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F. E. ARNOLD
R. L. VAN DEUSEN

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. R. L. Van Deusen, Project Scientist.

This report covers work conducted in this Laboratory from April 1967 to March 1968.

The work was supported, in part, by Air Force Materials Laboratory Director's Discretionary Funds.

This technical report has been reviewed and approved.

R. L. Van Deusen

R. L. Van Deusen
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The ladder polymer, BBL, has been formed into thin films by collecting suspensions of the polymer obtained from acid reprecipitations upon a fritted glass funnel. After drying, the polymer can be removed in the form of a film with thickness dependent upon the amount of material used. The film can be freely handled and very advantageously used for obtaining infrared spectra. 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. The films are dark with an intense golden luster which gives the appearance of a metal foil. Other aromatic heterocyclic polymers were examined to compare film formation with molecular structure.

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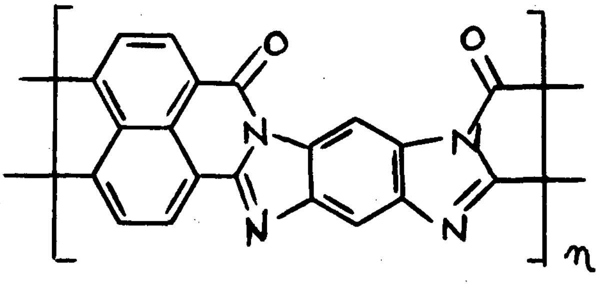
INTRODUCTION

The current literature reflects a growing interest in the synthesis and properties of aromatic heterocyclic ladder polymers (Reference 1 through 4). Polymers possessing the complete double strand structure are predicted (References 5 and 6) to be more resistant to degradation than analogously structured nonladder systems.

Although the aromatic heterocyclic ladder polymers are attractive for high temperature applications, they are soluble only in strongly acidic solvents which makes their 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 due to the corrosive nature of the acidic solvents. Nevertheless, results of this investigation indicate that some means to circumvent this problem may be available.

Results of an in-house research investigation (Reference 7) on the synthesis of high molecular weight poly [7-oxo-7_H_, 10_H_-benz [de] imidazo[4', 5':5, 6] benzimidazo [2, 1-_a_] isoquinoline-3, 4:10, 11-tetrayl-10 carbonyl], referred to as BBL (I), has uncovered a very unusual phenomenon which could make aromatic-heterocyclic ladder polymers more amenable to fabrication. The BBL ladder polymer can be formed into tough, durable films upon 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 of the polymer one is able to obtain films and coatings with relative ease and without residual acid impurities. Aspects of this unusual film-forming property of



Structure I

BBL also seems to be inherent in other aromatic heterocyclic ladder polymers.

With regard to problems being encountered or anticipated in the applications of high temperature nonmetallic materials, ladder polymers which are of interest due to their high thermal stabilities have been found to be polyheterocycles with highly fused ring systems. Unfortunately the fused and highly aromatic nature of these ring systems which give them their exceptional stability tend to render them intractable. The predicament this presents when one considers applications is obvious, and compromises are sought which usually involve tradeoffs of stability for processability. Compromises often entail the alteration of polymer structure in order to improve processability even at the expense of much desired thermal stability. Another approach to the problem is to modify an existing method of processing in the hope that loss of thermal stability can be avoided. Furthermore, in any attempt to solve a fabrication problem the practicability of processing methods must be born in mind continually. Processes requiring extraordinary conditions are seldom accepted as feasible. With respect to this, the best solution processability problems would probably be the development of some new method for handling thermally stable materials which would require relatively mild conditions but not require a compromise of stability.

The work on BBL described here is an approach along the line of establishing new and facile methods for fabricating complex ladder polymers without having to sacrifice thermal stability as a result of structural alterations or chemical impurities. Discussed are the first steps taken toward obtaining film of BBL ladder polymer under unusually mild and practical conditions.

SECTION II

DISCUSSION AND RESULTS

A. SYNTHESIS AND PROPERTIES OF BBL

Earlier work in this Laboratory has shown that the ladder polymer BBL (I) can be prepared from the polymerization of 1, 4, 5, 8-naphthaline tetracarboxylic acid with 1, 2, 4, 5-tetraaminobenzene in polyphosphoric acid (PPA). The polymer is completely soluble in methane sulfonic acid, exhibiting intrinsic viscosities as high as 6.0. Thermal properties of this material are excellent, showing initial weight loss by thermogravimetric analysis at 550 and 700°C in air and in nitrogen respectively. Isothermal aging of the polymer at 370°C in air shows weight loss of only 10-15% after 500 hrs. Poor quality fibers have been spun from methane sulfonic acid, but reasonably good films have been cast from methane sulfonic acid, although the low vapor pressure of this solvent make casting generally impractical.

Work with BBL in our laboratory has also led to the discovery of a rather unique property for this polymer and possibly for other ladder or semi-ladder polymers. This is the tendency for the polymer slurries to form films when collected during the removal of nonsolvent; this differs greatly from the usual techniques of casting from solutions.

B. METHODS OF OBTAINING FILMS

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 by 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 methane sulfonic acid solutions (0.05-0.5%) of ladder polymer were used which gave finely dispersed solid precipitates. These 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 whichever nonsolvent was being used to remove all occluded acid prior to film formation. The films which formed upon filtration provided excellent samples for obtaining the infrared spectra of the BBL polymer (Figure 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 filter cake or film to be 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 at the exposed cake surface such that subsequent addition of more slurried polymer does not adhere or coalesce to form a uniform film. Instead, definite layers form if intermittent drying occurs which 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. In this sense the dried surface can be thought to be deactivated. Once exposed it cannot be built up further. Contrarily, BBL freshly precipitated from methane sulfonic acid can be considered active, and keeping it wet is a requirement for uniform film formation.

Examination of the nature of wet precipitate (slurry) proved to be very interesting. When observed under magnifications up to 500X 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 but readily undergo fragmentation during rinsing and stirring. Despite folding and wrinkling the two-dimensional (sheetlike) 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 appearance of freshly precipitated or active BBL is such that it does not stretch the imagination to visualize these thin, sheetlike pieces of material being laid down to form a fairly uniform, compact mass upon filtration.

The sizes of fragments or sheetlike 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 sheetlike forms measure from 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 subtrates such as a metal surface was also accomplished. Filmlike coatings were obtained by spraying active, 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 of 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 intermittent 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.

Another variation in polymer deposition utilized concentrated acid solutions of about 1.0 to 2%. These were "doctored on" to glass plates and the coated plates were immersed in anhydrous methanol to cause the precipitation of the polymer. The specimen appeared to be continuous films on the glass. After leaching the films free of acid by several washes in methanol, the glass plates were air dried. These coatings took on a gold luster when dry and could be separated from the plates by immersing again into methanol or warm water.

The thicknesses of the resulting films were dependent upon the concentration of polymer in the initial acid solutions.

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, and both of these types were much stronger than the films formed by doctoring techniques. 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 other four methods, the suction filtration exerted pressure on the film during both the final deposition and the drying cycles. This surely aided in achieving film strength, 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 needed to accomplish film formation for BBL was represented by a solution viscosity of about 0.5 dl/g in methane sulfonic. Films formed from lower polymers could not withstand ordinary creasing.

C. FILM COMPARISONS

Since films of BBL could also be cast from methane sulfonic acid, a comparison between properties of cast film versus 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 methane sulfonic acid. The cast films were obtained from polymer dissolved in methane sulfonic acid where this acid solvent was removed in a sublimator at 60°C under a reduced pressure 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 as viewed through an electron microscope. Photomicrographs of both films were taken

TABLE I

PROPERTIES OF FILMS

Type[a] Film	Density g/cm³	Tensile Strength[b] lbs/in²	Rupture Elongation %	Initial Modulus lb/in²
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 ml average.
b. Tensile data obtained on a Instron / 1 inch G.L. /0.2 inch per min.

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

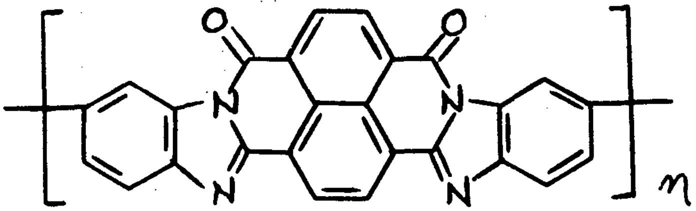
As might be expected, the amount of surface structure or lack of smoothness was found to be dependent in part upon the smoothness of the surface on which the film was deposited. The size of the particles of dispersed solid used was also found to be a factor. Figures 4 and 5 show the photomicrographs of both sides of a film deposited by the spraying method. The side facing the glass plate substrate (Figure 4) exhibited a bright metallic sheen comparable to the high sheen of a cast film and the appearance of its surface in the photomicrograph was much like that of a cast film. The opposite side of the film (Figure 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 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 (Figure 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. It should be noted that films composed of very definitely defined layers could be prepared by allowing the surface of the collected film to dry before adding more wet polymer to thicken it. After it has been dried the polymer surface no longer retains its activity or ability to form film with uniform cohesiveness.

X-ray diffraction studies (Reference 8) on the BBL polymer have shown it to exhibit Bragg spacings at 3.45 and 7.5A. 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 methane sulfonic 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 molecular 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.

D. 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-dioxobis-bensimidazo [2, 1-b:1', 2'-j] -benzo [lmn] [3, 8] phenanthroline-3, 12-diyl) (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 (Reference 9) by methods analogous to those used for BBL, but instead of employing 1, 2, 4, 5-tetraaminobenzene as the tetramine monomer, 3, 3'-diaminobenzedine is used. The polymer has been prepared in high molecular weight and is in the development state (Reference 10) as an Air Force high temperature fiber.



Structure II

Dilute methane sulfonic acid solutions (0.05 to 0.3%) of BBB are precipitated in methanol and 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 are obtained. This material when collected on a frit does show tendencies for film formation. The polymer cake film does not crumble when it dries, but shrinks 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.

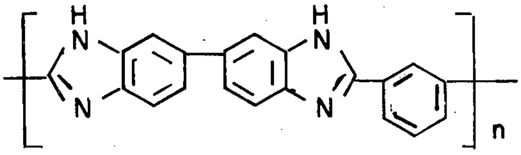
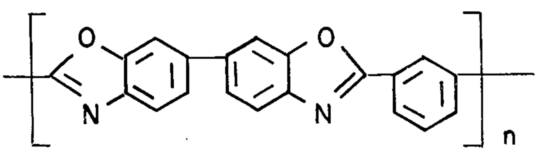
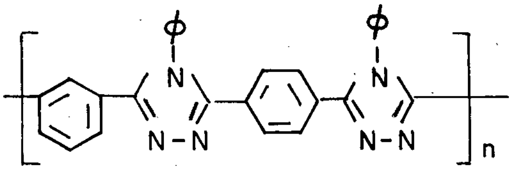
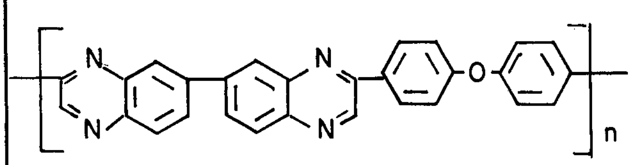
By considering model forms of the BBL chain structure, one expects that this ladder polymer closely resembles a rigid rod. There is very little opportunity for bending or twisting except where cyclization to completely fused ring structure has not been accomplished as previously discussed (Reference 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 notated with respect to each other. Although highly unlikely, it would be possible in the extreme for a segment of BBB chain to loop back upon itself within a distance of about six unit structures (Figure 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 (Reference 11) 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. It was found that there are probably no more than two per chain present (Reference 7), however. Even this chain structure with imperfections (either an aromatic imide or imidazole link) does not give rise to kinks in the chain which approaches the angle magnitudes of those you would expect for BBB chains. 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 inplane kinks that can be expected for BBB chains. These considerations which tend to negate possibilities that BBB is rodlike are now being born out by experimental data (Reference 11).

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.

Other nonladder aromatic heterocyclic polymers which were examined in this work were polymers containing imidazole, oxazole, N-phenyl triazole, and quinoxaline ring structures. Table II shows the structures, viscosities, and references for their preparation. The samples were obtained from Dr. G. F. L. Ehlers and Dr. T. E. Helminiak, both of our laboratory. The polymers were precipitated from methane sulfonic acid at a concentration of 0.5 to 1% into anhydrous methanol. The materials did not precipitate in the form of two dimensional sheets as noted above for ladder polymers. At lower concentrations the precipitates were in a particular or globular form and at higher concentrations in a form appearing to be fibrous in nature. None of the four polymers showed tendencies to form solid-phase films as did the sheetlike precipitates of BBL.

TABLE II

OTHER NONLADDER AROMATIC HETEROCYCLIC POLYMERS EMPLOYED

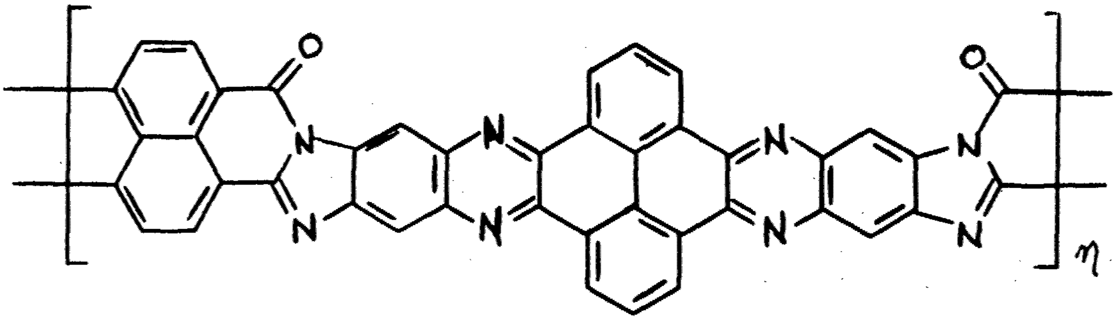
Structure	Viscosity	Reference
	$[\eta] = 0.8$	12
	$\{\eta\}^{a} = 1.2$	13
	$\{\eta\}^{b} = 1.1$	14
	$\{\eta\}^{c} = 1.6$	15

a. Inherent viscosity taken in sulfuric acid (0.5% solution at 30°C).

b. Inherent viscosity taken in formic acid (0.5% solution at 30°C).

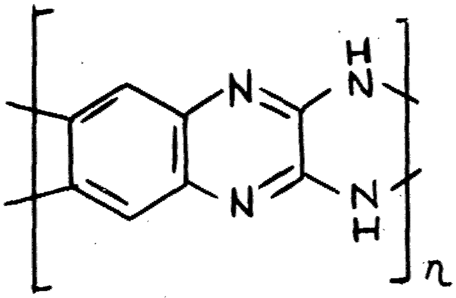
c. Inherent viscosity taken in hexamethylphosphoramide (0.3% solution 30°C).

Attention was then 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 (Reference 6) with intrinsic viscosities up to 1.2. The polymer was obtained from the condensation of tetraaminodiquinoxalpyrene and 1,4,5,8-naphthalinetetracarboxcyclic 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.



Structure III

A sample of polyfluoflavine (IV) having an inherent viscosity in methane sulfonic acid of 2.5 was obtained from Dr. C. S. Marvel, University of Arizona. This ladder polymer was prepared (Reference 7) from the A-B polycondensation of 2,3-dihydroxy-6,7-diaminoquinoxalines hydrochloride in PPA. Transparent blue sheets were observed on precipitation of this polymer from methane sulfonic acid and, when processed in the above manner, formed gold films much like the color of the BBL films.



Structure IV

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 all 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.

E. LADDER POLYMERS AS POTENTIAL HIGH TEMPERATURE COATINGS

It was realized that the uniqueness by which ladder polymers can be deposited on surfaces might offer an approach to circumvent various processing problems encountered with high temperature polymers. Instead of laborious removal of any of the high boiling solvents required to dissolve aromatic-heterocyclic polymers in order to prepare coatings, polymers with ladder structure could be sprayed to obtain coatings. This could be done over large surface areas of substrates without being confined to oven dimensions. Currently the processing of any ladder type polymer as a coating presents a difficult problem since such materials are only soluble in strong acidic solvents which are corrosive to most metallic surfaces. By the development of a solid phase technique all traces of acid could be removed prior to polymer deposition and solvents (actually polymer nonsolvents) which are volatile at room temperature could be used.

To follow-up this possibility, a scouting effort was undertaken to gain some preliminary information on the coating capabilities of the BBL polymer. It was found that BBL could be deposited on a variety of metallic substrates by either spraying a polymer slurry or successively dipping a substrate into a nonsolvent dispersion containing 60% solids. Metallic substrates that were coated were copper wire, titanium 8Al-1MO-1V, 304 stainless steel, and aluminum.

Adhesion of the coatings on metals was inspected by the standard tape test (Reference 14) and found to be poor. This was disappointing, but the extent of our work was not adequate enough to eliminate all possibilities. The adhesive bond strengths of ladder polymers to substrates presents a challenging problem both to the coating and synthetic polymer chemists. It may be feasible to devise ladder polymer systems in which units having good adhesive properties can be incorporated into the ladder backbone. Secondary low temperature reactions such as chelation may be applicable for bonding polymer to substrate where a nonsolvent could be employed as the ion carrier.

Adhesion of BBL polymer to substrates was increased substantially by the introduction of commercially available "Skybond 700" (a prepolymer curable to an aromatic polyimide) to the coatings. The Skybond 700 was dissolved in methanol and this solution was used as the nonsolvent with precipitated BBL. Various mixtures of Skybond 700 to BBL were sprayed then cured at 400°F for 3 hrs. Along with the metallics a Teflon substrate was also sprayed in an effort to obtain film by which the curing step could be followed spectroscopically. The infrared spectra of the films before and after the curing step are shown in Figure 9. Infrared absorption bands due to the presence of the prepolymer (uncured) were essentially concealed by intense absorptions of the excess BBL. As the films were thermally cured, the absorption bands at 4.5 and 5.6 μ appeared, characteristic of the imide carbonyl (Reference 11). Introduction of an amount as small as 10% of Skybond 700 into the coating resulted in good adhesion to the metallic surfaces. Although adhesion was good, the fact that the coating had to be at relatively high temperatures detracted from the processing advantages offered by the room temperature deposition technique.

It was also determined that films and coatings could be prepared with polymers other than Skybond 700 even though they were not soluble in the nonsolvent. Nonladder polymers such as BBB and PBI were dissolved in methane sulfonic acid along with BBL and coprecipitated with BBL into methanol. The codispersions of polymers were washed free of acid and deposited as above by filtration or spraying. Film formation occurred with both coprecipitates

(BBL-BBB and BBL-PBI) with as high as 50 weight percent of the nonladder polymer present. Coatings could also be obtained by spraying the coprecipitates; however, adhesion to the substrates was relatively poor.

The two-component films obtained by filtration gave excellent infrared spectra (Figures 10 and 11) showing the characteristic absorptions of both polymeric components. By comparison a cast film prepared from methane sulfonic acid containing 50% PBI and 50% BBL gave similar infrared spectra (Figure 12). The ratio of intensities for the N-H stretching vibration at 3.2μ of PBI to the 5.9μ carbonyl absorption of BBL were approximately the same for both types of films. This similarity to a cast film would tend to indicate that the PBI is evenly dispersed in the film prepared in the solid phase.

Since BBL is insoluble in sulfuric acid, the two-component films were leached with sulfuric acid in an attempt to remove the soluble nonladder polymers. After the acid treatment, the appearance of the BBL/PBI film had changed from bronzelike to goldlike, whereas the gold luster of the BBL/BBB film did not seem to change. No traces of either BBB or PBI were observable by the electron microscope; however, any effects due to the selective dissolution and removal of the nonladder materials were not discernible. This is probably because the BBL surface underwent swelling effects in the presence of sulfuric acid. It is recalled that low molecular weight BBL can be dissolved in this strong acid.

SECTION III

SUMMARY AND CONCLUSIONS

The greater part of this experimental work was spent in preparing films of BBL. Film preparation by filtration of reprecipitated polymers was given the most attention. The fact that films were obtained which had reasonably good strength and did not require casting from solution was of special interest. Adequate experimental data to explain the mechanism of this phenomena has not been obtained; however, some ideas which should prove useful in future attempts are summarized here.

The process of this solid phase film formation as performed in our laboratory may be thought to entail four steps: (1) precipitation of polymer from an acid solution by the use of a nonsolvent, (2) removal of residual acid by nonsolvent washing without exposing the precipitate to the atmosphere, (3) collection of the precipitate on a frit still in nonsolvent environment, and (4) removal of nonsolvent resulting in compaction of the solid and exposure to the atmosphere. Steps (2) and (3) seem to be primarily manipulatory and of less consequence than either (1) or (4).

In the first step, the process of precipitating polymer from solution is accomplished by pouring polymer solution into excess nonsolvent; then the polymer chains associate as their solvent environment is diluted. By the time precipitation has occurred, the polymer-polymer interactions which replace the polymer-solvent interactions have already been established. Although significant polymer-polymer interactions may have existed previously in the concentrated acid solution, this precipitation step may then be looked upon as a change in environment which enhances any tendency of chains to align or orient. Different polymer precipitates vary in the nature or degree of internal order which results. Microscopic examination indicates that the precipitates with the strongest film-forming tendencies have been formed into the two-dimensional or sheetlike solid phases described above. At this stage it can be predicted that these types of polymer precipitates will be film forming. On the contrary those which appear to exist in the particular or globular forms will either not produce films or will produce relatively poor film. Our experience further reveals that nonladder aromatic-heterocyclic polymers such as PBI give the nonfilm-producing precipitates, whereas ladder polymers give the film-forming type. BBB, which is a nonladder polymer but possesses a very high degree of fused ring ladder-type structure, seems to fall between. This near-ladder structure is film forming provided the initial solution is prepared at a concentration of 0.4% or higher. Apparently the tendency for these polymer chains to associate in the precipitated state is greatly enhanced if more concentrated solutions are used for the precipitations.

The second and third steps amount to a means of washing away acid without exposure to the atmosphere and of getting the desired amount of polymer into a desired slurry volume. This is varied by the size of filter fused to lay down a film and the amount of polymer required to get a desired thickness. The suction filter is never allowed to go dry before the entire quantity of precipitate to be used has been added. The building up of the wet filter cake is done without direct exposure to the atmosphere.

The significance of the fourth step is in question. It is a continuation of the third where the filtration is completed and the filter cake is compacted to a film as a result of the suction forces. As the film dries it loosens from the ground glass surface (cohesion exceeds adhesion) so that it is readily handled. The outer edges of the film tend to dry first on the frit, and if this occurs before all polymer solids are added, then layers with individual, nonadhering surfaces are formed. A question which arises about this fourth and last step asks whether the film formation is a simple laying down of the sheetlike fragments to produce a film much like felt with most of its strength dependent upon gross entanglements with some due to molecular entanglements from shrinkage or whether the film derives its strength from the formation of molecular interactions. If the latter is true, then the additional question arises as to whether or not polymer chain interactions similar to those formed in step (1) are continuing to form or whether different interactions acting between polymer surfaces come into play.

Whichever the process, it is very sensitive to the effects of drying. This gives rise to another unanswered question which asks whether the drying or shrinking of the wet film surface is most significant or whether the adsorption of gas molecules on the liquid free surface is responsible for surface deactivation. It is not unreasonable to suspect that the reason why BBB does not produce films of the quality of BBL is that swollen BBL does not undergo extensive shrinkage when reprecipitated. The ladder backbone is extended whereas the BBB backbone has much freedom of rotation (relative to BBL) to permit chains to collapse on themselves. When filter cakes prepared from BBB are dried, shrinkage is grossly apparent and resulting films are brittle, often cracking on the filter from internal stresses.

From the above investigation it seems reasonable to conclude that processing of BBL and possibly BBB into films or coatings under mild conditions will be possible without any sacrifice in thermal stability. The findings indicate that comparable results will be attainable for any polyheterocycle ladder polymer. Processing techniques described here may provide the ground work for solving certain fabrication problems, although the films and coatings produced thus far have neither the adequacy in strength, abrasion resistance, nor adhesive properties to suggest immediate applications. Nevertheless, it should be beneficial to study further about the processes described and the chances for enhancing the properties of products.

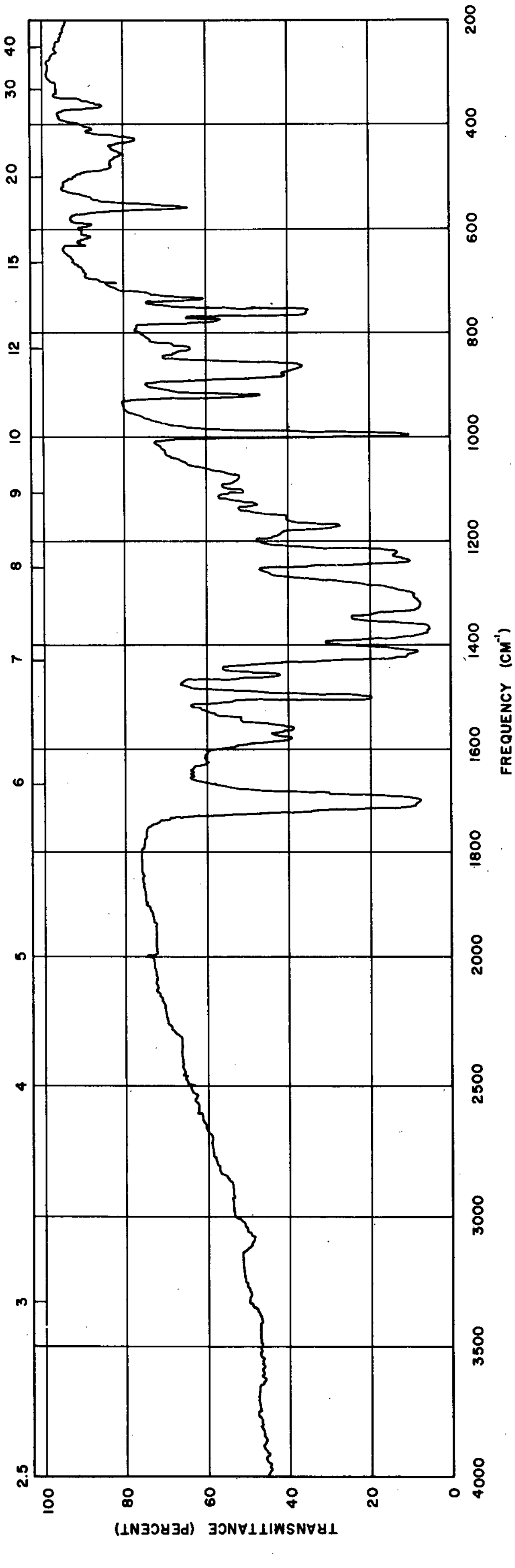
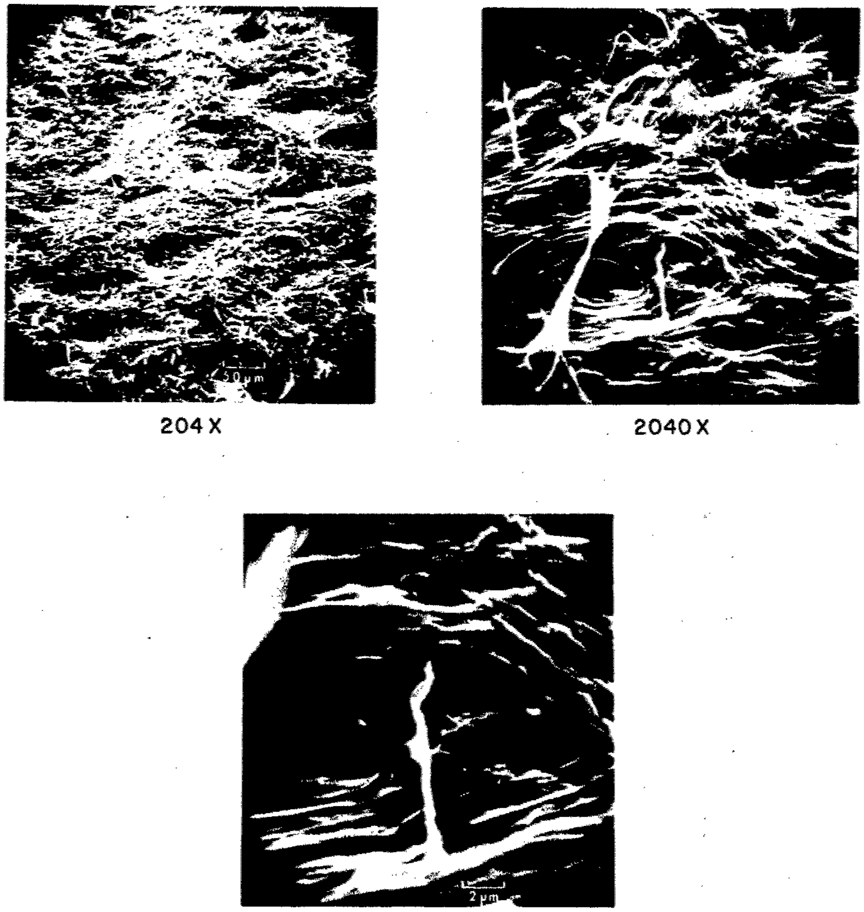


Figure 1. Infrared Spectrum of BBL Polymer (Film)

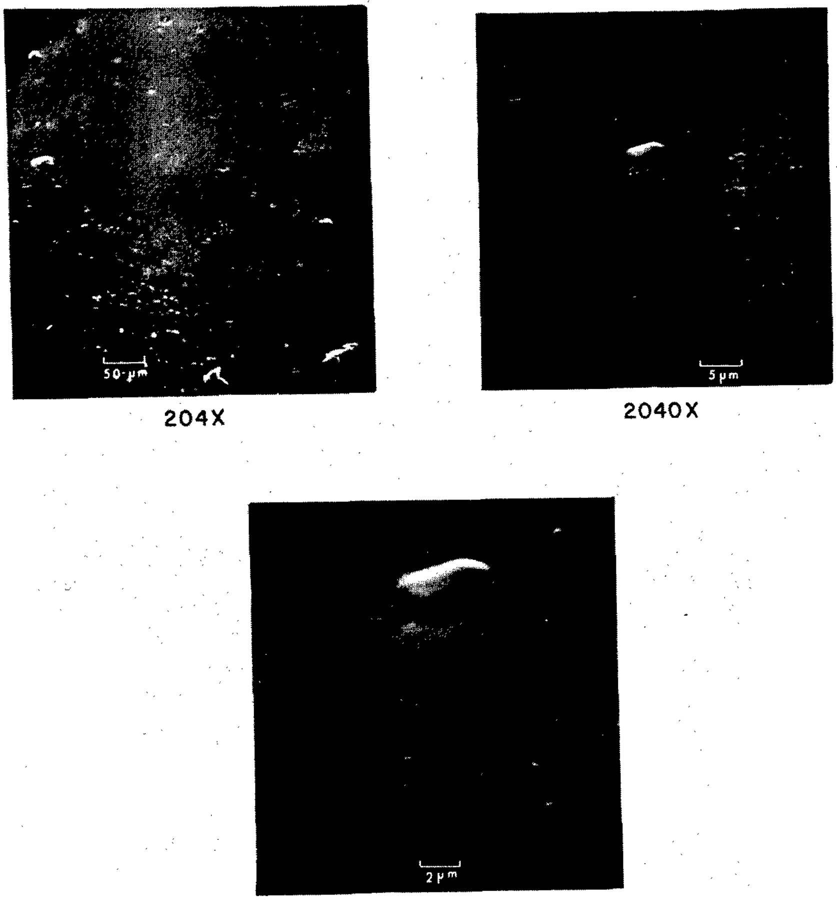


204X

2040X

5100X

Figure 2. Photomicrographs of Filtration Film at 204X, 2040X, and 5100X

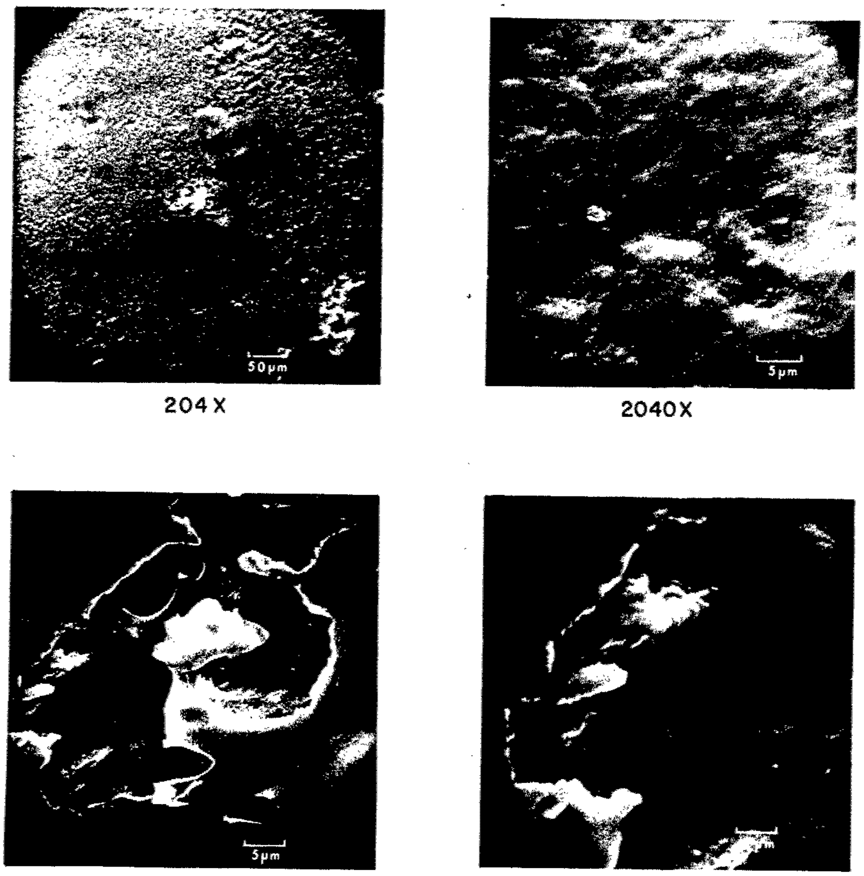


204X

2040X

5100X

Figure 3. Photomicrographs of Cast Film at 204X, 2040X, and 5100X



204X

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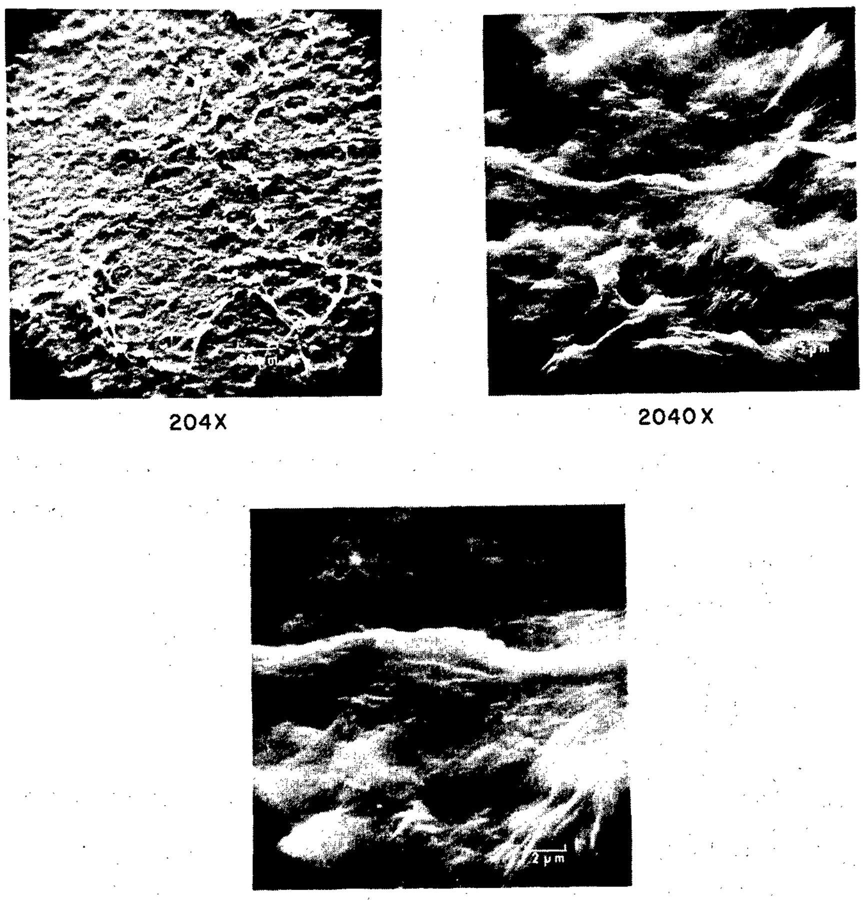
5100X

Figure 4. Photomicrographs of Sprayed Film (Side Facing Glass) at 204X, 2040X, and 5100X



204X

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Figure 5. Photomicrographs of Sprayed Film (Side Opposite Glass) at 204X, 2040X, and 5100X

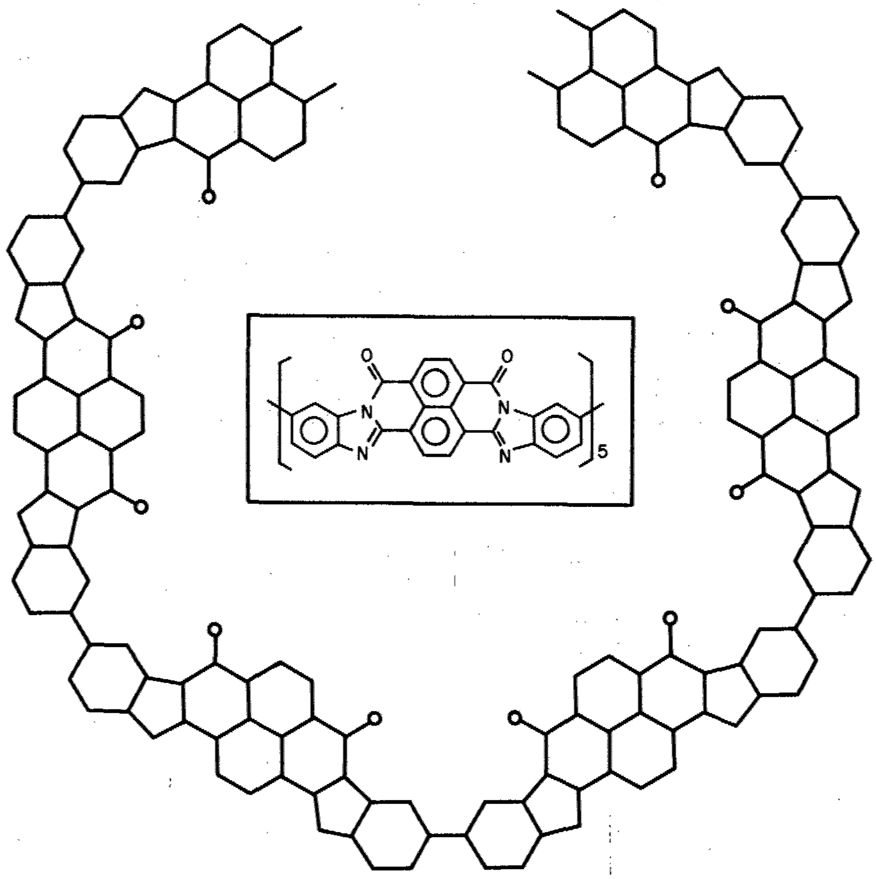
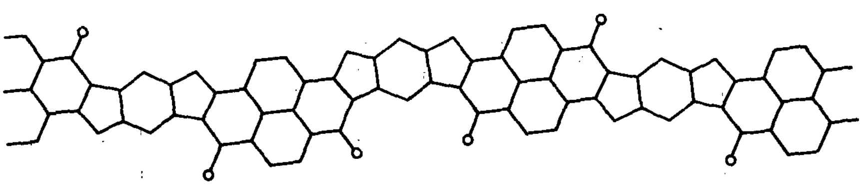
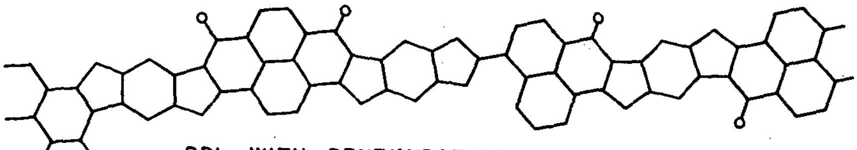


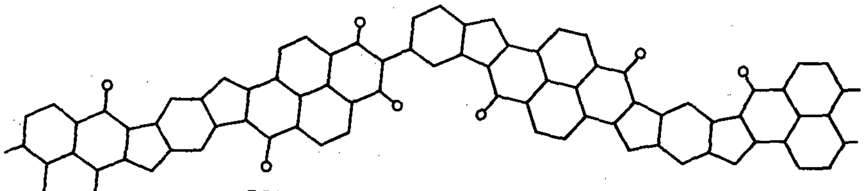
Figure 6. Diagrammatic Example of BBB Loop



COMPLETELY CYCLIZED BBL



BBL WITH BENZIMIDAZOLE IMPERFECTION



BBL WITH IMIDE IMPERFECTION

Figure 7. Diagrammatic Example of BBL Chains

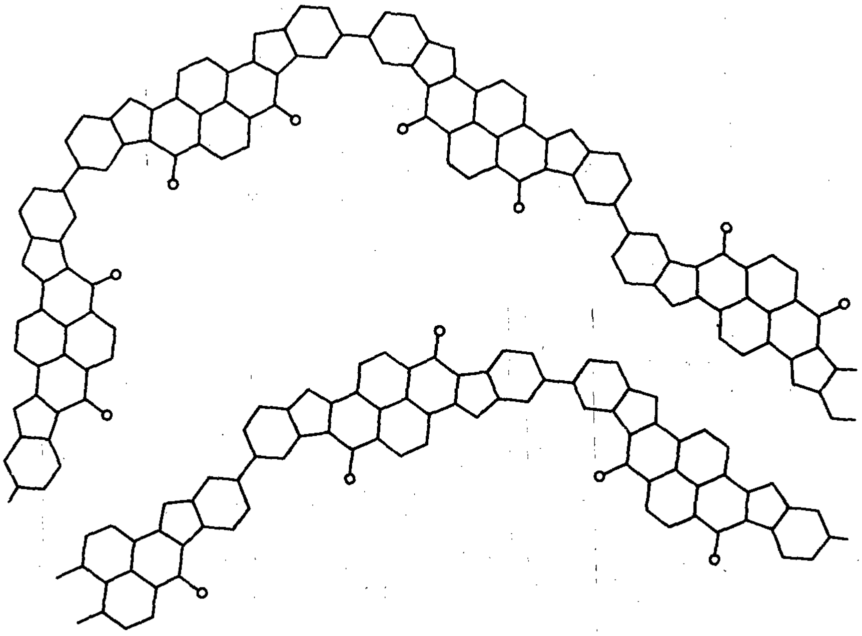


Figure 8. Diagrammatic Example of BBB Chains

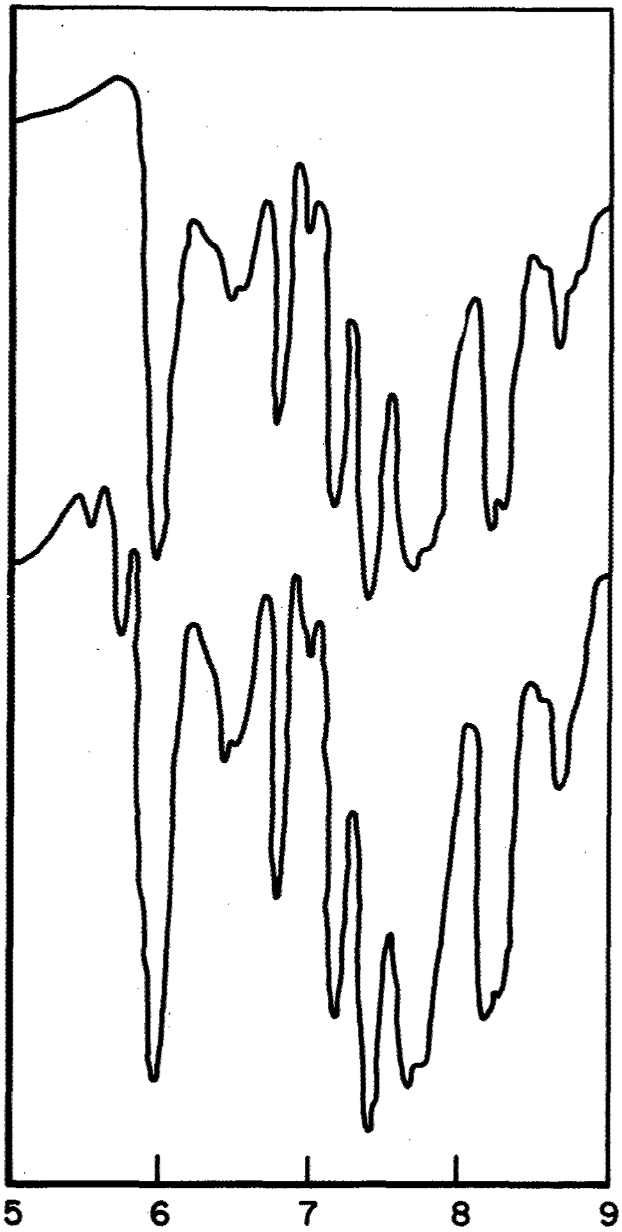


Figure 9. Comparison of Spectra (5-9μ) of a Film Containing 20% "Skybond 700": Before (Top) and After (Bottom) Thermal Cure

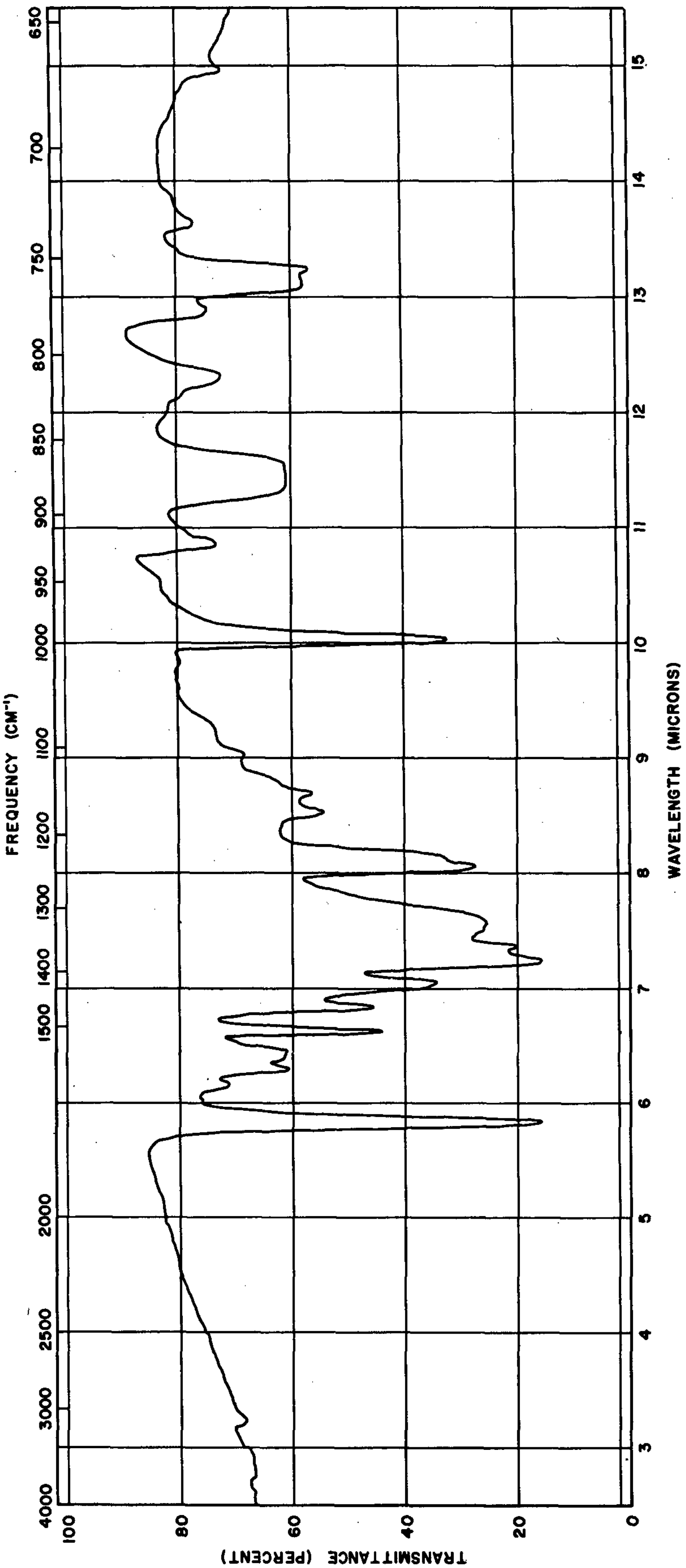


Figure 10. Infrared Spectrum of 50 BBL/50 BBB Film

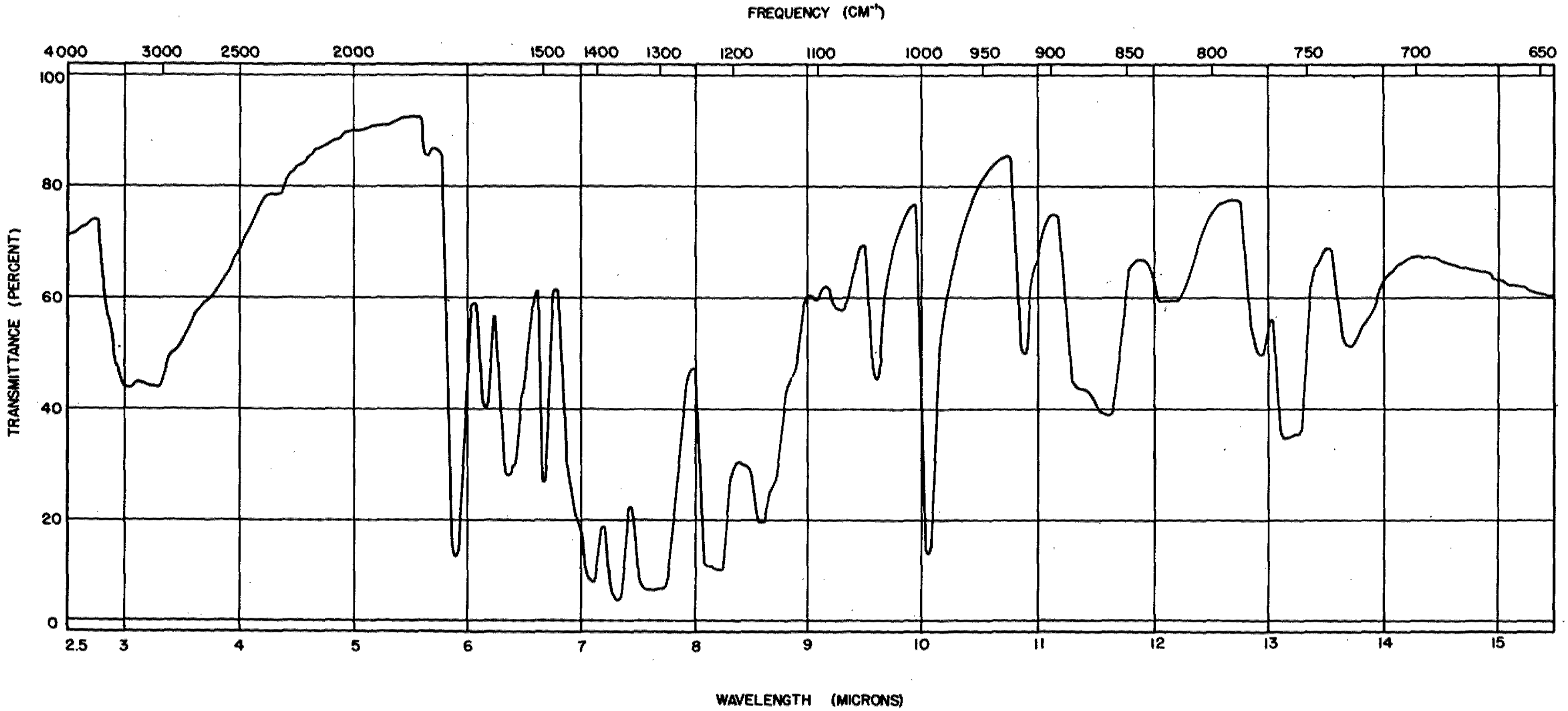


Figure 11. Infrared Spectrum of 50 BBL/50 PBI Film

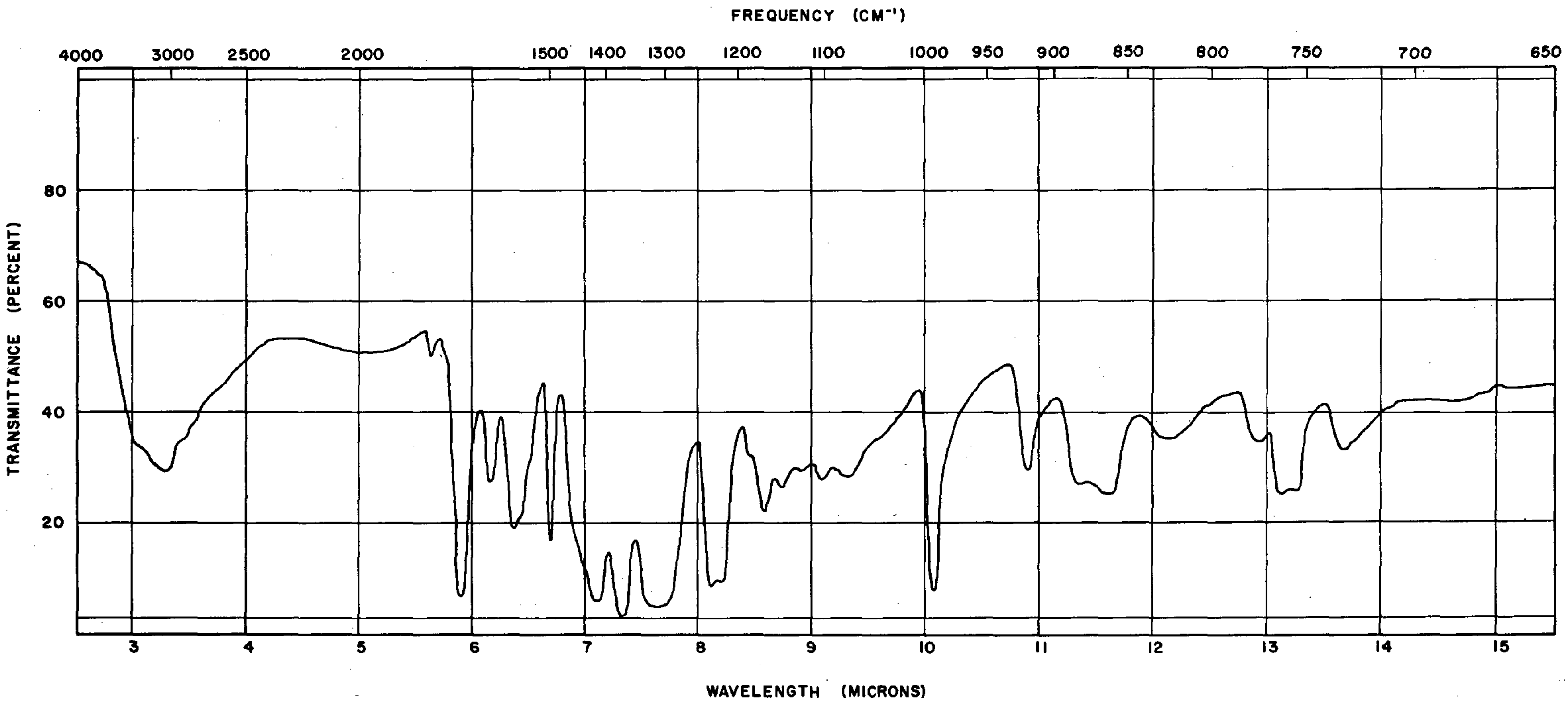


Figure 12. Infrared Spectrum of 50 BBL/50 PBI Cast Film

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13. ABSTRACT

The ladder polymer, BBL, has been formed into thin films by collecting suspensions of the polymer obtained from acid reprecipitations upon a fritted glass funnel. After drying, the polymer can be removed in the form of a film with thickness dependent upon the amount of material used. The film can be freely handled and very advantageously used for obtaining infrared spectra. 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. The films are dark with an intense golden luster which gives the appearance of a metal foil. Other aromatic heterocyclic polymers were examined to compare film formation with molecular structure.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ladder Polymers						
Film Formation						
Heterocyclic						