incorporates a single bond link in the chain between each unit structure which can produce kinks in the chain of up to about 75 degrees, depending upon the specific unit structure isomers being linked and the way units are rotated with respect to each other.   Although highly unlikely, it would be
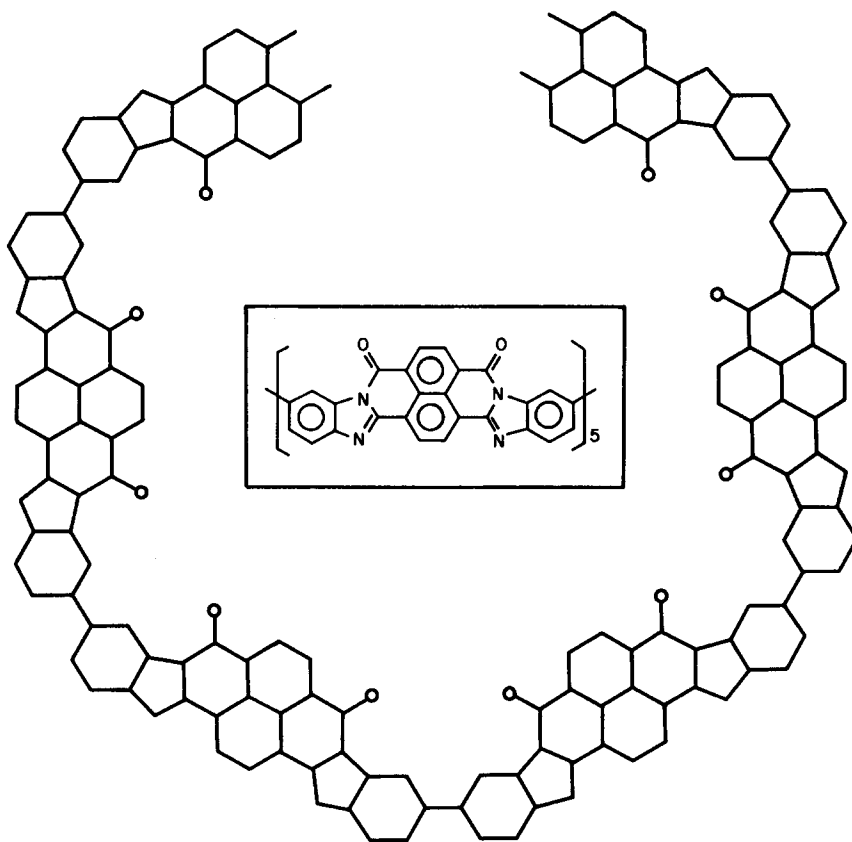
Fig. 6. Diagrammatic example of BBB loop.

possible in the extreme for a segment of BBB chain to loop back upon itself within a distance of about six unit structures (Fig. 6). To put this into context, the mole weight for a BBB unit structure is slightly above 400. A number-average molecular weight above 40,000 is not unreasonable[10] for the BBB samples we use. Such a polymer can therefore be expected to have more than 100 single-bond links in an average chain. A comparable molecular weight for a BBL polymer represents an entirely different case, since there should be no single-bond links in the chains. Nevertheless, the previous work in this laboratory on BBL supports the idea that some few single-bond links are present in the fused-ring heterocycle structure as imperfections, but that there are probably no more than two per chain.[7] Even this chain structure with imperfections (either an aromatic imide or imidazole link) does not give rise to kinks in the chain that approach the angle magnitudes of those to be expected in BBB.

Some comparisons of structure can be made by noting the drawings in Figures 7 and 8. Imide and imidazole structures would give rise to small out-of-plane chain bends but would not incorporate the in-plane kinks

COMPLETELY CYCLIZED BBL

BBL WITH BENZIMIDAZOLE IMPERFECTION
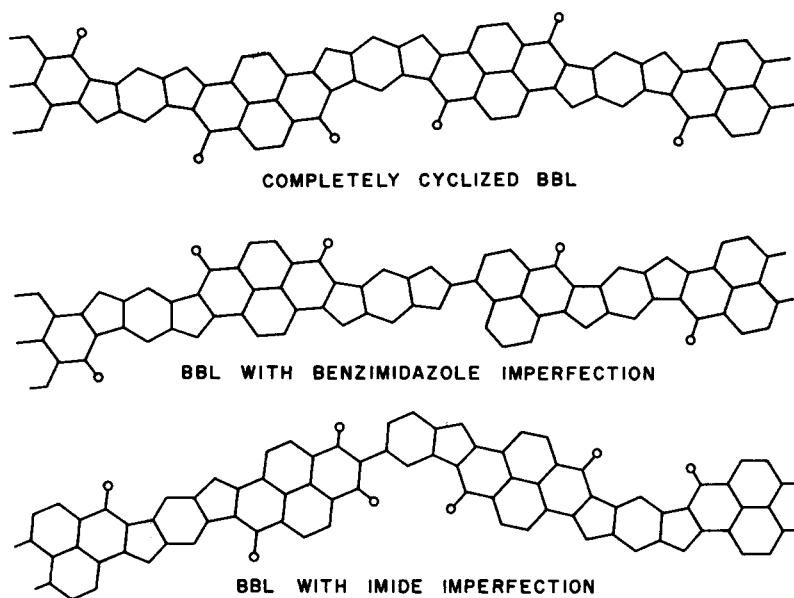
BBL WITH IMIDE IMPERFECTION

Fig. 7. Diagrammatic example of BBL chains.

that can be expected for BBB chains. These considerations which tend to negate possibilities that BBB is rod-like are now being born out by experimental data.[10]

Certain deductions can be made by comparing the BBB and BBL polymers. Both materials precipitate in the two-dimensional form of sheets. The ladder polymer BBL must surely have extended chain structure and on drying has relatively little tendency (capability) to shrink. BBB, on the other hand, with its backbone containing many single bonds, is able to coil in a nonsolvating environment to make shrinkage much more pronounced. In BBB, most of the stress of shrinkage is probably relieved by cracking at periodic intervals, and this of course is very detrimental to film formation.

Attention was also turned to aromatic heterocyclic ladder polymers other than BBL. Due to complexities in their synthesis, ladder polymers are not reported extensively in the literature, and in addition they are generally difficult to obtain in high molecular weight. In our laboratories, a novel ladder polymer consisting of alternating BBL and diquinoxalpyrene units (III) had been prepared[11] with intrinsic viscosities of up to 1.2:
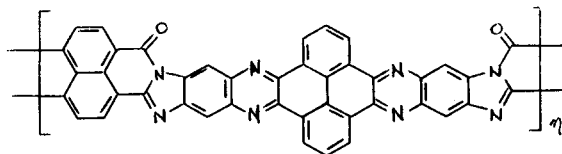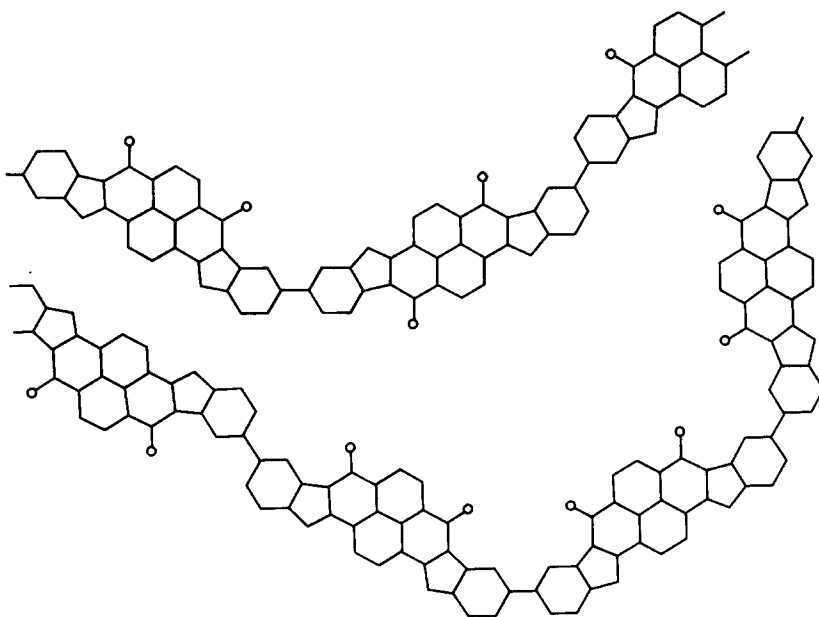
Fig. 8. Diagrammatic example of BBB chains.

The polymer was obtained from the condensation of tetraaminodiquinoxal-pyrene and 1,4,5,8-naphthalenetetracarboxylic acid in PPA. It was found that such a ladder structure also precipitates from dilute methane-sulfonic acid solution in the form of sheets, as above. They are red and transparent. When the precipitate was collected and dried on a glass frit, a film with a metallic silver luster was formed. Films could also be obtained by spray deposition onto a glass plate and immersing the coated plate into methanol. The films from this ladder polymer were not as strong as the BBL films, most likely because of a lower molecular weight of the new polymer.

A sample of polyfluoflavine (IV) having an inherent viscosity in methane-sulfonic acid of 2.5 was obtained from Prof. C. S. Marvel, University of Arizona:
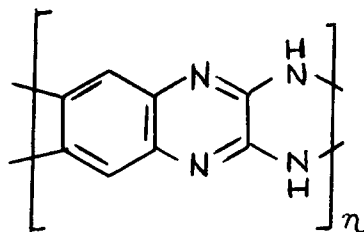
This ladder polymer was prepared[12] from the A-B polycondensation of 2,3-dihydroxy-6,7-diaminoquinoxaline hydrochloride in PPA. Transparent blue sheets were observed on precipitation of this polymer from

methanesulfonic acid, and when processed in the above manner it formed gold films much like the color of the BBL films.

The results obtained above in our examination of film-forming properties for the various ladder and nonladder polymers appear to be consistent. Thus, within the limits of the types of polymers investigated, it can tentatively be concluded that aromatic heterocyclic ladder polymers of sufficiently high molecular weight will form films from the solid phase. The limits of molecular weight are difficult to define since no molecular weights have been determined for polymers I, III, and IV and solution viscosity determinations are not a direct measure of molecular weights. Film formation is also surely dependent upon the extent of perfection in the ladder chain structure. Incomplete cyclization resulting in single links would enable the polymer chain to coil and thus undergo excessive shrinkage upon drying to hinder film formation. The fact that a material precipitates in thin sheets rather than a globular form must also play an important role.

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