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Complexation-Mediated Solubilization and Processing of Rigid-Chain and Ladder Polymers in Aprotic Organic Solvents

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ABSTRACT: A reversible electron donor–acceptor complex formation between heterocyclic polymers and Lewis acids in aprotic organic solvents is used to solubilize otherwise insoluble thermally stable rigid-chain polymers, exemplified by benzimidazole–benzophenanthroline-type ladder (BBL) and semiladder (BBB) polymers, poly(*p*-phenylene-2,6-benzobisthiazole) (PBT), poly(*p*-phenylene-2,6-benzobisoxazole) (PBO), and related model compounds and polymers. It is shown that the soluble complexes arise from a Lewis acid–base reaction at specific heteroatom nonbonded electron pair donor sites (N, S, O) on the polymer chains rather than from a π-electron charge-transfer reaction. The resulting solutions of the rigid-chain macromolecules in organic solvents were investigated by spectroscopic and rheological measurements. In the case of polymers with rodlike structure in solution, such as BBL and PBT, liquid-crystalline solutions in aprotic organic solvents can be obtained at high concentrations. The isotropic and anisotropic solutions of the rigid-chain polymers can be processed into films, coatings, and fibers, taking advantage of the facile and complete regeneration of the pure polymers from their soluble complexes by precipitation in nonsolvents that are stronger Lewis bases than the polymers. Films and coatings so prepared were characterized and shown to be identical with the pristine polymers. Thus, complexation-mediated solubilization of rigid-chain heterocyclic polymers in organic solvents represents a novel and promising approach to solution processing of heretofore difficult to process high-temperature polymers. The results also have important implications for the understanding of intermolecular interactions in polymers, their effects on structure and properties, and origins of intractability of rigid-chain polymers.

Introduction

Many heat-resistant or high-temperature polymers,[1–13] such as aromatic polyimides, polyquinoxalines, polybenzothiazoles, polybenzimidazoles, polybenzoxazoles, and aromatic heterocyclic ladder polymers, have been synthesized and widely studied in the past 3 decades. Some of these high-temperature polymers already find wide applications but are still being developed for uses in electronics, aircraft and aerospace vehicles, engine components, engineering structures, heat-resistant coatings, molecular composites, and other high-performance technological applications.[9–16] In addition to their generally excellent thermal stability, which suggests upper use temperatures in the range 250–500 °C, these polymers in the form of film or fiber also exhibit good mechanical properties (high tensile strength, high modulus) and exceptional solvent and chemical resistance. Recently, some of these polymers that are highly conjugated are also attracting scientific and technological interests because of their electronic and nonlinear optical properties.[16–24]

Rigid-chain structures containing aromatic or heterocyclic rings together with such chemical factors as introduction of groups that promote strong primary and van der Waals bonding forces, hydrogen bonding, resonance stabilization, molecular symmetry, or cross-linking have been used to achieve this combination of thermal stability and physical properties in polymers.[9–13] Unfortunately, these structural features, which endow the desirable physicochemical properties in thermally stable rigid-chain polymers, also cause processing difficulties due to insolubility in organic solvents and the extremely high glass transition, softening, or melting temperatures (>250–300 °C). Insolubility of these rigid-chain polymers is not due simply to high molecular weight since even their low molecular weight structural analogues or model compounds are equally insoluble in common organic solvents. Thus, of the numerous rigid-chain and high-temperature polymers that have been synthesized and investigated in the last 3 decades, only a small number of them are commercially available materials due largely to intrinsic processing problems and consequent high cost. Also, progress in the technological applications of the existing rigid-chain polymers is slow due to their lack of or poor processability.

All current or prior approaches to the solubilization and processing of rigid-chain polymers are variations of the following three basic concepts: (1) synthetic modification of the basic rigid-chain structures by introduction of flexibilizing linkages (e.g., –O–, –CO–, $-CH_2-$, $-SO_2-$, etc.) or molecular asymmetry (ortho, meta, versus para linkages) into the backbone or addition of bulky side groups to improve solubility;[10–12,25,26] (2) synthetic routes involving a soluble intermediate or precursor polymer that can be converted to the rigid-chain structure, after processing, by using a thermally activated cyclization or similarly simple reactions;[9–11] and (3) dissolution in strong protonic acids such as methanesulfonic acid (MSA), chlorosulfonic acid (CSA), triflic acid, and concentrated sulfuric acid.[6,27–31] The success and utility of these three approaches vary widely. The major disadvantage of the first strategy is that processability is achieved at the expense of reduced thermal stability, chemical resistance, or mechanical properties. The second approach is exemplified in the commercial processing of polyimides via soluble polyamic acid precursors.[32–34] The soluble precursor approach has also recently been explored in heteroaromatic ladder polymers.[35] Although these two synthetic approaches to solution processing of rigid-chain polymers have been successful to some extent, they are severely limited in scope and applicability in that the chemistry of each particular polymer must be reinvestigated from monomer synthesis to polymerization to characterization.

The known solubility of many rigid-chain polymers in strong protonic acids such as MSA and CSA has been established to be due to *protonation* of the polymer

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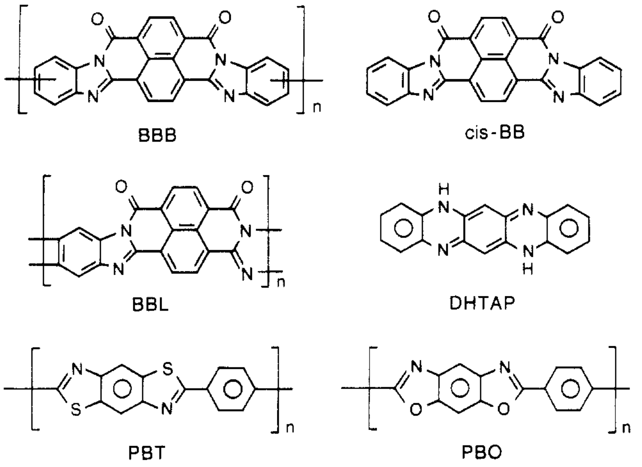


Figure 1. Structures of rigid-chain polymers and model compounds investigated.

chains,[27,28] thereby forming polyelectrolytes and consequently reduction of intermolecular attractions and chain stiffness. Acid solutions of rigid-chain polymers have been extensively investigated by Berry's research group,[27-31] especially their spectroscopic and rheological properties. Lyotropic liquid crystallinity has been observed in acid solutions of several rigid-chain polymers.[6,36,37] However, some of the polymers that are truly rodlike in acid solution, such as benzimidazole–benzophenanthroline-type ladder polymer (BBL), have not yet been shown to exhibit liquid crystallinity because of their poor solubility even in protonic acid solvents.[37] Although fibers of rigid-chain polymers have been spun from acid solutions on a large scale,[37-39] processing of acid solutions into films and coatings is more difficult because of the nonvolatile nature of such acid solvents.

Our work on the complexation chemistry and processing of rigid-chain polymers, whose initial results are communicated here, was motivated by the need to explore novel nonsynthetic approaches to the solubilization and processing of rigid-chain polymers in aprotic organic solvents. It is also of interest to investigate the dilute and concentrated solutions of these polymers in aprotic organic solvents, many of which are expected to be rodlike in solution, especially isotropic/anisotropic phase equilibria and lyotropic liquid crystallinity. We hope that a better understanding of the structure/solubility/processing relationships for rigid-chain polymers might emerge.

In this paper we report a new general approach to the solubilization and processing of rigid-chain polymers, including ladder polymers, in *aprotic organic solvents*. It is demonstrated that the reversible formation of electron donor–acceptor complexes of these polymers with Lewis acids allows dissolution to form viscous solutions, which can be processed by conventional methods. The polymers and model compounds investigated to illustrate the approach include (Figure 1) the following: benzimidazole–benzophenanthroline-type ladder (BBL) and semiladder (BBB) polymers, poly(*p*-phenylenebenzobisthiazole) (PBT), poly(*p*-phenylenebenzobisoxazole) (PBO), and 5,12-dihydro-5,7,12,14-tetraazapentacene (DHTAP). Our study of the solubilization, solutions, and processing of PBT in aprotic organic solvents using the approach reported here is presented elsewhere.[40] Our preparation and initial study of purely liquid-crystalline solutions of PBT in organic solvents is also reported elsewhere.[41]

A New Approach to Solubilization of Rigid-Chain Polymers. Melting or dissolution of rigid-chain polymers, such as BBL, BBB, PBT, and others in Figure 1, does not readily occur because each is a thermodynamically unfavorable process; the unfavorable free energy is due largely to the little gain in entropy when a solid form of a rigid-chain polymer is converted to its molten state or solution. The general intractability of these rigid-chain macromolecules is thus ultimately due to their unique structural features compared to the readily soluble and fusible flexible-chain polymers. The two main structural factors are (1) *intra*molecular or conformational effects, particularly the rigidity of the chains and (2) *inter*molecular effects, especially interchain attractions. A successful method of solvation must provide a favorable polymer–solvent interaction that at once mitigates against all causes of insolubility of the polymer.

Our proposed method of solubilization of these heteroaromatic rigid-chain polymers is to form *electron donor–acceptor complexes* of the polymers. One way of viewing complexation-mediated dissolution of otherwise insoluble rigid-chain polymers is that complex formation introduces molecules or ions of the complexing agent between chains and adds charge to or distributes charge on the macromolecular chain. The net result of such a process would be reduction of intermolecular attraction between chains and reduction of chain stiffness, allowing solvation of the chains by solvent. The feasibility of forming various electron donor–acceptor complexes of the heteroaromatic rigid-chain polymers with metal halide Lewis acids (MX_n) is excellent in view of the rich nonbonded electron pair donor sites on the polymer chains, such as the heteroatoms (O, S, N, C=O), which contain unshared electron pairs. Furthermore, some of the polymers have highly conjugated structures and hence are also strong π-electron donors. Thus, these heterocyclic rigid-chain polymers are Lewis bases by virtue of their heteroatoms, which contain unshared electron pairs, as well as their extensive π-electron conjugated structures.

Experimental Section

Polymers and Model Compounds. The polymers (BBB and BBL) and model compounds (*cis*-BB and DHTAP) were synthesized in our laboratory by using literature methods.[1-4,7,8] The two BBB polymer samples (BBB-1 and BBB-2) had intrinsic viscosities, $[\eta]$, of 2.66 and 2.72 dL/g, respectively, in concentrated (96%) sulfuric acid at 30 °C; the intrinsic viscosity of BBB-1, 2.66 dL/g, translates to a M_w of 97 300 using the known Mark–Houwink relation.[28] The two BBL samples (BBL-2 and BBL-1) had $[\eta]$ values of 4.78 and 7.91 dL/g, respectively, in methanesulfonic acid at 30 °C. The PBT sample, which had an $[\eta]$ value of 18.3 dL/g in methanesulfonic acid at 30 °C, was provided by the Polymers Branch, Air Force Materials Laboratories, Dayton, OH.

Lewis Acids and Organic Solvents. The metal halide Lewis acids (MX_n) used were of reagent grade, including $AlCl_3$, $GaCl_3$, $FeCl_3$, $SbCl_3$, $SbCl_5$, SbF_5, AsF_3, and $InCl_3$. All organic solvents (or nonsolvents) used were of spectroscopic grade or higher purity. Some of the aprotic and protic solvents investigated as solvents or nonsolvents for mediated solubilization and processing of rigid-chain polymers are shown in Table I. In addition, other organic solvents investigated are methylene chloride, toluene, *p*-xylene, benzene, and chlorobenzene. Deuterated nitromethane was used for ^{1}H NMR spectra.

Solubilization Studies and Solution Preparation. Due to the moisture sensitivity of most metal halide Lewis acids, all solution preparations were done in a glovebox filled with dry nitrogen. Our Vacuum Atmospheres Dri Lab glovebox was equipped with a Dri Train to remove residual water vapor or oxygen to below 1–5 ppm. Once prepared, all solutions were stored in the glovebox. Some solutions such as $FeCl_3$/nitroalkanes were also prepared and stored in air.

The organic solvent systems investigated were prepared by adding a known amount of metal halide Lewis acid (MX_n) to the

Table I
Properties of Solvents

	solvent	bp,[a] °C	ϵ'[a]	donor no.[b] (DN)	acceptor no.[b] (AN)
1.	nitromethane (NM)	101	35.9	2.7	20.5
2.	nitroethane (NE)	114	28.06		
3.	1-nitropropane (1-NP)	131	23.24		
4.	2-nitropropane (2-NP)	120	25.5		
5.	nitrobenzene (NB)	211	34.82	4.4	14.8
6.	*N,N*-dimethylformamide (DMF)	153	36.7	26.6	16.0
7.	*N,N*-dimethylacetamide (DMAc)	166	37.78	27.8	13.6
8.	*N*-methyl-2-pyrrolidone (NMP)	202	32.0	27.3	13.3
9.	acetonitrile (MeCN)	81.6	37.5	14.1	18.9
10.	dimethyl sulfoxide (DMSO)	189	46.68	29.8	19.3
11.	methanol (MeOH)	65	32.63	19.1	41.5
12.	acetone	56	21.6	17.0	12.5
13.	water	100	78	16.4	54.8
14.	acetic acid	118	6.15		52.9
15.	1,2-dichloroethane (DCE)	83.5	10.36	0.0	16.7
16.	$SbCl_5$/DCE				100.0
17.	sulfuric acid				
18.	methanesulfonic acid (MSA)				126.1
19.	trifluoroacetic acid	71.78	8.55		105.3
20.	trifluoromethanesulfonic acid	161			131.7

[a] Riddick, J. A.; Bunger, W. B. Techniques of Organic Chemistry. *Organic Solvents*, 3rd ed.; Wiley-Interscience: New York, 1970; Vol. 2. [b] Gutmann, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

organic solvents or vice versa. Most of these organic solvent Lewis acid systems have an exothermic heat of mixing and thus require no heating for ready dissolution. For a given organic solvent/MX_n pair, for example $AlCl_3$/nitromethane, a range of solvent systems with varying solvating powers is obtained by varying the concentration of the Lewis acid up to its solubility limit in the organic solvent.

Initial polymer and model compound solubilization studies were qualitative in nature and aimed to determine the most effective organic solvent Lewis acid pairs for a more detailed study. The qualitative solubility tests were done by placing about 5–10 mg of the polymer or model compound in about 6–10 mL of solvent systems prepared by using the Lewis acids and organic solvents listed previously. To aid in the dissolution of the samples, the vials were heated to about 40–60 °C on a hot plate while the solution was stirred with a magnetic stir bar. The solid/solvent samples were monitored for signs of dissolution with time (swelling, solvent color changes, viscosity changes, etc.). The results of the qualitative solubility tests showed that all the polymers and model compounds in Figure 1 can be solubilized in some of the Lewis acid/aprotic organic solvent pairs. The amount of polymer or model compound dissolved increased with increasing concentration of Lewis acid in solution. Furthermore, some of the Lewis acids were effective to different degrees in different solvents and some were totally ineffective in all solvents. All the preliminary results showed that the most effective aprotic organic solvents, for a given effective MX_n, had a combination of low donor number (DN) with a high dielectric constant. Thus, we decided to investigate several Lewis acids in nitroalkanes and nitrobenzene in detail.

In order to determine the minimum amount of Lewis acid necessary for complete dissolution of a given amount of polymer or model compound, 2 wt % solutions or mixtures with a stoichiometric ratio of Lewis acid/polymer repeating unit or model compound of 1:1, 2:1, 3:1, 4:1, and 5:1 were prepared in widemouth jars at room temperature or up to 50 °C. All subsequent polymer solutions were prepared in such a way as to have at least the minimum MX_n: polymer stoichiometry to ensure complete solubility. In general the dilute solutions (<2–3 wt %) could be stirred with a magnetic stirring bar. The concentrated and more viscous solutions, which could not be stirred, took longer to form homogeneous solutions.

All the polymer and model compound solutions so prepared in aprotic organic solvent/Lewis acid were quite stable when stored at room temperature. No visible changes were observed in over 6 months if solvent evaporation is prevented by sealing solution-containing jars or vials with tape. Evaporation of the solvent, however, leaves behind the solid polymer complex and any uncomplexed Lewis acid.

Rheological Measurements. Intrinsic viscosity, $[\eta]$, of the polymers in the different solvents was measured at 30 ± 0.1 °C by using Cannon–Ubbelohde capillary viscometers and a constant-temperature bath. The polymer solution concentrations were adjusted such that the elution times were between 1.1 and 1.8 times the elution time of the pure solvents. No further kinetic correction to the data was made. The concentration-dependent and shear rate dependent viscosities of the concentrated polymer solutions were measured at 25 ± 0.1 °C by using a Wells–Brookfield cone and plate digital viscometer Model RTV DV-II. Various cone angles and angular rotation speeds allowed the variation of shear rate ($\dot{\gamma}$, s^{-1}) over about 3 decades. In the case of nitromethane solutions, rapid transfer of solution to the cone and plate, prealignment, and care were essential to obtaining accurate and reproducible viscosity data prior to any significant solvent evaporation.

Investigation of Solution Liquid Crystallinity. Thin layers of polymer solutions at rest were observed under crossed polarizers in transmitted light by using an Olympus Model BHSP 300 polarized light microscope. The thin films of solutions were also observed visually; transparent appearance indicated isotropic solutions whereas turbid appearance suggested possible solution anisotropy to be confirmed by polarized light microscopy. Orientation of films prepared by shearing solutions between glass slides was also used as an indication of the morphology of the solutions.

Instrumental Characterization. Electronic absorption spectra of solutions and films were obtained by using a Perkin-Elmer Lamda 9 UV–vis–near-IR spectrophotometer. The ^1H NMR spectra were taken at 300 MHz by using a General Electric Model QE300 instrument. FTIR spectra were taken at room temperature by using either free-standing films or coatings on sapphire or KCl disks and either a Nicolet Model 2SXC or Digilab Model FTS-14 Fourier transform infrared (FTIR) spectrometer. Thermal analysis was done by using a Du Pont thermal analyst Model 2100 based on an IBM PS/2 Model 60 computer and equipped with a Model 910 differential scanning calorimeter (DSC) and a Model 951 thermogravimetric analyzer (TGA). DSC and TGA runs were done in flowing nitrogen and at a heating rate of 20 °C/min.

Processing to Films and Coatings. The viscous solutions of the rigid-chain polymers in Figure 1 were readily processable to free-standing films or coatings using conventional solution processing techniques, including solution casting onto substrates, spin-coating deposition, and spray coating. An important step in the processing of these solutions of rigid-chain polymer complexes is *decomplexation* or *regeneration*, which was achieved by precipitation in a nonsolvent such as water or methanol. Coatings on glass or other substrates were typically obtained by solution casting on the substrate and evaporation of the organic solvent (e.g., nitromethane). The resulting solid film on the substrate is the polymer/Lewis acid complex, which when immersed in water precipitates a continuous coating of the pure polymer on the substrate. The nonsolvent or water was also sprayed onto the solid complex to similarly precipitate the pure polymer. Free-standing films were similarly prepared, except that the films were peeled from the substrate while still wet with precipitating nonsolvent.

Results

Solubilization of Rigid-Chain and Ladder Polymers in Organic Solvents. The polymers (BBB, BBL, PBT, and PBO) and model compounds (*cis*-BB and DHTAP) in Figure 1 were found to dissolve in aprotic organic solvents, such as nitroalkanes and nitrobenzene, containing metal halide Lewis acids (MX_n) as the complexing agents.

The complexation-mediated solubilization of the polymers and model compounds was found to depend on a number of critical factors: the ratio MX_n/polymer repeating unit; the nature of MX_n; and the nature of the aproptic organic solvent.

Although most of the Lewis acids investigated so far have been effective in forming soluble complexes of these rigid-chain polymers and model compounds, some were found to be more effective than others at similar concentrations in organic solvents. For example, the effectiveness of the following Lewis acids in promoting solubilization of BBL in nitromethane was in decreasing order: GaCl > $AlCl_3$ > $FeCl_3$ > $SbCl_5$ > $SbCl_3$. In the same solvent $InCl_3$ was ineffective in dissolving BBL. At room temperature and in all the organic solvents, $GaCl_3$ was the most effective in terms of the dissolution rate of all polymers and model compounds investigated. In principle, one might use a kind of Lewis acidity scale to predict the relative effectiveness of the various Lewis acids in promoting solubilization via complex formation. On the basis of one such Lewis acidity scale based on the electron acceptor strength of the pure Lewis acids, one would expect the relative effectiveness of the present metal halides in solubilizing the polymers to be in the decreasing order: AlX_3 > FeX_3 > GaX_3 > SbX_5 > AsX_3. Such an order was not found; in fact, $GaCl_3$ > $AlCl_3$. The main reason is that the electron acceptor properties, and hence Lewis acidity, of a given Lewis acid MX_n are significantly modified by the organic solvent in which it is dissolved. In practice, the choice of a Lewis acid for solubilizing a polymer in organic solvents will also depend on other factors such as the properties of the resulting solutions.

Many of the organic solvents (Table I) investigated as complexation and solubilization medium for the rigid-chain polymers were either not effective or only partially so. BBB, BBL, and PBT were insoluble at 1–2 wt % concentration in DMF, DMAC, NMP, DMSO, MeCN, acetone, methanol, acetic acid, benzene, chlorobenzene, toluene, and *p*-xylene containing various concentrations of MX_n = $AlCl_3$, $GaCl_3$, $SbCl_5$, $FeCl_3$, $SbCl_3$, SbF_5, or AsF_3.

It appears from the solubilization results that suitable organic solvents, which in the presence of MX_n, would dissolve the rigid-chain polymers and model compounds, are those that combine low donor number (DN) with a high dielectric constant (Table I), i.e., the nitroalkanes and nitrobenzene. Although the dielectric constant of the solvent might be expected to be an important factor especially since the polymer/Lewis acid complex might be a highly polarized species, isodielectric constant solvents can exhibit significantly different electron donor and acceptor properties as revealed by the values of empirical acceptor and donor numbers (AN and DN; Table I). Thus, DMF, MeCN, DMAc, etc., that are highly polar solvents with dielectric constants greater than 30 do not dissolve the polymers in the presence of Lewis acids because of their equally high donor number compared to nitromethane, which does. On the other hand, the requirement of a high dielectric constant is revealed by insolubility in low donor number solvents such as benzene (DN = 0.1), toluene, and chlorobenzene, which also have a low dielectric constant.

It is clear from these results that it is the solvation properties of the organic solvent/Lewis acid system that determine solubility of the rigid-chain polymers. The properties of such a solvent system, including AN, DN, and dielectric constant values, are significantly different from those of the neat organic solvent without added MX_n. The radical change in the acceptor properties of an organic solvent by adding a Lewis acid is illustrated by comparing 1,2-dichloroethane (DCE) and the composite liquid DCE/$SbCl_5$ shown in Table I. The acceptor properties of DCE as measured by the empirical acceptor number are increased 6-fold to 100 upon addition of $SbCl_5$. It is noteworthy that strong concentrated protic acids, which are the only prior solvents for these rigid-chain polymers, have acceptor numbers in the range 105.3–131.7 (Table I). Thus, by adding Lewis acids to organic solvents, aprotic organic liquids with solvation properties as powerful as those of concentrated protic acids can be obtained without the drawbacks of the latter.

Table II
Theoretical Maximum Polymer Solubility in Organic Solvents Containing Lewis Acids

solvent syst, wt % MX_n	solubility, wt % polym BBL	BBB	PBT	PBO
$AlCl_3$/NM 9	5.34	6.47	4.30	3.80
12	6.99	8.45	5.65	5.01
18	10.14	12.16	8.25	7.32
25	13.54	16.12	11.10	9.89
30	15.82	18.75	13.03	11.64
40	20.07	23.57	16.65	14.93
$GaCl_3$/NM 9	4.10	4.98	3.29	2.90
12	5.38	6.52	4.33	3.84
18	7.86	9.49	6.37	5.64
25	10.59	12.70	8.63	7.67
30	12.45	14.86	10.18	9.07
40	15.95	18.90	13.13	11.74

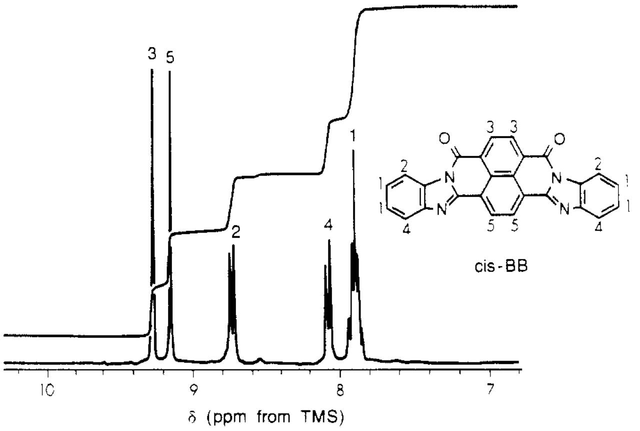


Figure 2. ^1H NMR spectrum of *cis*-BB in deuterated NM/$AlCl_3$.

One of the important findings of the solubilization studies with $AlCl_3$ and $GaCl_3$ in nitroalkanes was that a threshold stoichiometric Lewis acid MX_n/polymer (repeating unit) ratio of 4:1 was needed to form a solution. At MX_n/polymer ratios of 1:1, 2:1, and 3:1 the mixtures formed insoluble gels. Initially, each of the mixtures below the 4:1 threshold appeared to start to dissolve as judged by the color change of the solvent. However, as time proceeds the whole volume of the mixture gelled. In contrast, at 4:1, 5:1, and higher ratios the mixtures formed solutions without prior gel formation. These results suggest that the MX_n/polymer ratio of 4:1 or greater is maintained in solution. One consequence of this is that it places a theoretical limit on the polymer solubility at a given concentration of MX_n in solution as shown in Table II.

Solution Properties in Organic Solvents. Spectroscopic Properties. Figures 2 and 3, respectively, show the ^1H NMR spectra of *cis*-BB and BBB in deuterated nitromethane containing $AlCl_3$. The observed sharp resonances in Figure 2 were readily assigned to the *cis*-BB structure. The resonances of the BBB polymer are broader than its model compound, and they are largely overlapped. A small downfield shift of the resonances in

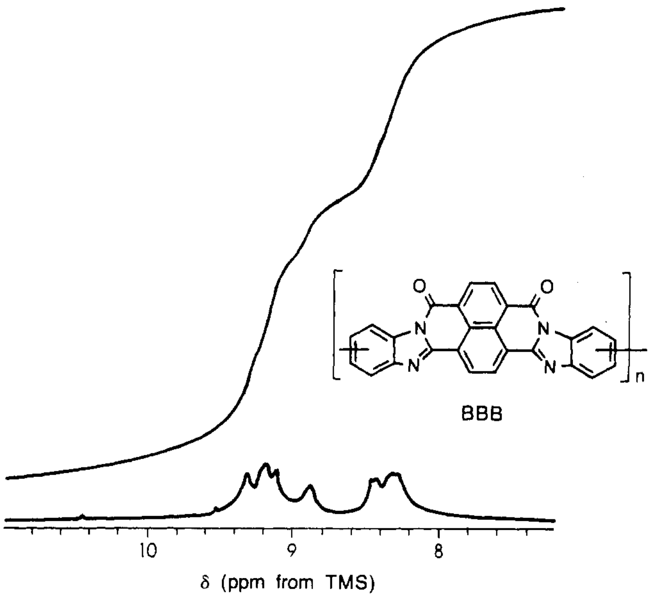


Figure 3. ^{1}H NMR spectrum of BBB in deuterated NM/$AlCl_3$.

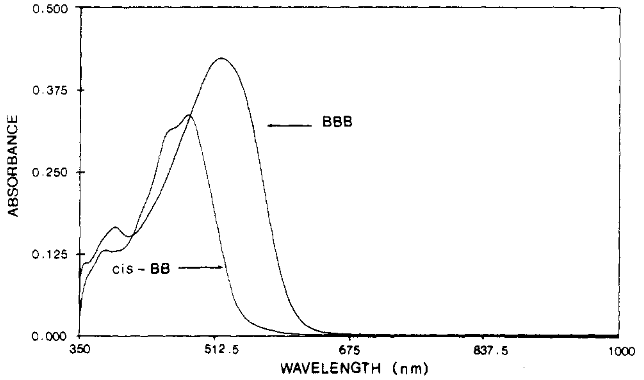


Figure 4. Electronic absorption spectra of *cis*-BB and BBB in NM/$AlCl_3$.

BBB relative to those of its model compound is also observed. However, the correct number of protons (10 H) in BBB was obtained from Figure 3. The broad *overlapped* resonances of BBB relative to its pure cis model compound suggest the presence of both cis and trans isomers of BBB repeating units randomly distributed in the chain. In fact, there is a total of 6 possible structural isomers of BBB repeating units depending on the placement of linkages through the two phenylene rings during condensation polymerization. Although the possible presence of mixed structural isomers of BBB and BBL repeating units in the polymers samples has previously been suggested from their X-ray powder diffraction patterns and physical properties,[28] this is the first direct spectroscopic evidence of such structural heterogeneity of the polymer chains. Planned further work on the structural properties of the rigid-chain polymers BBB and BBL will include a detailed NMR characterization of the trans model compound (*trans*-BB) and polymers prepared from isotropic and liquid-crystalline solutions in the case of BBL.

All the solutions of DHTAP in nitroalkane/MX_n ($AlCl_3$, $GaCl_3$, $FeCl_3$, or $InCl_3$) were deep blue. All the isotropic solutions of BBB, BBL, or *cis*-BB in nitromethane/MX_n ($AlCl_3$, $GaCl_3$, or $FeCl_3$) were red. Solutions of PBT were yellow to brown. Solutions of PBO were gold yellow. Figure 4 shows the solution electronic absorption spectra of *cis*-BB and BBB in nitromethane containing $AlCl_3$. Similar solution electronic absorption spectra of BBL in nitromethane containing 0.05 M $FeCl_3$ are shown in Figure 5. The second and third spectra of Figure 5 were obtained at two different times (and hence dissolved polymer concentrations) after adding a solid sample (~5 mg) of BBL into a neat $FeCl_3$/nitromethane liquid. The dissolution kinetics at room temperature was conveniently followed by monitoring the absorbance of the λ_{max} at 546 nm. After about 35 min, dissolution was complete, but the absorbance exceeded the limit of the instrument and went off scale relative to Figure 5. The solution electronic absorption spectrum of DHTAP in $AlCl_3$/nitromethane is shown in Figure 6. All these solution electronic spectra of the rigid-chain macromolecules in Lewis acid/nitroalkanes are similar to both the solution spectra in concentrated sulfuric acid or methanesulfonic acid and solid-state spectra. The optical absorption maximum (λ_{max}) and molar extinction coefficient (ϵ) of *cis*-BB, DHTAP, BBB, and BBL in both Lewis acid/organic solvent and protonic acids (H_2SO_4 or CH_3SO_3H) are collected in Table III. For example, the λ_{max} of BBL is 546 nm in nitromethane/$FeCl_3$, 544 nm in MSA, and 560 nm in the solid state. The similarity of the electronic spectra of the rigid-chain macromolecules in the solid state and the various solvent systems suggests similarity of the electronic structures of the chains in solution in the two solvent systems and the solid state. We also note that new absorption bands that might indicate π-electron charge-transfer effects such as radical cations (polarons) or dications (bipolarons) are absent in the electronic spectra of the polymers and model compounds (Figures 4–6).

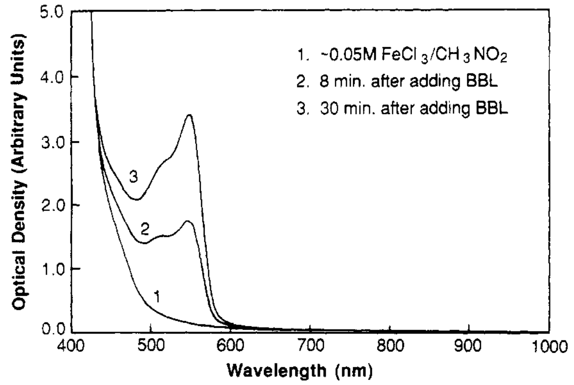


Figure 5. Electronic absorption spectra of BBL in NM/$FeCl_3$.

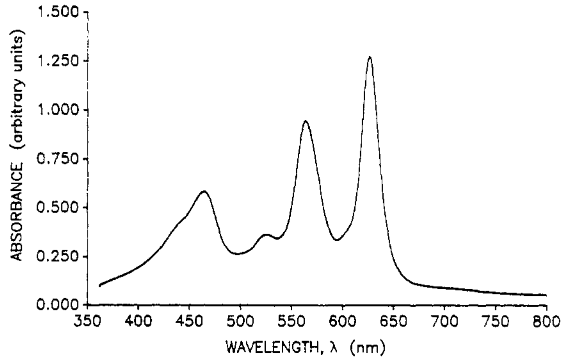


Figure 6. Electronic absorption spectrum of DHTAP in NM/$AlCl_3$.

Intrinsic Viscosity, [η]. The intrinsic viscosity of BBB in various Lewis acid/nitromethane (NM) solvent systems and in concentrated H_2SO_4 and CH_3SO_3H (MSA) at 30 °C is shown in Table IV. No systematic trend in the value of the intrinsic viscosity as a function of the Lewis acid concentration is observed in either $AlCl_3$/NM or $GaCl_3$/NM. However, a significant difference between the value of [η] in $AlCl_3$/NM and in $GaCl_3$/NM is observed; the averages of the three [η] values in each Lewis acid/

Table III
Spectroscopic Properties of Rigid-Chain Polymers and Model Compounds

model compd or polym	^{1}H NMR, ppm	UV–vis–near-IR
cis-BB	7.84 (4 H), 8.02 (d, 2 H), 8.67 (d, 2 H), 9.09 (s, 2 H), 9.21 (s, 2 H)	H_2SO_4, λ_{max} = 486 nm (ϵ = 32 400 M^{-1} cm^{-1}); $NM/AlCl_3$, λ_{max} = 482 nm (ϵ = 50 700)
DHTAP		H_2SO_4, λ_{max} = 628 nm, 576 nm, 456 nm; NM/$AlCl_3$, λ_{max}= 627 nm, 564 nm, 465 nm
BBB	5 broad overlapping resonances similar to *cis*-BB and 10 H indicated	H_2SO_4, λ_{max} = 527 nm (ϵ = 19 500); $NM/AlCl_3$, λ_{max} = 520 nm (ϵ = 52 000)
BBL		100% MSA, λ_{max} = 544 nm; $NM/FeCl_3$, 546 nm; $NM/AlCl_3$, 546 nm; NM/$SbCl_3$, 550 nm; $NB/AlCl_3$, 557 nm; $NB/SbCl_5$, 557 nm

Table IV
Intrinsic Viscosities, [η], of BBB and BBL in Various Protic Acids and Aprotic Organic Solvents at 30 °C

polymer	solvent	solvent viscosity, mPa s	[η], dL/g
BBB	concd H_2SO_4 (96%)	24.5	2.72
BBB	100% MSA (CH_3SO_3H)	10.5	5.24
BBB	30 wt % $AlCl_3$/NM	2.2	4.21
BBB	18.2 wt % $AlCl_3$/NM		3.53
BBB	9.0 wt % $AlCl_3$/NM		3.54
BBB	30 wt % $GaCl_3$/NM		5.51
BBB	18.2 wt % $GaCl_3$/NM		4.62
BBB	9.0 wt % $GaCl_3$/NM		5.23
BBL	100% MSA (CH_3SO_3H)	10.5	7.91

nitromethane system are 3.76 and 5.12 dL/g in $AlCl_3$/NM and $GaCl_3$/NM, respectively. These [η] values are also to be compared to those in concentrated H_2SO_4 and MSA.

Using rheological, light scattering, and other measurements, Berry et al.[27-31] have extensively studied the dilute and concentrated solutions of the polymers in Figure 1 (BBB, BBL, PBT, and PBO) in *protonic acid* solvents, including concentrated H_2SO_4, MSA, and CSA. They have shown that BBB in dilute solution behaves as a flexible coil whereas BBL, PBT, and PBO are rodlike in solution. Our previous studies of the solution properties of PBT in Lewis acid/nitroalkanes confirmed that PBT was also rodlike in these organic solvents.[40,41] For example, it was found that the intrinsic viscosity of PBT was constant in all the Lewis acid/nitroalkanes regardless of the nature and concentration of the Lewis acid, as expected for a true rodlike molecule in solution.[31] In contrast, the observed significant variation of [η] of BBB in the different organic solvent systems confirms that BBB is also coillike in these solvents and suggests that $GaCl_3$/nitromethane ([η] ~ 5.12 dL/g) is a thermodynamically better solvent for the polymer than $AlCl_3$/nitromethane ([η] ~ 3.76 dL/g). The rate of dissolution of BBB in the two solvent systems seems to confirm that $GaCl_3$/nitromethane is a thermodynamically better solvent; BBB dissolves in $GaCl_3$/NM about twice as fast as in $AlCl_3$/NM.

Rheological Properties of Concentrated Solutions. The steady shear viscosity of BBB solutions, $\eta(\dot{\gamma})$, in the Lewis acid/organic solvents of Table IV were measured at concentrations up to 5 wt % BBB and shear rates in the range $1 < \dot{\gamma} < 800\ s^{-1}$. Parts A and B of Figure 7 show the steady shear viscosity of 2% (w/w) BBB, respectively, in 30% $AlCl_3$/NM and 18.2% $GaCl_3$/NM as a function of shear rate. In both $AlCl_3$/NM and $GaCl_3$/NM solutions Newtonian flow behavior was generally observed in the shear viscosity until ~5% BBB when significant shear thinning was observed. It is noteworthy from Figure 7 that the zero shear viscosity (η_0) of 2% BBB in $AlCl_3$/NM is about twice the η_0 in $GaCl_3$/NM. The disparity in the viscosity of BBB solutions in $AlCl_3$/NM versus $GaCl_3$/NM becomes larger at higher polymer concentrations. For example, at 5% BBB, the $AlCl_3$/NM solutions are about 1 order of magnitude more viscous than $GaCl_3$/NM solutions.

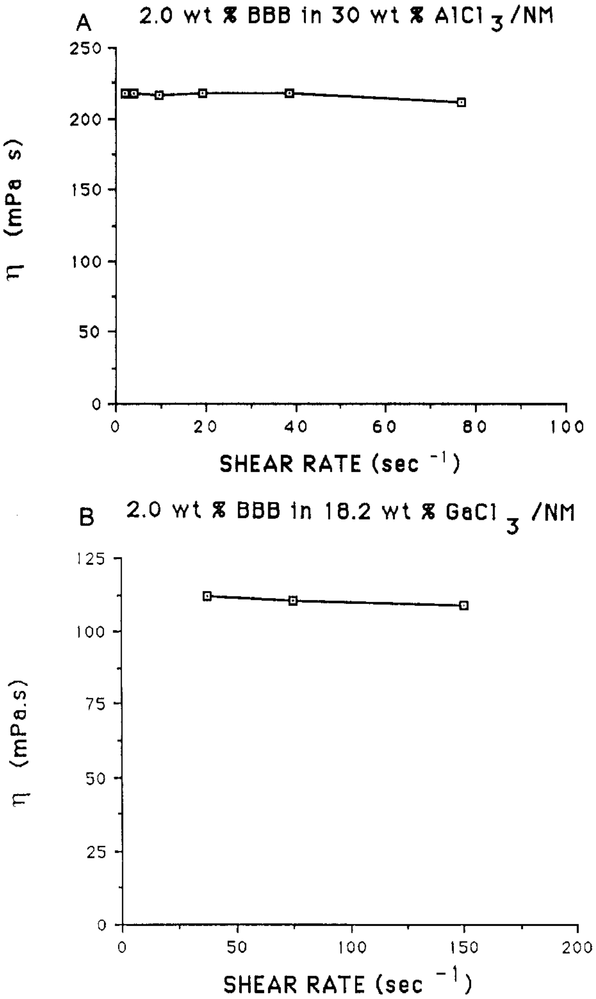


Figure 7. (A) Shear rate dependence of the steady viscosity of 2% BBB solution in 30% $AlCl_3$/NM. (B) Shear rate dependence of the steady viscosity of 2% BBB solutions in 18.2% $GaCl_3$/NM.

The concentration-dependent zero shear viscosities of BBB solutions in $GaCl_3$/NM and $AlCl_3$/NM are shown, respectively, in Figures 8 and 9; in the case of the 5% solution in $AlCl_3$/NM where a true η_0 could not be readily obtained due to shear thinning, the viscosity at the smallest accessible shear rate ($1\ s^{-1}$) was used. From Figures 8 and 9 the increase of solution viscosity with polymer concentration is seen to be more rapid in $AlCl_3$/NM compared to $GaCl_3$/NM. The observed larger viscosity (e.g, η_0) of concentrated BBB solutions in $AlCl_3$/NM compared to $GaCl_3$/NM is the exact opposite of the observed behavior of [η] in dilute solutions. A similar behavior of η_0 in $AlCl_3$ solutions versus $GaCl_3$ solutions was observed in concentrated solutions of the rigid-rod polymer PBT.[40,41] However, the intrinsic viscosity of PBT in MX_n/NM was

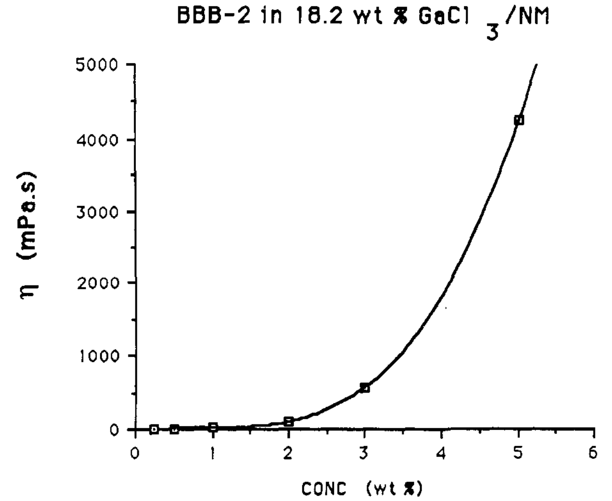


Figure 8. Concentration dependence of the zero shear viscosity of BBB solutions in 18.2% $\mathrm{GaCl_3}$/NM.

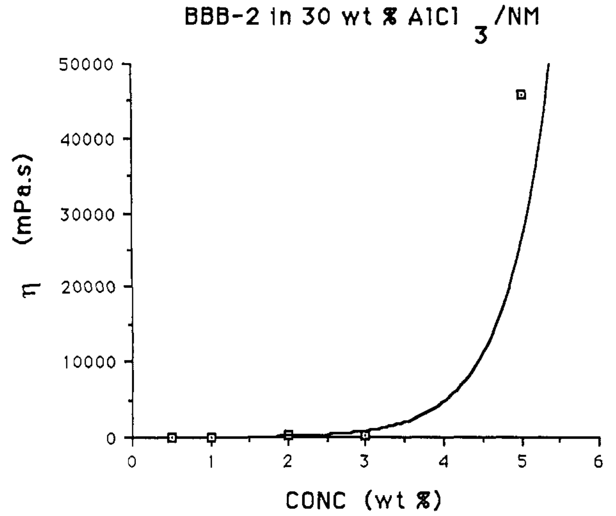


Figure 9. Concentration dependence of the zero shear viscosity of BBB solutions in 30% $\mathrm{AlCl_3}$/NM.

independent of the nature and concentration of the Lewis acid. The observed variation of the rheological properties of the concentrated solutions of BBB and PBT with the nature and concentration of the Lewis acid suggests ways of readily adjusting the polymer solutions to desired practical film, coating, and fiber processing conditions. Theoretically, a full understanding of why the rheological properties of concentrated solutions of $\mathrm{AlCl_3}$ complexes are significantly larger than $\mathrm{GaCl_3}$ complexes is still under investigation at this time.

Solution Liquid Crystallinity. As expected from the flexible-coil nature of BBB in solution, no evidence of liquid crystallinity was found in its concentrated solutions in nitromethane/MX_n (=$\mathrm{AlCl_3}$ or $\mathrm{GaCl_3}$). In contrast, 8–9% BBL-1 ($[\eta]$ = 7.91 dL/g) solutions in 28% $\mathrm{AlCl_3}$/NM contained both isotropic and liquid-crystalline phases. Solutions in the same solvent system with greater than 10% BBL-1 were largely liquid crystalline. PBT solutions in 18% $\mathrm{AlCl_3}$/NM similarly exhibit liquid crystallinity, becoming completely anisotropic solutions at 6.5% PBT or greater.[41] Onset of isotropic to biphasic phase separation in PBT solutions in 30% $\mathrm{GaCl_3}$/NM occurs at about 8% polymer.

The important conclusion from this initial investigation of liquid crystallinity in organic solvent solutions of the rigid-chain polymers in Figure 1 is that liquid-crystalline solutions can be obtained in the case of polymers with rodlike structure in solution, i.e., BBL, PBT, and PBO. Furthermore, the liquid crystallinity and isotropic/anisotropic phase equilibria of the solutions of rigid-chain polymers in organic solvents containing Lewis acids depend on both the nature (i.e., $\mathrm{AlCl_3}$ versus $\mathrm{GaCl_3}$) and concentration of the Lewis acid solution. Of special interest is the observation of liquid crystallinity in solutions of BBL in $\mathrm{AlCl_3}$/NM. Previously, truly liquid-crystalline solutions of BBL have not been achieved in protonic acids (MSA and CSA) because of poor solubility, except in polyphosphoric acid (PPA), which is the polymerization solvent.[37]

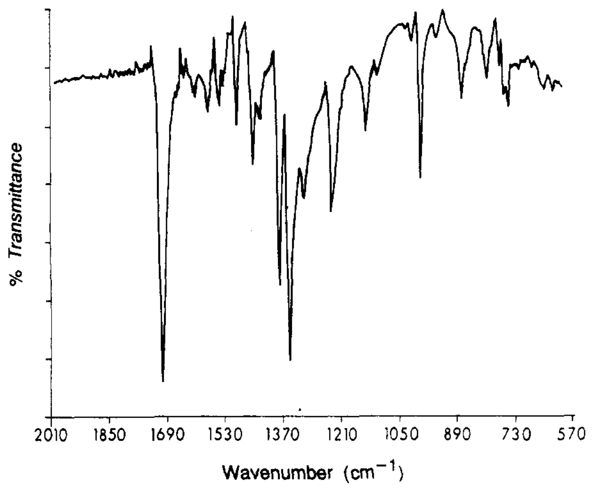


Figure 10. FTIR spectrum of BBB thin film recovered from an $\mathrm{AlCl_3}$/NM solution by precipitation in water.

Solution Processing to Films and Coatings. The viscous solutions of all the polymers investigated were readily processed into free-standing films or coatings on various substrates (glass, silicon wafers, sapphire) by conventional polymer solution processing techniques, including solution casting, spin coating, and spray coating. The main novel feature of the processing of these rigid-chain polymers from their soluble complexes in organic solvents is the *decomplexation* step, which consists of precipitation in nonsolvents, primarily water or methanol. Free-standing films were obtained by peeling off supported films from the substrate while still wet with precipitating nonsolvents.

Elemental analysis, infrared and electronic absorption spectra, and thermal analysis (DSC and TGA) of the *regenerated* polymers and model compounds were obtained to confirm the complete recovery of the pure materials from their soluble complexes. Visually the regenerated polymers and model compounds were similar in appearance to the pristine uncomplexed samples. In all cases, the analytical results showed only trace amounts of residual Lewis acid (~0.039–0.44 atomic % Cl) when either water or methanol at room temperature is used as the decomplexation or precipitation liquid.

Figure 10 shows the FTIR spectrum of a free-standing BBB film cast from an $\mathrm{AlCl_3}$/NM solution and precipitated in water. The spectrum is in excellent agreement in every detail with the previously reported spectrum of BBB.[1,2] Figure 11 shows the FTIR spectra of two BBL films: the pristine film (Figure 11A) was obtained from a uniaxially rolled as-synthesized BBL/PPA dope repeatedly extracted with boiling water and dried in vacuo; the regenerated film (Figure 11B) was cast from a 0.1 M $\mathrm{FeCl_3}$/NM solution, precipitated in methanol, and dried in vacuo. The two FTIR spectra in Figure 11 are very similar, suggesting the similarity of the regenerated and pristine BBL samples. One important detail from the FTIR spectra of Figures 10 and 11 is that the C=O absorption

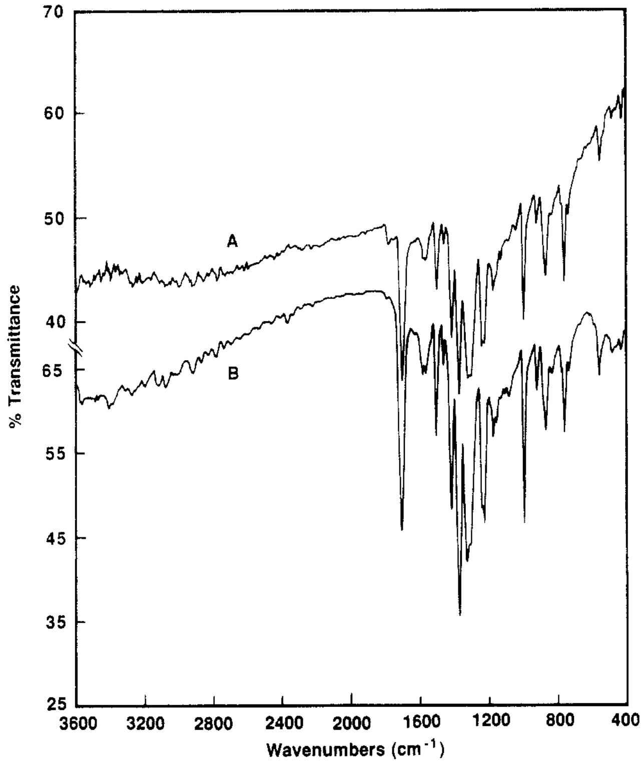


Figure 11. FTIR spectra of BBL thin films: pristine (A) and film regenerated from an FeCl$_3$/NM solution by precipitation in methanol (B).

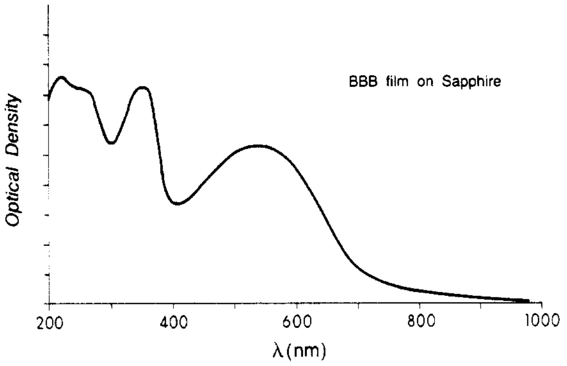


Figure 12. Electronic absorption spectrum of BBB thin film cast from AlCl$_3$/NM solution.

band is at ~1700 cm^{-1} in both regenerated and pristine samples of BBB and BBL. In contrast, the IR spectra of the Lewis acid complexes of BBB and BBL are expected to show a large shift of C=O absorption band to lower frequencies (~1600–1650 cm^{-1}) if the anticipated coordinated covalent bond is made to oxygen site, i.e., $C{=}O^{+}{-}MX_n$.

The electronic absorption spectra of BBB and BBL thin films cast from AlCl$_3$/NM solutions are shown in Figures 12 and 13, respectively. The visible absorption bands in the spectra of BBB and BBL have a λ_{max} at 540 nm (2.30 eV) and 560 nm (2.21 eV), respectively, that can be attributed to π–π^* transitions. The optical absorption edge in both spectra is at ~700 nm, which gives a solid-state semiconductor band gap of 1.77 eV for both conjugated polymers. These results are those expected for the pure conjugated rigid-chain polymers.

Figure 14 shows the thermogravimetric analysis (TGA) of a pristine BBB sample and that regenerated from AlCl$_3$/NM solution. The onset of thermal decomposition in flowing nitrogen in both BBB samples is ~700 °C. These TGA results show that the regenerated polymer is not degraded by complex formation. Similar results were found for PBT and BBL.

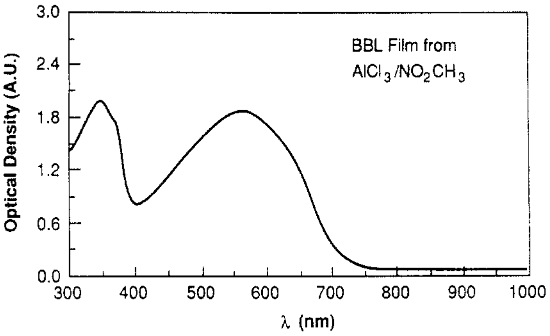


Figure 13. Electronic absorption spectrum of BBL thin film cast from AlCl$_3$/NM solution.

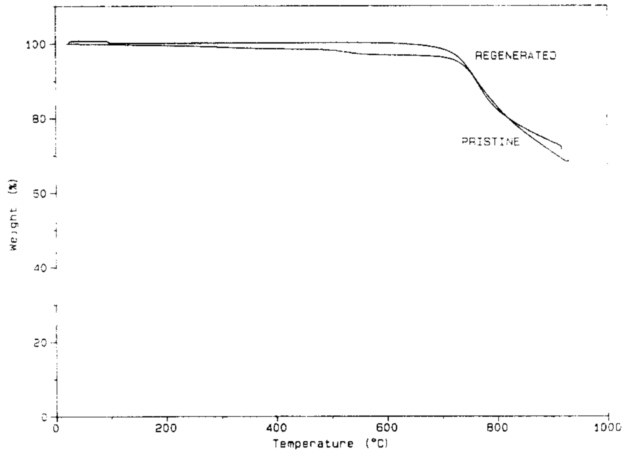


Figure 14. TGA thermograms of pristine and regenerated BBB samples at a heating rate of 20 °C/min.

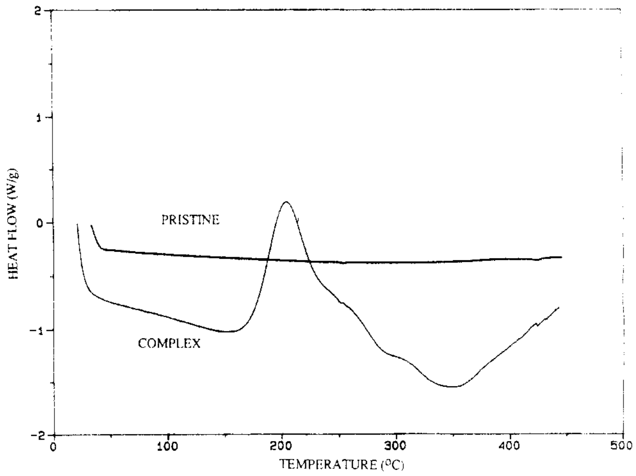


Figure 15. DSC thermograms of a pristine BBB sample and a 4:1 AlCl$_3$/BBB complex.

Figure 15 shows the DSC thermograms of a pristine BBB sample and that of the pure 4:1 AlCl$_3$/BBB (repeating unit) complex. No transitions are observed in the DSC thermogram of BBB up to 450 °C. However, over the same temperature range the DSC thermogram of the AlCl$_3$ complex exhibits both an exothermic and an endothermic transition with peaks at ~210 and ~350 °C, respectively. Precipitation of such AlCl$_3$ complexes in water or methanol and complete recovery of the pure polymer was ascertained by a DSC thermogram identical with that of the pristine BBB in Figure 15. Partially decomplexed AlCl$_3$/BBB samples had DSC thermograms that fall between the two extremes shown in Figure 15. Similar results were observed for all the other polymers investigated and both $AlCl_3$ and $GaCl_3$ complexes. Detailed studies aimed at elucidation of the origins of observed DSC transitions as well as the solid-state structure and properties of the Lewis acid complexes of the rigid macromolecules in Figure 1 are currently in progress and will be reported elsewhere.

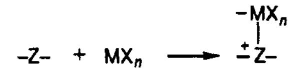
Overall, these analytical, spectroscopic, and thermal analysis results for the polymers regenerated from their Lewis acid complexes by precipitation in nonsolvents (water and methanol) show that the pure polymers are recovered. Thus, complexation-mediated solubilization of the rigid-chain polymers in Figure 1, forming their viscous solutions processable by conventional polymer processing techniques and the facile recovery of the pure polymers in the form of free-standing films and coatings from their soluble complexes, substantiate the basic concept.

Discussion

Nature of Lewis Acid Complexes and Mechanism of Solubilization. The basic complex-forming reaction between the metal halide Lewis acids (MX_n) and the polymers or model compounds of Figure 1 is a Lewis acid–base reaction. There are two possible Lewis acid–base reactions of these macromolecules since they are highly conjugated structures on the one hand and contain non-bonded electron pair donor atoms on the other. The polymer (P) can donate π-electrons to the Lewis acid, resulting in the formation of a π-electron charge-transfer (CT) complex (eq I). Alternatively, the Lewis acid–base

$$P + MX_n \rightarrow P^+(MX_{n+1}^-) \qquad (I)$$

reaction can occur site-specifically at the heteroatom donor sites (-Z-) on the macromolecules



$$-Z- \;+\; MX_n \longrightarrow \overset{-MX_n}{\overset{|}{\pm Z-}} \qquad (II)$$

where -Z- = -S-, -O-, =N-, >C=O, -NH-, or >N-. The resulting product of the reaction of eq II is an electron donor–acceptor (EDA) complex in which a localized coordinated covalent bond is formed between the metal atom of MX_n and the donor heteroatom Z. Both the CT complex (eq I) and the EDA complex (eq II) are highly polarized species relative to the pristine materials of Figure 1. However, the CT complex is ionic in nature and hence is a polyelectrolyte whereas the EDA complex is a neutral molecular adduct compound.

The CT complex of eq I is similar to the product of well-known redox reactions of "doping" phenomena in conjugated polymers. For example, $AlCl_3$, $FeCl_3$, and other metal halide Lewis acids (MX_n) in organic solvents are known to react with polyacetylene, $(CH{=}CH)_n$, and other conjugated polymers to form electrically conductive CT complexes.[42,43] Similarly, liquid AsF_3/AsF_5 mixture reacts with poly(*p*-phenylene sulfide) (PPS) to form conductive and soluble CT complexes.[44] Other examples of soluble "doped" conjugated polymers include polycarbazoles doped with liquid I_2[45] and poly(3-alkylthiophenes) doped with I_2 or $SbCl_5$ in organic solvents.[46] Some of the characteristic features of such CT complexes include the following: (1) a new absorption band in the electronic spectrum due to the π-electron charge transfer forming radical cations (polarons) or dications (bipolarons); (2) a high dc conductivity of the solid-state CT complex; (3) the ratio of MX_n to the polymer repeating unit being generally less than 1; (4) the complex-forming reaction of eq I only being partially or at best completely reversed by another redox reaction using a strong reducing agent. These features were not observed. On the basis of these considerations in conjunction with all our results, we rule out the CT complex and eq I.

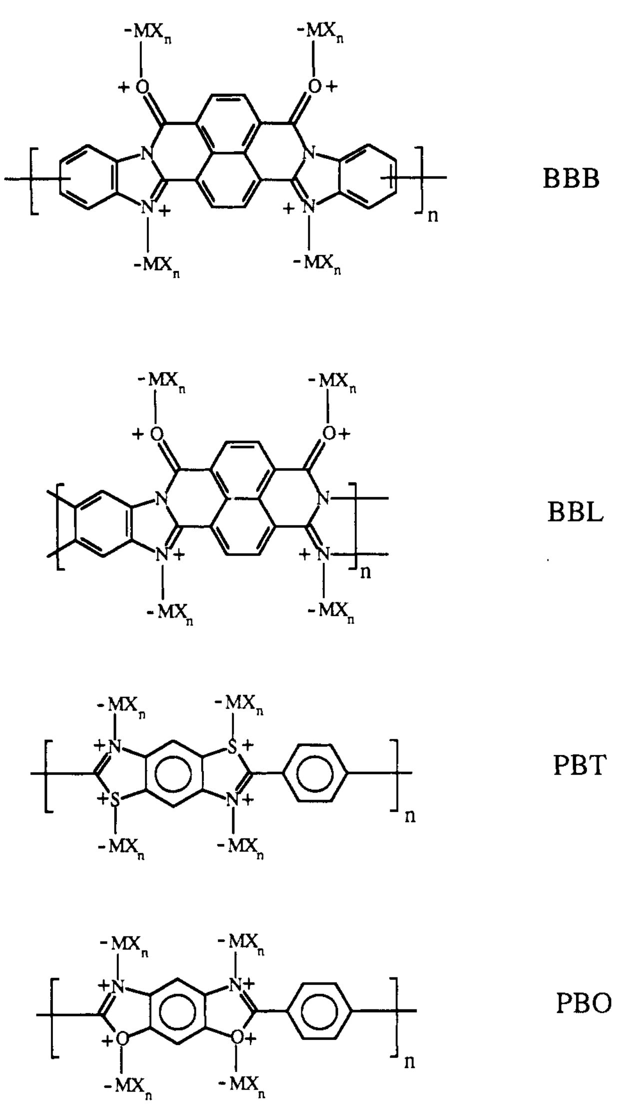


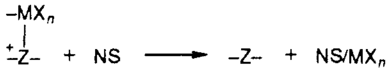
Figure 16. Structures of the soluble Lewis acid (MX_n) complexes of rigid-chain polymers.

The results of solubilization studies and characterization of the Lewis acid complexes in solution and solid state directly support eq II, i.e., a site-specific Lewis acid–base reaction forming an EDA complex. The isolated Lewis acid complexes of the polymers and model compounds are not conductive; they all have the 4:1 MX_n/polymer (repeating unit) stoichiometry, except in MX_n/DHTAP where the ratio is 2:1. The observed compositions of the complexes show that all the complexable Lewis base sites in PBT (4), PBO (4), BBB (4), BBL (4), *cis*-BB (4), and DHTAP (2) are actually complexed by MX_n. In the case of the two secondary amine sites (-NH-) in DHTAP and two tertiary amine sites (>N-) each in BBB, BBL, and *cis*-BB, the unpaired electrons are not readily available for complexation. The Lewis acid complexes of the rigid-chain polymers are shown in Figure 16. The observed solution electronic absorption spectra of the Lewis acid complexes were similar to the solid-state spectra of the pristine polymers. The facile recovery of the pure polymers from their complexes is a further direct evidence for the EDA nature of the complexes as will be discussed in more detail below. FTIR studies of the Lewis acid complexes of these and related polymers also confirm the site specificity of the complexation reaction as will be reported elsewhere:[47] IR absorption bands at 1700 cm^{-1} due to C=O in the pristine and regenerated materials are shifted to lower frequencies (~1615 cm^{-1}) in the complexed polymers due to $C{=}O^{+-}MX_n$.

The highly polarized EDA complex of eq II suggests the requirement of a polar organic solvent (high dielectric constant) and a low donor number (Table I) for solvation in accord with the solubilization results. The reason why a low donor number solvent, such as the nitroalkanes or nitrobenzene, is necessary is due to the possible competing complexation reaction of solvent (S) with the Lewis acid:

$$S + MX_n \rightarrow S/MX_n \qquad \text{(III)}$$

This explains why, in the presence of such highly polar organic solvents as DMF, DMAc, DMSO, MeCN, and NMP, the Lewis acids preferentially complex the solvent *rather than the polymer. The high donor number solvents* are stronger Lewis bases than the polymers. This also explains the facile decomplexation reaction of the EDA complexes with nonsolvents (NS) such as water and methanol that are stronger Lewis bases than the polymers:



$$\overset{-MX_n}{\overset{|}{\overset{+}{-}Z-}} + NS \longrightarrow -Z- + NS/MX_n \qquad \text{(IV)}$$

Thus, in addition to water and methanol other high donor number solvents (Table I), such as DMF, DMAc, MeCN, and NMP, are excellent precipitating nonsolvents for the recovery of the pure polymers from their soluble complexes (eq IV).

The present mechanism of solubilization of rigid-chain polymers via site-specific Lewis acid–base reactions that form EDA complexes (eq II; Figure 16) is to be contrasted with the previously known solubilization of aromatic polyamides in LiCl/DMF, LiCl/DMAc, and related solvent systems.[38,39] Not surprisingly, the polymers in Figure 1 are insoluble in such LiCl/amide solvent systems. However, we expect polyamides to be soluble in the present Lewis acid (MX_n)/low donor number aprotic organic solvent systems.

Concluding Remarks

A new general approach to the solubilization and processing of heretofore insoluble rigid-chain and ladder polymers in aprotic organic solvents is reported. It is demonstrated that a reversible, nondegradative formation of electron donor–acceptor complexes of rigid-chain polymers with metal halide Lewis acids (MX_n = $AlCl_3$, $GaCl_3$, etc.) allows their solubilization in organic solvents and subsequent conventional solution processing to films, coating, and fibers of the pure polymers. Among the rigid-chain macromolecules that have been dissolved in organic solvents by this approach are the following: BBL, BBB, *cis*-BB, DHTAP, PBT, and PBO. In the case of polymers with rodlike structure in solution, such as BBL and PBT, liquid-crystalline (nematic) solutions can be obtained at high concentrations. The liquid crystallinity, isotropic/anisotropic phase equilibria, and rheology of the concentrated solutions of the rigid-chain polymers in aprotic organic solvents containing Lewis acids were found to depend on both the nature (MX_n = $AlCl_3$ or $GaCl_3$) and concentration of the Lewis acid in solution.

The Lewis acid complexes of these rigid-chain polymers (eq II and Figure 16) are of interest in their own right. They are excellent model systems for the study of intermolecular interactions in polymers and the role of such secondary bonding forces in shaping structure and properties. The present results demonstrate the significant effect of such intermolecular interactions on polymer solubility. The complexes may also be melt processable or find applications as polymer catalysts or reagents. It also appears that the Lewis acid–base reaction of eq II might apply to other classes of polymers that contain the relevant electron donor heteroatom sites: for example, polyamides, aromatic polyimides, polyureas, polypeptides, and proteins.

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