The jacket temperature was controlled with a Hallikainen Instrument Co. Model 1053A controller.

Combustion measurements were made by accurately defining the initial linear slope of the time–temperature relationship (caused by the difference in temperature between the jacket and bucket temperature), firing the bomb, and obtaining the final linear slope (caused by the heat of rotation of the bomb). These two linear slopes were extrapolated to the ordinate of the midpoint of the bucket temperature rise and thus a corrected temperature difference was obtained from combustion. This value was then corrected for all energy added to the system (fuses, H_2O added to the bomb, specimen holders, energy equivalent of the bomb itself, etc.). Washburn correction and correction for heat capacity of sample (E_c) were made. The resulting energy was then calculated as heat of combustion of the specimen in calories per gram.

Acknowledgments. The author is indebted to Mr. J. Baldt for the calorimetric measurements, to Mrs. Janet Willoughby, Mr. J. F. Grezlikowski, Jr., Mr. John Bair, and Dr. H. Eatough for technical assistance. and to various colleagues for lactone samples.

Preparation and Properties of High Molecular Weight, Soluble Oxobenz[*de*]imidazobenzimidazoisoquinoline Ladder Polymer

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ABSTRACT: The synthesis of double chain or ladder polymers from 1,2,4,5-tetraaminobenzene and 1,4,5,8-naphthalenetetracarboxylic acid has been optimized. High ladder polymers of high quality were obtained from the free tetraamine, as well as its hydrochloride salt, in polyphosphoric acid polycondensations at 180°. These ladder polymers were completely soluble in methanesulfonic acid and had intrinsic viscosities ranging from 1 to 6 dl/g. Film-forming and fiber-forming properties were demonstrated. TGA weight losses of less than 10% at 600° in air and less than 5% at 700° in nitrogen were observed. Low-viscosity ladder polymers were obtained from polycondensations in methanesulfonic acid.

Polycondensations of aromatic acids and amines have given rise to several thermally stable polyheterocycles including the conventional polyimides as well as naphthalene imide polymers[1,2] and the polybenzimidazoles as well as tetraazopyrene polymers.[3,4] More recently related ladder polymers referred to as pyrrones,[5-7] BB polymers,[8,9] and polyperimidines[6,10] have been synthesized which are comprised of these same ring systems fused.

Of this group of related polycondensates the ladder types have most recently generated the greatest research interests since they are relatively novel and appear to have potential for applications. Nevertheless due to their complexities, they have not yet been well characterized nor have they yet been developed to any great extent. A primary problem in characterization has been the great difficulty of obtaining high quality linear polymers with reasonably high molecular weights.

One from this group of ladder polymers, the benzimidazobenzophenanthroline-type ladder polymer (BBL), has now been synthesized possessing a combination of properties which appear to be significantly better than the others reported. The synthesis and properties of BBL comprise the subject of this report.

Discussion

From investigations of the polycondensation of aromatic tetraamines and tetraacids or their derivatives, the synthesis of four types of ladder polymers have been studied. Using the currently acceptable structure-based nomenclature[11] these are poly[(10-oxoimidazo[4,5-*f*]isoindolo[2,1-*a*]benzimidazole-1,2(10H):7,8-tetrayl)-8-carbonyl] (I), poly[(7-oxo-7H,10H-benz[*de*]imidazo[4′,5′:5,6]benzimidazo[2,1-*a*]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (II), poly[(11-oxoisoindolo[2,1-*a*]pyrimido[4,5,6-*gh*]perimidine-1,2(11H):8,9-tetrayl)-9-carbonyl] (III), and poly[(13-oxo-1H,13H-benz[4,5]isoquino[2,1-*a*]pyrimido[4,5,6-*gh*]perimidine-1,2:910-tetrayl)-10-carbonyl] (IV).[12] All possess excellent thermal stability, but in terms of attempting to obtain a high degree of perfection in structure each system differs in its characteristics.

The polymers possessing the perimidine structures (III, IV) are derived from 1,4,5,8-tetraaminonaph-

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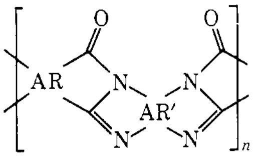
(12) Polymer names were provided through the courtesy of Nomenclature Committeeman Kurt L. Loening, Nomenclature Director, American Chemical Society, Chemical Abstracts Service.

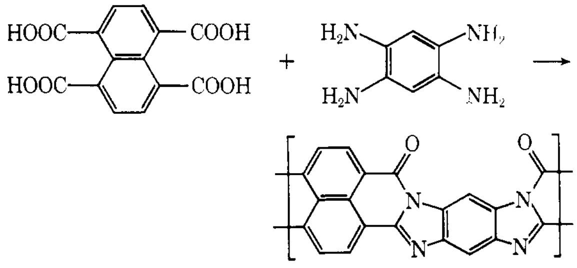
thalene or 5,8-diaminonaphthalic acid derivatives[6,10] and this aspect is unattractive. The *peri*-aminonaphthalene monomers are relatively less reactive and either unstable or very difficult to purify. Consequently, prospects of obtaining high DP with the III and IV types of ladder structure are not good. Best efforts reported to date are represented by inherent viscosities in sulfuric acid of 0.2–0.4 dl/g.[6,10] The remaining two types (I, II) appear more promising although the nature of these systems also varies.

The general class of type I polymers can be synthesized[5-7] by two-step methods starting with aprotic solution reactions near room temperature and followed by a solid phase step at high temperature. Polyphosphoric acid (PPA) and melt polymerizations can also be used.[6] The ladder polymer of this class (I) has been difficult to work with because there is a strong tendency to produce insoluble polymer indicating the production of network or nonlinear structure. This of course severely complicates purification and characterization with regard to structure–property relationships.



I, AR = 1,2,4,5-C_6H_2; AR′ = 1,2,4,5-C_6H_2
II, AR = 1,4,5,8-$C_{10}H_4$; AR′ = 1,2,4,5-C_6H_2
III, AR = 1,2,4,5-C_6H_2; AR′ = 1,4,5,8-$C_{10}H_4$
IV, AR = 1,4,5,8-$C_{10}H_4$; AR′ = 1,4,5,8-$C_{10}H_4$

The BB-ladder polymer (II) synthesis[8,9] does not exhibit the strong tendencies to form insolubles. This is particularly true when the polycondensations are performed in PPA and is quite possibly due to the favorable spacial arrangements for forming the six-membered ring imide structure as an intermediate backbone structure. Considering the steric features, the final step cyclodehydration can be expected to proceed intramolecularly and this does not appear to be in conflict with experimental results. Nevertheless, in preceding work[9] on the synthesis of BBL (II) it was found that the physical properties did not measure up to what one might expect for the double strand structure. The ladder polymer gave solution viscosities less than 1.0 dl/g in concentrated sulfuric acid, somewhat poorer TGA than the nonladder analog and infrared spectra which contained absorptions suggestive of incomplete cyclization.



II

In this study of the BBL system, significant improvements have been realized. Much higher molecular weights have been obtained as indicated by high solution viscosities (Table I). These are believed to be approximately four times higher than those previously reported although a direct comparison is not possible since these higher polymers are not soluble in concentrated sulfuric acid. They are, however, completely soluble in methane sulfonic acid which has been found to be a much better solvent for these polymers. The free base form of 1,2,4,5-tetraaminobenzene (TAB) gave high-viscosity polymers (Table I). The tetrahydrochloride salt of TAB was used with comparable success provided the hydrogen chloride was thermally liberated by heating in PPA before the acid monomer 1,4,5,8-naphthalenetetracarboxylic acid (NTCA) was added. Lower viscosity polymers were obtained when hydrogen chloride was liberated in the presence of NTCA during the initial stages of the polymerization as was reported previously.[9] It is noted that these findings for the BBL system differ from those found for the polybenzoxazinone system.[13] In the latter, the use of a hydrochloride salt is reported to aid the polymerization process by enhancing monomer diffusion or mobility in media during the HCl volatilization. In our case, the absence of HCl with the monomers was preferred. The special care taken to achieve high monomer purities and exact stoichiometries was surely a contributing factor to the optimization and the higher molecular weights obtained.

Table I
BBL Synthesis

Tetraamine	Reaction time,[a] hr	Intrinsic viscosity[b]
TAB	1.5	1.34
TAB·4HCl	6	3.93
TAB·4HCl	10	5.25
TAB·4HCl	36	6.12
TAB	10	5.00
TAB·4HCl[c]	10	1.86

[a] Reaction temperature maintained at 180°. [b] Intrinsic viscosities (deciliters per gram) were obtained in methanesulfonic acid. [c] The hydrogen chloride was not thermally liberated prior to polycondensation.

The favorability of linear propagation and intramolecular cyclocondensation processes for this system is apparent since all of these ladder polymer products were completely soluble. The possibility of network structures arising from undesirable side reactions is thus excluded. Methanesulfonic acid solutions as high as 5% were obtainable with little difficulty despite the expectation that ladder structure renders high melting, stiffer chain polymers with poorer solubilities. The lower molecular weight ladder polymers were also soluble in phosphoric and sulfuric acids (*e.g.*, intrinsic viscosity of 1.7 dl/g in concentrated sulfuric acid); however, the higher polymers were only swollen in these solvents. Lower polymers which were soluble in concentrated acid (96–97%) showed higher intrinsic viscosities in the methanesulfonic acid, approximately 1.6 times higher. It is noted that viscosity ratios for the nonladder BBB are quite similar, approximately 1.4 times higher in methanesulfonic acid than in concentrated sulfuric acid. Solutions of ladder polymers in concentrated sulfuric acid,

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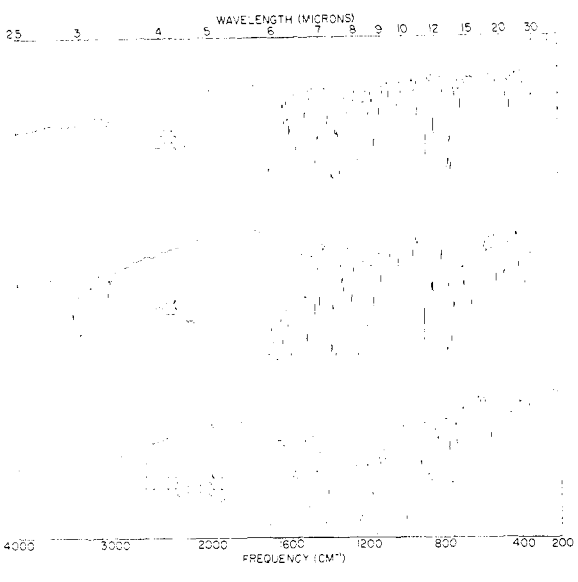
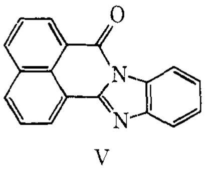


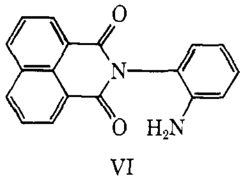
Figure 1. Comparison of spectra for model compounds V and VI and BBL polymer.

PPA, and methanesulfonic acid were all of an intense red color. Film cast from methanesulfonic acid solution was dark with an intense golden luster which gave the appearance of a metal foil. A 0.3-mil film (1.3 g/cm^3) cast from methanesulfonic acid solution near 60° and 0.05 mm was found to have an initial modulus of 1.1×10^6 psi. Tensile strength averaged 16,600 psi with rupture elongation of 2.9%.

A comparison of the infrared spectra of the ladder polymer and the model compounds V and VI is shown in Figure 1. Spectra of high-viscosity BBL closely resembled the spectra of model compound V in the 5.9–6.5-μ region. Intense absorptions in the 6.0–6.1-μ region which are very prominent in the spectra of VI are indicative of incompletely cyclized structure and these are not observed in the polymer spectra. It should be noted that the previously reported spectra of low-viscosity BBL polymers showing absorptions (unresolved peaks) in the 2.7–3.0- and 6.0–6.2-μ regions as indicated in Figure 2 were thought to be due to incompletely cyclized backbone links. However, in this investigation, the use of films to obtain spectra gave better resolution and led to some different conclusions. When a film sample was made from the same low viscosity polymer sample and infrared spectrum taken, the absorptions just below 3 μ and just above 6 μ no longer appeared (Figure 2). This difference seemed to be attributed to the elimination of some form of water which was present. It is likely associated with the preparation of KBr pellets since these absorptions reoccurred when the film was ground to obtain another KBr pellet spectrum. Reduction of the particle size of the polymer to 200 μ or less for pellet preparation is difficult and requires vigorous grinding in a metal apparatus to the point of generating easily detectable heating of the sample.



V



VI

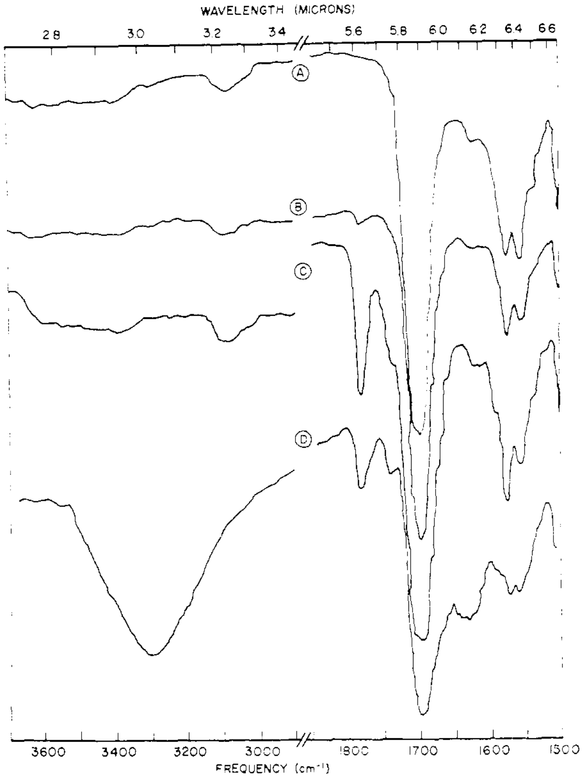


Figure 2. Comparison of spectra in the 3- and 6-micron regions: (A) high viscosity BBL after end capping (film); (B) high viscosity BBL before end capping (film); (C) low viscosity BBL (film); (D) low viscosity BBL (KBr pellet).

Absorption bands at 5.6 and 5.8 μ which are quite prominent for low-viscosity BBL (Figure 2) were found to be due to anhydride end groups. Identification was made from chloroform solutions of model compound V containing small amounts of 1,8-naphthalic anhydride. They are less prominent in the spectra of high-viscosity polymer and are not found in the spectra after subjecting the polymer to *o*-phenylenediamine end-capping conditions in PPA. The similarity in spectra between low- and high-viscosity polymers indicates that even the low BBL has ladder structure as opposed to incompletely cyclized prepolymer structure.

Molecular weight determinations on BBL polymers have not been attempted in this laboratory due to the lack of a suitable solvent in which to make conventional measurements. Nevertheless, some qualitative evidence that high polymers have been obtained is rather convincing and further work to determine physical and mechanical properties more extensively is anticipated.

Experimental data now available seem to reflect some very worthwhile indications upon which to assess the synthetic results. BBL with an inherent viscosity of only 0.9 dl/g in concentrated sulfuric acid at 0.5 g/dl (equivalent to approximately 1.5 dl/g in methanesulfonic acid) was film forming. This suggests that solution viscosities of 1.5 dl/g or higher are indicative of at least moderate molecular weights. BBL polymer with a comparable intrinsic viscosity of 1.86 dl/g in methanesulfonic acid exhibited good fiber-forming properties when spun from this solvent. The as-spun BBL fiber

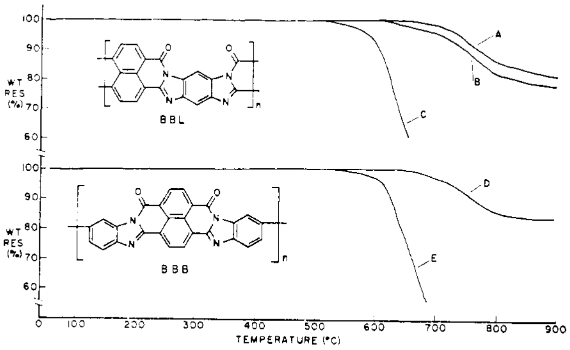


Figure 3. TGA comparison of BBL and BBB: (A) BBL-end capped (N_2); (B) BBL (N_2); (C) BBL (air); (D) BBB (N_2); (E) BBB (air); $\Delta T = 3°$/min.

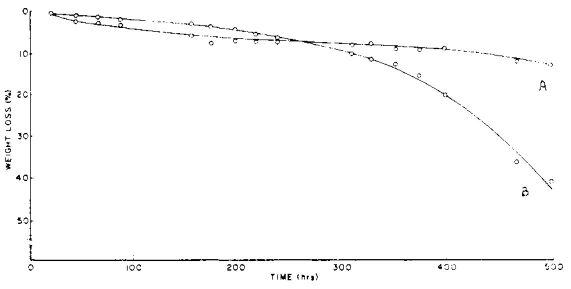


Figure 4. Isothermal aging of BBL (A) and BBB (B) at 370° in static air as powders (particle size of 177 μ or less).

showed strength properties about as good as those obtained for the first nonladder BBB polymer fibers[14] which are now under development.[15] Compared to the other BBL samples listed in Table I, these samples with viscosities less than 2.0 are relatively low polymers but still they possess film and fiber properties similar to polymers with fairly high molecular weights. Since the lower polymers of Table I can be cast and spun, the higher polymers with solution viscosities up to 5.0 and 6.0 are thought to be reasonably high polycondensates.

Barry and Yen[16] have investigated some dilute solution parameters of BBB, the nonladder analog of BBL, and a comparison of these data is enlightening. A BBB whole polymer sample having an intrinsic viscosity of 2.66 dl/g in methanesulfonic acid was found to have a weight average molecule weight of 97,000 by adapting laser techniques to light-scattering methods.[16] If one assumes a usual molecular weight distribution then a number average molecular weight of about one-half, or an average degree of polymerization a little above 100, is indicated. In our laboratory a film of this BBB polymer sample exhibited a 5.6-μ anhydride absorption which we believe is due to end group as in the case of BBL above. The intensity of anhydride absorption appeared to be of the same relative order of magnitude as that found for the high-viscosity BBL (Figure 2) which, in turn, would tend to indicate a similar degree of polymerization for the BBL. In such comparisons, the relative magnitudes of anhydride were based upon the absorbance found for the 5.6-μ peak relative to the absorbance exhibited for the 5.9-μ BB carbonyl peak. The degree of polymerization which is thus indicated to be near 100 for BBL would represent a number average molecular weight near 82,000.

Another interesting, albeit qualitative, observation was made. The relationship of carbonyl absorptions due to the anhydride (5.6 μ) and the BB (5.9 μ) structures in chloroform solutions was determined for solutions of naphthalic anhydride and model compound V. Solutions 9.25×10^{-2} M in V were prepared to contain anhydride in concentrations varying between 5.01×10^{-4} and 2.02×10^{-2} M to establish the relationship of the absorbances *vs.* concentrations. Comparisons of the absorbances ratios obtained from these solutions with those from films of high viscosity BBL polymer indicated an anhydride concentration in BBL commensurate with a degree of polymerization between 30 and 60, depending upon whether one or both chain ends were assumed to possess the anhydride structure. A direct comparison was not possible since the polymer is not soluble in conventional solvents. The comparison of spectra of model compounds in chloroform solutions with those of a polymer as a film is likely less valid than the first-mentioned comparison with the BBB molecular weight data. Although both are qualitative, these comparisons of BBL, in conjunction with the findings of high solution viscosities and the film- and fiber-forming properties of the polymer, provide support for our belief that a ladder polymer with exceptional properties has been obtained.

The thermal stability of BBL polymers was excellent and definitely improved over those previously obtained (Figure 3). Typically, the TGA weight loss curves of high molecular weight BBL prepared here showed breaks in the regions of 550 and 700° in air and nitrogen, respectively. These TGA curves are very similar to those currently obtained for the analogously structured nonladder BBB (Figure 3) so no significant improvement in thermal stability appeared to be attributable to ladder structure. The end-capped ladder polymer exhibited less than 10% weight loss at 750° in nitrogen TGA (Figure 3) which may be indicative of a slight improvement. Unlike TGA, isothermal aging experiments in an air atmosphere at 370° of some samples of both BBB and BBL did show a significant difference between the ladder and nonladder polymers. BBL lost only 10–15% of its initial weight after aging 500 hr in the thermooxidative environment whereas the BBB loss was greater than twice that under the same conditions (Figure 4). This finding tends to support the idea that increased life at temperature should be realized for polymers with ladder structure. Although both polymers analyzed for high-quality samples so that the results seem valid, substantiation of this would require quantitative degradation studies beyond the scope of this work for verification.

The solubility of BBL in methanesulfonic acid was investigated in conjunction with isothermal aging. Solubility decreased as expected with progressive thermal aging. The completely soluble ladder polymer which had an intrinsic viscosity of 5.2 was found to be 20% soluble after aging 240 hr at 370° in air. The soluble portion had an intrinsic viscosity of 1.76. Solubility was lowered to 5% after aging for 500 hr. Isothermal aging was also carried out on films which could be ex-

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(16) G. C. Berry and S.-P. S. Yen, National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

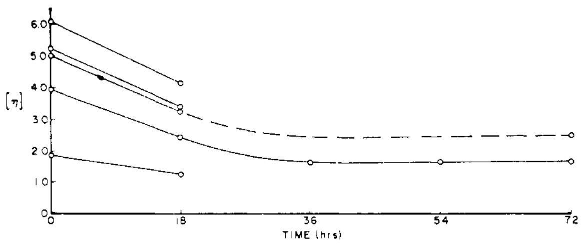

Figure 5. Effect of caustic hydrolysis (in refluxing 1 *N* NaOH) upon intrinsic viscosities (in methanesulfonic acid) of BBL.

amined periodically for spectral changes. This was done hoping that the nature of cross-link structures could be identified. However, except for expected losses in the intensity and resolution of characteristic bands, no changes were detected by routine infrared analysis which could be attributed to changes in molecular structure, even after aging for 500 hr. The nonvolatile residues produced by the thermooxidative decomposition tended to be infrared opaque. This in addition to the fact that degradative structural changes appear to be below the usual level of detection for ir indicates that a more refined analytical approach will be required to obtain additional information.

Quantitative assessments of structural perfection (or imperfection) of complex ladder polymers are seldom offered in the literature because of the great difficulties associated with obtaining substantiating analytical proof. Nevertheless, as a preliminary measure to gain qualitative information about the BBL structure, we have conducted some investigations related to the chemical stability of the polymer. As discussed previously[9] imperfections in the BBL ladder structure resulting from incomplete cyclization are likely to be imide although imidazole structures could be present. Directing our attention to the former, samples of BBL were subjected to vigorous conditions of caustic hydrolysis to cleave imide linkages and reduce the molecular weights. Model compound N-phenylnaphthalimide was hydrolyzed under these conditions. Determinations of molecular weights and distributions of the whole polymers after hydrolysis were not attempted, but since solution viscosity determinations provide a sensitive measure of molecular weight changes, we related the intrinsic viscosities of hydrolyzed samples to the time variable of hydrolysis (Figure 5).

Polymers were mixed with 1 *N* NaOH and the heterogeneous system was heated to reflux for periods up to 72 hr. After hydrolysis, the samples were collected and reprecipitated from methanesulfonic acid before their solution viscosities were determined. The results (Figure 5) were encouraging since the reductions in molecular weight reflected by solution viscosity decreases (approximately 50%) quite certainly do not indicate the occurrence of several cleavages per chain. On the contrary, the data are more suggestive that few hydrolyzable imperfections per chain existed. Further, it appears from the leveling off of viscosity values beyond 36 hr that remaining polymer is exceptionally stable to base hydrolysis. Some complications have arisen, however, which are not readily explained. The TGA curve in nitrogen of hydrolyzed polymer showed a gradual weight loss of approximately 1% per 100° temperature rise up to 600°. This was not typical for BBL as evidenced by the much better curve found in Figure 3. Also questionable, the absorption band at 6.4 μ of BBL spectra (Figure 1) was found to be intensified after hydrolysis. These unexpected results suggest the presence of impurities or possibly chain end fragment structures generated during the base hydrolysis.

Additional information was gained from model compound work. The BBL type ring structure (V) was not hydrolyzed by 1 *N* NaOH after 72 hr at reflux. The addition of approximately 10% by volume of ethyl alcohol to a mixture of V with 1 *N* NaOH produced a solution so a similar homogeneous reaction was carried out for 72 hr without causing cleavage. Having demonstrated the stability of the BBL-type structure the incompletely cyclized model structure (VI) was examined. Hydrolytic cleavage by homogeneous reaction occurred to the extent of 80% after 72 hr, but in the heterogeneous media the cleavage did not occur. Instead, cyclization of the imide amine VI to produce V occurred quantitatively in the refluxing 1 *N* NaOH. Since the conditions were identical with those used for the polymers above it is not unreasonable to assume that imide amine structures in the polymer backbones could have been cyclized as opposed to being cleaved. This leads to the tentative conclusion that imperfections cleaved to reduce the polymer molecular weights are the result of triamine impurity in the tetraamine monomer or incompletely cyclized imide amine units in which the amine group functionality has been destroyed. The latter could result from oxidative processes.

Since IV was found to cyclize in aqueous NaOH and had been previously found to cyclize in PPA and glacial acetic acid,[9] the cyclization was also attempted in concentrated H_2SO_4 and methanesulfonic acid. Both of these acids were found to support the cyclodehydration quantitatively. Since methanesulfonic acid is a good solvent, the polymerization of naphthalic dianhydride and free tetraaminobenzene was carried out in this solvent. Monomers were treated in methanesulfonic acid solution at 120° for 12 hr to produce BBL with an inherent viscosity in the acid of 0.3 at 0.25 g/dl. Even this low polymer had surprisingly good TGA. Although a gradual weight loss occurred between 300 and 550° amounting to about 3%, the polymer resisted catastrophic degradation in air up to 600°. Weight losses of 10% were found to occur a little above 600° in air and 700° in nitrogen. This tends to support the previously reported ir findings which indicate that highly cyclized structure is present even in low polymers prepared in protic media.

Experimental Section

Polyphosphoric Acid (PPA). PPA (Practical) was purchased from Matheson Coleman and Bell and used as received.

1,4,5,8-Naphthalenetetracarboxylic Acid (NTCA). The polymerization grade monomer was obtained through Celanese Research Co. and used as received.

1,2,4,5-Tetraaminobenzene Tetrahydrochloride (TAB·4HCl). The monomer was purchased from Burdick and Jackson. It was purified by treating an aqueous solution with activated charcoal and precipitating the material by addition of concentrated hydrochloric acid. The tetrahydrochloride salt was dried under reduced pressure (0.05 mm) over phosphorus pentoxide at 100°. The free amine obtained by the method of Vogel and Marvel[9] from the tetrahydrochloride salt was purified by sublimation at 150–160° (0.1 mm), mp 273–274° (lit.[9] mp 274–276°).

7H-Benzimidazo(2,1-*a*)benz(*de*)isoquinolin-7-one (V). This model compound was prepared as previously described.[9,17]

N-(2-Aminophenyl)naphthalimide (VI). This model compound was prepared as previously described.[9,17]

Polycondensation Using Free Tetraamine. To a 500-ml three-necked flask fitted with a trubore stirrer and nitrogen inlet and outlet was added 250 g of PPA. The PPA was deoxygenated by heating overnight at 110° with nitrogen bubbling through the stirred acid. Under a nitrogen atmosphere at 50° were added 1.38 g (0.01 mol) of TAB and 3.04 g (0.01 mol) of NTCA. The mixture was slowly heated (4°/min) to 180° and maintained at that temperature for 10 hr. The resulting viscous solution was poured out of the flask at 180° into a beaker and allowed to cool to room temperature. The polymer was precipitated in methanol, using a blender to facilitate mixing. The fibrous brown material was washed twice with 1-l. portions of anhydrous methanol and dried at 200° under reduced pressure (0.40 mm). Precipitation from 500 g of methanesulfonic acid and drying in the above manner gave 3.2 g (95%). An intrinsic viscosity of 5.00 dl/g in 100% methanesulfonic acid was determined.

Anal. Calcd for $C_{20}H_6N_4O_2$: C, 71, 86; H, 1.81; N, 16.76. Found: C, 70.08; H, 2.01; N, 16.08; residue, 0.9. Residue by emission spectra analysis contained mainly silicon and traces of various metals.

Polycondensation Using Tetraamino Tetrahydrochloride. Polymerizations using TAB·4HCl were carried out in a similar manner; however, the NTCA was not added until all the hydrogen chloride was thermally displaced from the tetraamine. This was accomplished by heating the tetraamino tetrahydrochloride in deoxygenated PPA overnight at 75–80°.

Polymer End Capping. To 100 g of deoxygenated PPA were added 0.500 g of polymer with intrinsic viscosity 5.00 dl/g and 2 g of *o*-phenylenediamine. The solution was slowly heated (4°/min) to 180° and 2 g of additional *o*-phenylenediamine was added. After 8 hr at 180°, the mixture was cooled to room temperature and precipitated into 2 l. of anhydrous methanol. The finely divided precipitated material was washed with methanol and dried under reduced pressure (0.40 mm).

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Sulfonyl Carbamate Derivatives of Cellulose[1]

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ABSTRACT: *p*-Toluenesulfonyl isocyanate (*p*-TSI) reacts with cellulose to produce a *p*-toluenesulfonylcarbamate derivative. O-Alkyl N-*p*-toluenesulfonylcarbamates exhibit pK_a's comparable to carboxylic acids; this represents a new acidic ionogenic group for cellulosic ion exchange resins. Treatment of a slurry of cotton linters in pyridine with 4 mol of *p*-TSI/mol of cellulose effects solution within 2 hr at 80°. A degree of substitution of 2.0 is attained rapidly but reaction times of 18 hr or more are required to achieve quantitative substitution. The formation of a pyridine–*p*-TSI complex decreases the activity of *p*-TSI at reaction temperatures below 70°, but inert solvents such as chlorobenzene or dioxane fail to dissolve the cellulose derivative and no substitution occurs. Neither $ZnCl_2$ nor dibutyltin dilaurate was effective in catalyzing the process. Derivatives with residual hydroxyl groups could be cross-linked with bis(4-isocyanatophenyl) isocyanate, *p*-(isocyanatophenyl)sulfonyl isocyanate, or chlorosulfonyl isocyanate to form resins which swell but do not dissolve in 2% NaOH. The ion exchange capacity of these resins was found to be 2.9 mequiv/g.

Recent improvements in the synthesis techniques of sulfonyl isocyanates indicate that a new look at their application to the modification of polymeric materials could be beneficial. Ulrich and Sayigh[3] have developed a procedure by which aromatic sulfonyl isocyanates can be prepared by the direct phosgenation of the corresponding sulfonamides in the presence of catalytic amounts of butyl isocyanate. Sulfonyl isocyanates exhibit enhanced reactivity toward nucleophilic attack by alcohols, amines, phenols, thiols, and some aromatic compounds containing activated carbon–hydrogen bonds. In contrast to aryl isocyanates, sulfonyl isocyanates react quantitatively with phenols and sterically hindered alcohols to produce sulfonylcarbamate derivatives.[4] This suggests that they would be sufficiently reactive to disrupt the crystallinity of native cellulose. We have found that *p*-toluenesulfonyl isocyanate (*p*-TSI) reacts with untreated cellulose to pro-

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