Lewis acid coordination complexes of polymers:

3. Poly(benzobisimidazobenzophenanthroline) ladder and semiladder polymers

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(Received 3 August 1993; revised 5 March 1994)

The structures, solution properties and solid state properties of complexes of poly(benzobisimidazobenzophenanthroline) ladder (BBL) and its semiladder analogue (BBB) with the Lewis acid aluminium(III) chloride ($AlCl_3$) and gallium(III) chloride ($GaCl_3$) are reported. At a 4:1 mole ratio of Lewis acid to polymer (BBB or BBL) repeat unit, electron donor–acceptor complexes of Lewis acid–base type, which are highly soluble in organic solvents, are formed. A detailed spectroscopic investigation shows that complexation of both polymers involves coordination of the Lewis acids to the electron-rich carbonyl oxygens and the imine nitrogens in the polymer backbones. The complexes of BBL exhibit the characteristic rigid-rod behaviour of the pristine ladder polymer. BBL complexes have rigid, rod-like chain conformations in dilute solution as evidenced by their solvent independent intrinsic viscosities. The complexes form liquid crystalline solutions above 8 wt% BBL in $AlCl_3$/nitromethane and above 9–9.5 wt% in $GaCl_3$/nitromethane. The solid complexes of BBL have slightly smaller optical absorption edges than BBL and ~50% larger absorption coefficients at λ_{max}. D.s.c. revealed a glass transition (T_g) of the 4:1 $GaCl_3$:BBL complex at 15°C. Dynamic mechanical experiments indicated the T_g, measured at the loss tangent peak, was in the range 29–37°C depending on frequency, with an activation energy of 448 kJ mol^{-1}. The complexes of BBB by contrast exhibit flexible-coil behaviour due to the polymer topology. In solution, BBB complexes have intrinsic viscosities which depend on the solvent and Lewis acid used, due to differing degrees of coil expansion in different solvent media. Coil expansion in solution leads to improved conjugation of BBB complexes as evidenced by comparison of the electronic absorption spectra with those of BBL. BBB complexes, like the pure polymer, are apparently not liquid crystalline at high concentrations in solution. The solid 4:1 $GaCl_3$:BBB complex has a T_g at 30°C, and a dynamic mechanical analysis T_g in the range 12–24°C. The T_g activation energy, at 293 kJ mol^{-1}, is lower than that of the BBL/$GaCl_3$ complex. The overall results of the present studies provide a basis for understanding the structure and properties of these polymers in terms of intermolecular interactions and also have implications for the processing of the polymers for diverse applications.

(Keywords: Lewis acid; coordination complexes; properties)

INTRODUCTION

Poly[(7-oxo-7H,10H-benz[de]imidazo[4′,5′:5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL, *Scheme 1a*) is a member of a class of polymers known as ladder polymers, so named because a schematic diagram of their molecular structures resembles a ladder (*Scheme 1b*)[1]. Poly(6,9-dihydro-6,9-dioxobis-benzimidazo[2,1-b:1′,2′-j]benzo[lmn][3,8]phenanthroline-2,13-diyl) (BBB, *Scheme 1c*) is known as a semiladder polymer for similar reasons (*Scheme 1d*). The synthesis of ladder polymers was motivated by the need for materials with increased resistance to thermal-oxidative degradation compared with conventional polymers[2–5]. Their double-stranded structures have reduced tendencies towards complete chain scission due to the necessity of breaking at least two adjacent bonds in a backbone ring to do so. BBB and BBL were first synthesized[2–4] in an effort to develop polymers with very high strength and high temperature resistance for use as structural materials in aerospace applications[5,6]. Although BBL has a fully fused structure and BBB does not, no significant differences in thermal and mechanical properties are observed[4]. Both polymers are thermally stable (i.e. exhibit no weight loss) to 550°C in air and 700°C in nitrogen. Various other polymers were also synthesized which are based on the bisimidazonaphthalamide structure[7–9].

Due to the difficulties encountered in processing, the mechanical properties which were reported[4,10] are low compared to theoretical estimates[11]. In the case of BBL, Young's moduli of 3.65 and 7.58 GPa and tensile strengths of 66.2 and 114.5 MPa were reported for films prepared by filtration of a suspension and acid processing, respectively[4,10]. Wierschke[11] has predicted a modulus of 720–745 GPa for BBL by AM1 calculations, which probably indicates that the experimental values achieved are suboptimal. Several studies have been carried out to characterize the morphology and thermal

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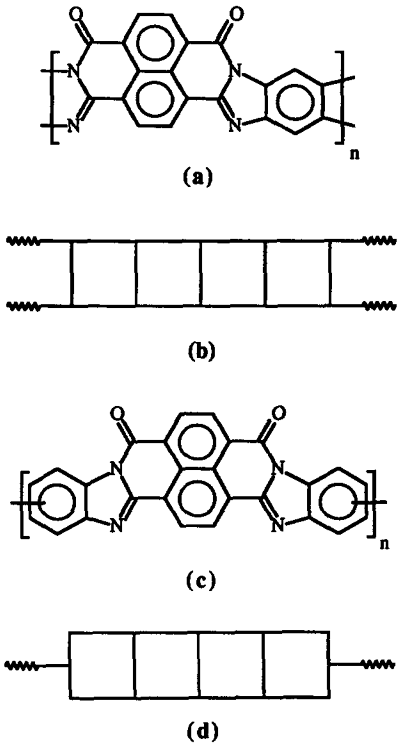

Scheme 1

transitions of such films[12–16]. X-ray diffraction studies[12–14] revealed that BBB is non-crystalline, although diffuse diffraction maxima indicated extensive short-range stacking of the repeat units with a very close intermolecular spacing of 3.5–3.6 Å (perpendicular to the plane of the repeat). Weaker reflections at 7.5 Å indicated some correlation of the molecules in the molecular plane and approximately perpendicular to the long axis of the repeat unit. Tensile and creep recovery[12–14] measurements in the range 30–500°C indicated that this 'supramolecular' structure is relatively insensitive to temperature and no glass or other transition was evident in this temperature range. As one might expect from its fused, rigid-rod structure, BBL is semicrystalline and exhibits sharp diffraction maxima at 3.4 and 8.4 Å[15,16]. A weak in-chain relaxation was detected for BBB at −120°C and for BBL at −50°C by dynamic mechanical methods[17]. This loss dispersion was assigned as a β-transition. No other transitions were detected in the temperature range −150°C to 250°C for either polymer. Nayak and Mark[18] have constructed molecular models for BBL and BBB and shown by their calculations that the intractability (as measured for example by the absence of any thermal transitions below 500°C) and poor solubility of these polymers is due to the very strong intramolecular and intermolecular forces which prevail in the solid polymers.

Berry and co-workers have carried out extensive studies of the dilute and concentrated solutions of BBB and BBL[19–24]. The poor solubility of both polymers limited the then available solvents to concentrated sulfuric acid, methanesulfonic acid (MSA) and molten antimony trichloride (m.p. 73.4°C). Dissolution in the protic acids was found to be accompanied by extensive protonation of the polymer chains[19–22]. Reduction of the carbonyl oxygens of BBB and BBL by sodium hydrosulfite also rendered the polymers soluble in an aqueous solution of sodium hydroxide and pyridine[19]. As expected from its non-fused structure, BBB behaves as a flexible coil polymer in solution[19,23,24]. BBL has a rigid-rod structure in solution[20,22–24] although liquid crystallinity was not observed due to the limited polymer solubility.

More recently there has been interest in the potential of BBB and BBL as electronic and optical materials[15,16,25–30]. Sulfuric acid doped films of BBL were produced with a conductivity of $2\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and lower conductivities were obtained with alternative dopants[25,26]. The doping mechanism has been probed by MNDO studies of the band structure of BBL[27]. Work in our group has shown that conductivities in the range $80–200\,\Omega^{-1}\,\mathrm{cm}^{-1}$ can be achieved for BBL by ion implantation doping[15,16,28]. Electrical conductivities as high as $20\,\Omega^{-1}\,\mathrm{cm}^{-1}$ were achieved in electrochemically doped BBL[16]. We have reported the third-order non-linear optical susceptibility ($\chi^{(3)}$) spectra of BBL, BBB and a model compound in the wavelength range 1.0–2.4 μm and analysed the results using an essential states model[29,30]. The magnitude of $\chi^{(3)}$ was found to be greater for BBL than BBB at all wavelengths and is in the range 0.96×10^{-11}–6.4×10^{-11} esu for both polymers. In our studies of the non-linear optical properties of these polymers, we employed a technique developed in our laboratory for processing of BBB and BBL[31,32]. The technique involves solubilization of BBB or BBL in an organic solvent, such as nitromethane, in the presence of a metal halide Lewis acid. The solutions produced are used to prepare films, coatings or fibres of the polymers by conventional techniques. Our success in processing these polymers via conventional organic solvents eliminates many of the difficulties associated with processing of ladder polymers[33], which stem from their insolubility and intractability.

In earlier papers we have reported how our soluble complexes approach may be applied to other classes of polymers such as rigid-rod polymers[34–38] (e.g. poly(*p*-phenylene benzobisthiazole) (PBZT)[36–38]) and polyamides[39,40]. In all cases we found on examining the complexes formed that the metal halide Lewis acids (e.g. BCl_3, $AlCl_3$, $GaCl_3$) coordinate to heteroatoms in the polymers (e.g. O, N, S) thus forming electron donor–acceptor complexes. In this paper, we examine the structures of the complexes of BBB and BBL with the Lewis acids $AlCl_3$ and $GaCl_3$ to elucidate the coordination sites, and we report on their solution and solid state properties. Apart from the practical interest in improving their tractability and processability, the two polymers BBB and BBL constitute a unique and interesting system for study, quite different from polymer systems whose complexes we have investigated previously[31,32,34–40]. Although the two polymers have very similar chemical structures, they have very different chain conformations due to differences in the chain topologies. BBL has a very rigid structure and is conformationally inflexible due to its completely formed ladder structure. On the other hand BBB does not have a completely fused structure and rotations about the single bonds at either end of each repeat unit give conformational flexibility to the polymer.

EXPERIMENTAL

BBB and BBL were synthesized according to literature methods[4]. The BBB sample had an intrinsic viscosity of $5.65\,\mathrm{dl\,g^{-1}}$ in 99% MSA at 30°C. The corresponding molecular weight (M_w) is 172 000 which we obtained by extrapolation of Berry and Yen's intrinsic viscosity–molecular weight data[19]. The BBL sample had an intrinsic viscosity of 8.2 dl g^{-1} in MSA at 30°C. The intrinsic viscosity–molecular weight relationship is not well established for this polymer and we estimate M_w is ~75 000 from Berry's plot of the Yamakawa–Fujii relationship[22] with an assumed hydrodynamic chain diameter of 12 Å. Polymer samples were dried thoroughly in a vacuum oven at 100°C and then stored under nitrogen prior to use. All organic solvents, Lewis acids and protonic acids were used as received without further purification: nitromethane, 99+% (Aldrich); dichloromethane, 99+% (Aldrich); $AlCl_3$, 99.99% (Aldrich); $GaCl_3$, 99.9999% (Alfa); MSA, 99% (Aldrich); sulfuric acid, 98% (Fischer).

Preparation of complexes

All polymer complexes were prepared in a Vacuum Atmospheres Dri-Lab filled with nitrogen due to the moisture sensitivity of the group III metal halides used. A Dri-Train assembly attached to the glovebox circulated the gas to remove residual oxygen and water vapour to a level of 1–5 ppm. Nitromethane was found to be the most suitable solvent for preparation of solutions of the polymer complexes due to its low electron donating ability and high dielectric constant which provide the right medium for the Lewis acid–base reaction and complex dissolution, respectively, as discussed in more detail elsewhere[37]. Solutions of the complexes of BBB or BBL with $AlCl_3$ or $GaCl_3$ were prepared as follows. A specific amount of Lewis acid was weighed and added to nitromethane. The mixture was stirred at room temperature until the Lewis acid was completely dissolved. A known weight of BBB or BBL was then added to the solution and the mixture was stirred until the polymer was completely dissolved. Polymer dissolution commences immediately at room temperature as indicated by the change of solution colour from colourless to deep purple within a few seconds of adding the polymer. In the case of concentrated solutions (e.g. $> \sim 3$ wt% polymer) complete dissolution took several days but could be accelerated by heating at 40–60°C. The amount of Lewis acid Y (g) necessary for complete polymer dissolution was calculated using the formula:

$$\frac{rX}{M} = \frac{Y}{M_r} \tag{1}$$

where X is the amount of polymer used (g), M is the molecular weight of the polymer repeat unit taken as 334 for BBL and 410 for BBB, M_r is the molecular weight of the Lewis acid and r is the minimum number of moles of Lewis acid required per mole of polymer repeat unit. We found r to be 4.0 ± 0.05 for $AlCl_3$ or $GaCl_3$ complexes of BBB or BBL. In the case of very concentrated solutions ($> \sim 4$ wt% polymer) which were very viscous, an r value of 6 or greater was sometimes used to accelerate polymer complexation and dissolution. Solutions of polymer complexes prepared in this way were stable over a period of many months without apparent losses in viscosity or visible polymer precipitation. Solid polymer/Lewis acid complexes were prepared from these solutions by slow evaporation of nitromethane in vacuum at 60°C for 10–12 h. (Throughout this paper, when a ratio 'Lewis acid:polymer' is referred to this always means moles of Lewis acid per mole of polymer repeat unit, unless otherwise specified, e.g. 4:1 $AlCl_3$:BBB means $r=4$ in equation(1)).

BBB or BBL complexes with $AlCl_3$ or $GaCl_3$ were also prepared in dichloromethane. In this case the complexes do not dissolve because of the low polarity of the solvent, and complexation proceeds by heterogeneous reaction of the Lewis acid with the solid polymer (dichloromethane also has a very low electron donating ability[37]). Complexes of BBB and BBL prepared in dichloromethane using $r > 4.0$ were soluble in nitromethane. For purposes of studying the details of the complexation process we also prepared several BBB/$GaCl_3$ complexes with r values between 0 and 4.0. The solubility of $AlCl_3$ in dichloromethane is limited to ~1 wt%. $GaCl_3$ dissolves readily in dichloromethane and solutions >20 wt% were easy to prepare. The solid complexes were removed from solution and dried in vacuum as described above.

Aliquots of solutions were pressed between microscope glass slides and coverslides for optical microscopy studies. The edges of the coverslides were then sealed to the slides using a Cytoseal 280 mounting medium to prevent solvent evaporation. As a simple shearing experiment, the coverslides of unsealed samples were made to slide over the solutions with the bottom glass slides held stationary. Complexes for i.r. spectroscopy were thin films cast on NaCl substrates from nitromethane solutions or free standing films prepared in dichloromethane. Solid samples for u.v.-visible (vis.) spectroscopy were on the order of 0.1 μm thin films sandwiched between optically flat fused silica substrates. Solutions for u.v.-vis. spectroscopy were 10^{-4}–10^{-5} M in polymer repeat unit, contained in quartz cells. Solutions for n.m.r. spectroscopy contained 1–2 wt% polymer in deuterated nitromethane. Samples for dynamic mechanical analysis (d.m.a.) were thin films (~1 μm thick) sandwiched between glass microscope slides (55 × 20 × 1 mm).

Instruments and methods

Fourier transform infra-red (*FT*i.r.) spectroscopy was carried out using a Nicolet 20SXC *FT*i.r. spectrometer at a resolution of 4 cm^{-1}. Sets of 32 scans were signal averaged and the resulting spectra were stored on disk. Internal calibration of the frequency scale was done to an accuracy of 0.2 cm^{-1} with a He-Ne laser. All spectra were taken at room temperature (25–27°C) under nitrogen purge. U.v.-vis. spectra were collected on a Perkin–Elmer Lambda 9 spectrophotometer. N.m.r. spectra were obtained with a General Electric model QE400 spectrometer. For ^{27}Al n.m.r. experiments, a 0.5 M aqueous solution of $AlCl_3$ was used to obtain a reference as described in a previous paper[37]. The sharp resonance of the $Al(H_2O)_6^{3+}$ ion was thus taken as the zero ppm reference on the chemical shift scale. Thermal analysis was done with a DuPont model 2100 TA system which is based on an IBM PS/2 computer. D.s.c. was also done under a nitrogen purge and at a heating rate of 20°C min^{-1}. An indium (m.p. 156.6°C) standard was used to calibrate the d.s.c. instrument. Intrinsic viscosities were measured at 30.0 ± 0.1°C by using Cannon–Ubbelohde capillary viscometers. Polymer concentrations were chosen such that the elution times were between 1.1 and 1.8 times the elution times of the pure solvents. Optical microscopy studies were carried out by using an Olympus model BH2 microscope equipped with polarizers which were set at the crossed (90°) position. D.m.a. experiments were done by using a Rheometrics

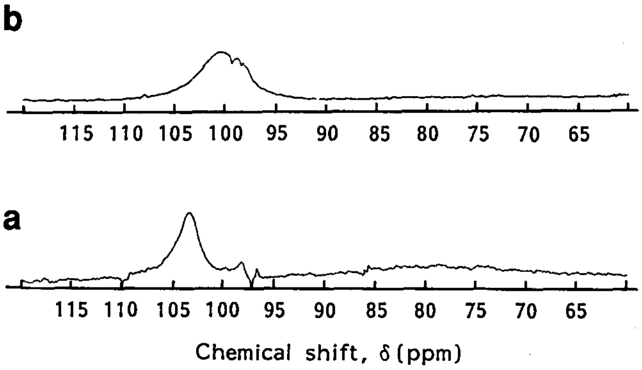

Figure 1 ^{27}Al n.m.r. spectra of (a) 4.10:1 $AlCl_3$:BBB and (b) 10.40:1 $AlCl_3$:BBB in deuterated nitromethane. Ratios are mole ratios of $AlCl_3$ to polymer repeat unit in solution

solids analyser model RSAII with liquid nitrogen as a coolant. Measurements were taken every 3°C with a thermal soak time of 1 min.

RESULTS AND DISCUSSION

Structures of BBB and BBL complexes

Solution studies. In an earlier paper we reported the ^{27}Al n.m.r. spectrum of an $AlCl_3$/nitromethane solution. The aluminium resonance observed was a sharp singlet shifted 98 ppm downfield of the reference $Al(H_2O)_6^{3+}$. The position of this resonance is in the expected region (40–140 ppm) for tetrahedral aluminium adducts[41] and Schmerling[42] has shown that the dissolved species is the addition complex $AlCl_3 \cdot CH_3NO_2$. In the following discussion we use the adjective 'free' for aluminium chloride which exhibits this 98 ppm resonance. 'Free' is used in the sense that the $AlCl_3$ is merely solvated by nitromethane and is not coordinated to any polymer.

Figure 1 shows ^{27}Al n.m.r. spectra of two different solutions of BBB in $AlCl_3$/nitromethane. *Figure 1a* is the spectrum obtained for a 4.10:1 $AlCl_3$:BBB solution in nitromethane. The largest resonance is a singlet at 103.5 ppm with a minor peak at 98 ppm. The 103.5 ppm resonance is due to $AlCl_3$ which is coordinated to BBB ('coordinated' $AlCl_3$). The species giving rise to the 98 ppm peak is free $AlCl_3$. Thus coordination to BBB causes a downfield shift of 5.5 ppm relative to the free $AlCl_3$. This shift is slightly larger than was seen in the case of coordination to PBZT[37] wherein the resonance of coordinated $AlCl_3$ was at 103 ppm, corresponding to a 5.0 ppm downfield shift. Integration of the 103.5 ppm and 98 ppm peaks gave an approximate ratio of 1:0.05. This implies that for each mole of BBB repeat unit in solution, the corresponding 4.1 moles of Lewis acid present is divided between free and coordinated species in the ratio 0.2:3.9. This means that there are 3.9 moles of Lewis acid coordinated to each repeat unit of BBB, which corresponds very closely with the 4:1 $AlCl_3$:BBB minimum stoichiometry necessary for polymer solubilization in nitromethane. The slight difference between actual $AlCl_3$ coordinated (3.9 moles) and necessary (4.0 moles) for dissolution may be attributable to the approximate nature of the spectral integration.

The solution of the BBB complex in *Figure 1b* had a stoichiometry of 10.4:1 $AlCl_3$:BBB in nitromethane. A very broad resonance with a peak between 100 ppm and 101 ppm is observed. In contrast to *Figure 1a*, the separate resonances of free and coordinated $AlCl_3$ cannot be easily deconvoluted from this spectrum. This is due to the large $AlCl_3$ excess in solution over the 4:1 $AlCl_3$:BBB complex stoichiometry. Consequently a large free $AlCl_3$ resonance overlaps with a coordinated resonance of similar broadness and intensity.

The results of similar experiments in solutions of BBL in $AlCl_3$/nitromethane are shown in *Figure 2*. *Figure 2a* shows the spectrum of a solution of 4.56:1 $AlCl_3$:BBL. The resonance of free $AlCl_3$ is again at 98 ppm and the resonance of $AlCl_3$ coordinated to BBL appears as a broad singlet at 103.5 ppm. Integration of coordinated and free resonances gave a ratio of 1:0.27. Thus the 4.56 moles of $AlCl_3$ per mole of BBL used to prepare this solution are divided in the ratio 3.6 moles coordinated to each mole of BBL repeat unit and 0.96 moles free. This corresponds approximately to the minimum of 4 moles of Lewis acid per mole of BBL repeat unit necessary for solubilization. The difference (i.e. 3.6:1 *versus* 4:1) may be due to the error in the integration since the baseline is quite erratic in the region of the resonances, or that a complex with stoichiometry slightly less than 4:1 is in fact soluble.

The stoichiometry used in the solution of *Figure 2b* was 7.06:1 $AlCl_3$:BBL. The resonances of free $AlCl_3$ at 98 ppm and of $AlCl_3$ coordinated to BBL around 103.5 ppm are visible in this spectrum also. The peak overlap and erratic baseline make it difficult to reliably deconvolute the signals for integration.

The results of *Figures 1* and *2* show that the stoichiometry of the soluble BBB and BBL complexes with $AlCl_3$ is close to 4 moles of Lewis acid per mole of polymer repeat unit. A question to be answered in the next section is how the Lewis acid coordinates to BBB or BBL and what the resulting complex structures are. We note from *Scheme 1* that there are six Lewis base heteroatoms in the repeat unit of each polymer (two carbonyl oxygens, two amide nitrogens and two imine nitrogens) which are possible coordination sites.

Solid state studies. The *FT*i.r. spectrum of BBB is shown in *Figure 3a* and that of BBL is shown in *Figure 4a*. The spectra of these polymers are complicated and unambiguous assignment of all of the bands would be very difficult. It is known that up to six isomers of the BBB and two isomers of the BBL repeat unit structures in *Scheme 1* may arise during synthesis[19,27]. These isomers contribute to the complexity of the *FT*i.r. spectra.

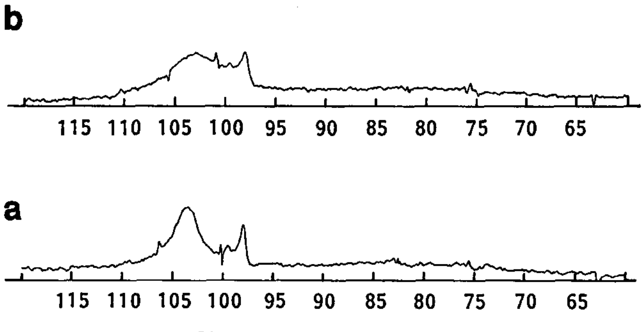

Figure 2 ^{27}Al n.m.r. spectra of (a) 4.56:1 $AlCl_3$:BBL and (b) 7.06:1 $AlCl_3$:BBL in deuterated nitromethane. Ratios are mole ratios of $AlCl_3$ to polymer repeat unit in solution

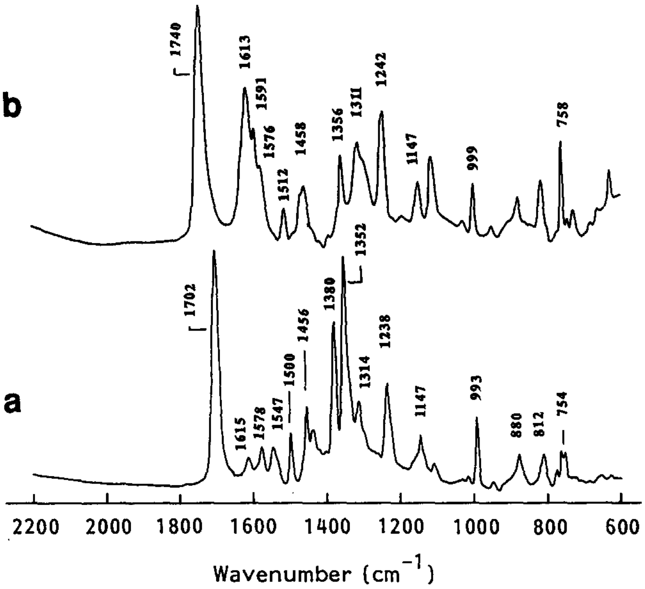

Figure 3 *FT*i.r. spectra of thin films of (a) BBB and (b) BBB/GaCl$_3$ complex with a 4:1 GaCl$_3$:BBB ratio

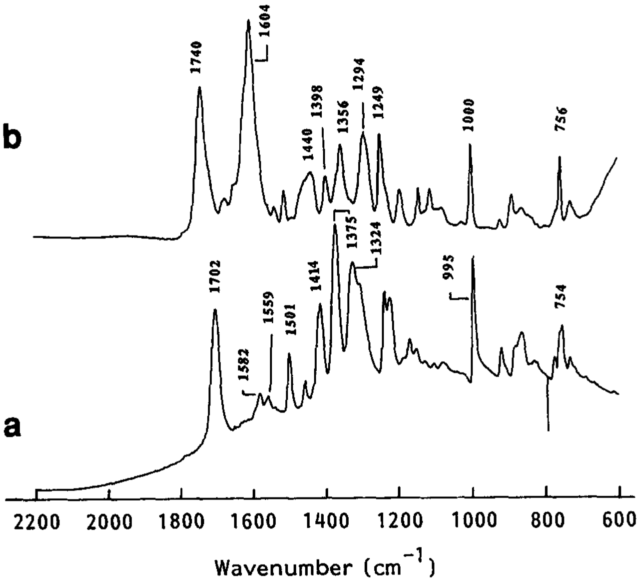

Figure 4 *FT*i.r. spectra of thin films of (a) BBL and (b) BBL/GaCl$_3$ complex with a 4:1 GaCl$_3$:BBL ratio

Nonetheless, several important bands may be assigned and provide sensitive probes of the polymer structures.

The most prominent band in the spectrum of BBB is at 1702 cm^{-1} and is due to carbonyl stretching, ν(C=O). In BBL this band also appears at 1702 cm^{-1}. There are several bands of lower intensity adjacent to this mode in BBB at 1615, 1578, 1547 and 1500 cm^{-1}. Similar bands appear in the spectrum of BBL at 1582, 1559 and 1501 cm^{-1}. Kim[25] has assigned the band at 1582 cm^{-1} in BBL to stretching of the imine carbon–nitrogen double bond, ν(C=N). The same assignment may be made for the 1578 cm^{-1} band of BBB. The surrounding bands (1615, 1547 and 1500 cm^{-1} in BBB, and 1559 and 1501 cm^{-1} in BBL) are due to aromatic carbon–carbon stretching and other skeletal modes associated with the C=N bonds.

At lower frequencies there are bands at 1456 and 1437 cm^{-1} in the spectrum of BBB, and at 1457 and 1413 cm^{-1} in that of BBL. The origin of these bands is, most probably, stretching of the amide carbon–nitrogen bonds, ν(C–N). Bands in the region 1380–1265 cm^{-1} are associated with carbon–nitrogen stretching in tertiary arylamines[43]. BBB exhibits bands at 1380, 1352 and 1314 cm^{-1}, and bands in this region appear at 1375, 1324 and 1307 cm^{-1} for BBL. Therefore these bands arise from stretching of the various carbon–nitrogen single bonds, ν(C–N), in the BBB and BBL structures. Skeletal vibrations also appear at 1238 and 993 cm^{-1} in the BBB spectrum, and at 1239, 1223 and 995 cm^{-1} in the BBL spectrum. An in-plane C–H bend[43] of BBB is at 1147 cm^{-1} and BBL has such bands at 1171 and 1152 cm^{-1}. Out-of-plane C–H wag modes of the phenyl rings are at 880 and 812 cm^{-1} in BBB, and at 919 and 864 cm^{-1} in BBL[43]. The 754 cm^{-1} band in both polymers is attributable to the out-of-plane C–H wag of the two adjacent carbon–hydrogen bonds on the naphthalene rings[43]. The preceding band assignments for BBB and BBL are summarized in *Table 1*.

The *FT*i.r. spectrum of the 4:1 GaCl$_3$:BBB complex is shown in *Figure 3b*. The spectrum is quite different from that of BBB in *Figure 3a*. To study the effects of coordination of GaCl$_3$ on the BBB spectrum, the 1:1, 2:1 and 3:1 GaCl$_3$:BBB complexes were also prepared and their spectra are shown in *Figures 5a, b* and *c*, respectively. The spectra of *Figures 3* and *5* were thus used to analyse the gradual structural changes as BBB is complexed with GaCl$_3$ from the pure BBB up to the 4:1 (stoichiometric) complex which is soluble in organic solvents.

At 1:1 stoichiometry in *Figure 5a*, the ν(C=O) band of BBB is split into two components, one at 1709 cm^{-1} and one at 1734 cm^{-1}. By comparing the band intensities of the sample of *Figure 5a* and that of the pure BBB subsequently regenerated from the same complex film, we found that the 1709 and 1734 cm^{-1} bands of the 1:1 complex are, respectively, 71 and 55% as intense as the 1702 cm^{-1} band of pure BBB. At 2:1 stoichiometry in *Figure 5b*, the ν(C=O) band is at 1739 cm^{-1} with a shoulder at slightly lower wavenumber. The 1739 cm^{-1} band is more intense (125%) than the ν(C=O) band of uncomplexed BBB. In the 3:1 complex of *Figure 5c* a single sharp band is observed at 1740 cm^{-1} with evidence of only a very minor shoulder to the lower frequency side. This band is again more intense (132%) than the

Table 1 Bands of the *FT*i.r. spectra of BBB and BBL and their assignments

BBB (cm^{-1})	BBL (cm^{-1})	Assignment
1702	1702	ν(C=O), carbonyl carbon–oxygen stretching
1578	1582	ν(C=N), imine carbon–nitrogen stretching
1615, 1547, 1500	1559, 1501	Aromatic carbon–carbon and carbon–nitrogen skeletal modes
1456, 1437	1457, 1413	ν(C–N) of amide carbon–nitrogen bonds
1380, 1352, 1314	1375, 1324, 1307	ν(C–N) of carbon–nitrogen single bonds
1238, 993	1239, 1223, 995	Mixed skeletal vibrations
1147	1171, 1152	In-plane C–H bending
880, 812	919, 864	Out-of-plane C–H wagging
754	754	δ(C–H), out-of-plane wag of naphthalene C–H bonds

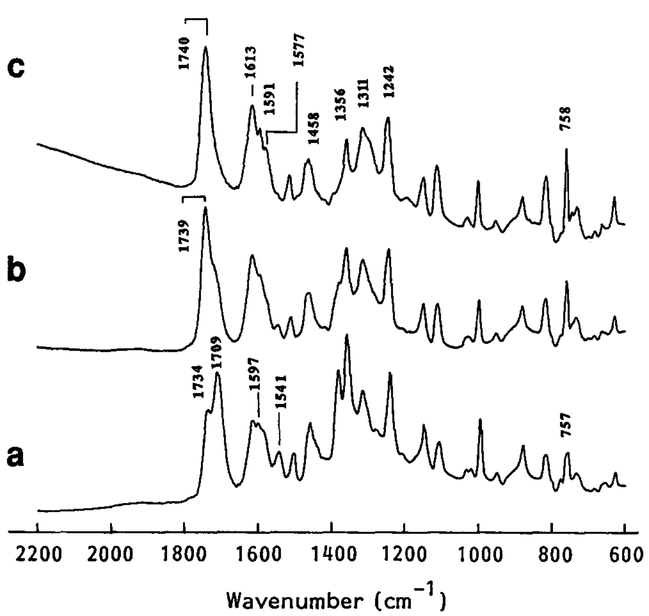

Figure 5 *FT*i.r. spectra of thin films of (a) 1:1 $GaCl_3$:BBB, (b) 2:1 $GaCl_3$:BBB and (c) 3:1 $GaCl_3$:BBB complexes

ν(C=O) band of BBB. Finally in the 4:1 complex (*Figure 3b*) the ν(C=O) mode is a single sharp band at 1740 cm^{-1} with 179% of the intensity of the same mode in BBB.

The gradual elimination of the 1702 cm^{-1} band of pure BBB, and its replacement by a band at 1740 cm^{-1} is evidence that the Lewis acid, $GaCl_3$, is coordinating to the carbonyl oxygens. Thus the band at 1740 cm^{-1} represents complexed carbonyl oxygen and the 1702 cm^{-1} band uncomplexed carbonyl oxygen. In the 1:1 complex there is a mixture of complexed and uncomplexed oxygens. As the $GaCl_3$:BBB ratio is increased, the uncomplexed oxygens are gradually complexed until none remain and the 1702 cm^{-1} band is completely eliminated at the 4:1 (stoichiometric) ratio. The shift of the ν(C=O) band to higher frequency on complexation indicates a net increase in the carbon–oxygen bond order. This is the opposite of what was seen in the case of coordination of $GaCl_3$ to the carbonyl oxygens of aliphatic polyamides. For example, in the case of nylon 6, complexation caused a decrease in bond order ($\Delta\nu = 25$ cm^{-1})[40]. This shift was rationalized on the basis of electron withdrawal by the Lewis acid leading to a reduced carbon–oxygen bond strength. The important difference between BBB and aliphatic polyamides which causes this difference in behaviour on complexation is that BBB has a highly conjugated structure whereas the polyamides do not. The availability of high energy π-electrons in the vicinity of the carbon–oxygen bonds results in an electron redistribution in the BBB structure when $GaCl_3$ coordinates to the oxygens. The net result is a strengthening of the carbon–oxygen bonds. This type of resonance stabilization has been predicted from MNDO calculations of the effect of oxidation on the chain geometry of BBL[27]. It has also been observed experimentally for complexes of aromatic Schiff bases[44,45] and related polymers[36–38,46] in the case of coordination of Lewis acids to imine nitrogens.

Concurrently with the shift of the ν(C=O) band to 1740 cm^{-1} as $GaCl_3$ is added to the BBB structure, there are changes in the bands at 1456 and 1437 cm^{-1}. In the 1:1 complex of *Figure 5a*, the 1437 cm^{-1} band has merged with the 1456 cm^{-1} band and is evident only as a broad shoulder to this band. In the 2:1 complex in *Figure 5b* the 1437 cm^{-1} band has disappeared and a sharp band is evident at 1458 cm^{-1} with a shoulder to the higher wavenumber side. This shoulder gradually emerges in the 3:1 and 4:1 complexes as a band at 1469 cm^{-1} which overlaps with the more intense 1458 cm^{-1} band.

The bands at 1437 and 1456 cm^{-1} in the spectrum of BBB are assigned to the carbon–nitrogen stretch of the amide (>CON<) units. The observed changes to these bands upon complexation indicate an increase in bond order. This may be the result of increased delocalization of the nitrogen lone pair electrons along the amide carbon–nitrogen bonds. Delocalization of the nitrogen lone pair electrons occurs for resonance stabilization of the amide units[47,48]. This resonance reduces the likelihood of electrophilic attack at the nitrogens. This is further ensured by the steric inaccessability of these nitrogens due to the very close surrounding atoms. Thus, as in the case of linear polyamides[39,40], complexation of the amide segments of BBB (there are two per repeating unit, as shown in *Scheme 1*) with $GaCl_3$ results in coordination of the Lewis acid to the carbonyl oxygens and not the nitrogens. This is accompanied by a rehybridization of the atoms and resonance stabilization of adjacent C=O and carbon–nitrogen bonds.

The 1578 cm^{-1} stretching mode of the imine carbon–nitrogen bonds, ν(C=N), of BBB is affected by complexation with $GaCl_3$. To examine the changes to this band it is necessary to also look at changes in the adjacent skeletal bands at 1547 and 1615 cm^{-1}. In the 1:1 complex of *Figure 5a*, the 1547 cm^{-1} band of BBB is still evident (at 1541 cm^{-1}), but the ν(C=N) band has merged with the 1615 cm^{-1} band and has shifted to 1597 cm^{-1}. This band has a broad shoulder at the lower wavenumber side. The 1615 cm^{-1} band has increased in intensity relative to BBB. In the 2:1 complex of *Figure 5b*, the 1547 cm^{-1} band becomes quite weak and the 1615 cm^{-1} band has gained further intensity. The new ν(C=N) mode appears at 1592 cm^{-1} in this spectrum. In the 3:1 complex of *Figure 5c* the 1547 cm^{-1} band has disappeared completely and a new band at 1577 cm^{-1} has emerged in its place. The ν(C=N) band is at 1591 cm^{-1}, overlapping with the other skeletal mode which is now at 1613 cm^{-1}. Finally, in the 4:1 complex (*Figure 3b*) there are bands at 1576, 1591 and 1613 cm^{-1} in this region of the spectrum. The other skeletal band in this region of the BBB spectrum, namely the 1500 cm^{-1} band, shifts to 1501 cm^{-1} in the 1:1 complex, 1508 cm^{-1} in the 2:1 complex, and 1512 cm^{-1} in the 1:3 and 1:4 complexes.

The shift of the 1576 cm^{-1} ν(C=N) band of BBB by 15 cm^{-1} to higher frequency in the spectrum of the 1:4 $GaCl_3$:BBB complex indicates coordination of the imine nitrogens by $GaCl_3$. The increase in frequency arises from a rehybridization of the nitrogen and adjacent atoms and a consequent increase in C=N bond order, caused by withdrawal of the nitrogen lone pair electrons by the Lewis acid. This type of shift to higher frequency has been observed on complexation of imine nitrogens by Lewis acids in many structures, e.g. complexes of conjugated Schiff bases with BF_3[44,45], polyazomethines complexed with $GaCl_3$[46] and complexes of poly(*p*-phenylene benzobisthiazole) with $AlCl_3$ and $GaCl_3$[37].

The carbon–nitrogen single bond stretching bands, ν(C–N) of BBB at 1380, 1352 and 1314 cm^{-1} exhibit small changes in their frequencies when the polymer is complexed with $GaCl_3$. In the 1:1 complex they are at

Table 2 U.v.-vis. absorption data for BBB, BBL and their complexes

	λ_{max} (nm)	ε ($l\,mol^{-1}\,cm^{-1}$)[a]	α (cm^{-1})[a]	E_g (nm)[b]
BBB in $GaCl_3$/NM[c]	517	3.9×10^4	–	606
BBB in $AlCl_3$/NM[c]	520	4.0×10^4	–	607
BBB[d]	518	–	5.7×10^4	686
BBB/$GaCl_3$[d]	531	–	8.7×10^4	621
BBB/$AlCl_3$[d]	531	–	8.7×10^4	621
BBL in $GaCl_3$/NM[c]	546	4.9×10^4	–	580
BBL in $AlCl_3$NM[c]	545	4.9×10^4	–	581
BBL[d]	561	–	5.8×10^4	704
BBL/$GaCl_3$[d]	557	–	8.7×10^4	645
BBL/$AlCl_3$[d]	544	–	8.5×10^4	666

NM, nitromethane

[a] Molar absorptivity (ε) and absorption coefficient (α) at λ_{max}

[b] Low energy absorption band edge

[c] 10^{-4} M solution

[d] Solid film

1379, 1355 and 1314 cm^{-1}, respectively. In the 2:1 complex they shift to 1375, 1356 and 1312 cm^{-1}, respectively. The 1375 and 1356 cm^{-1} bands overlap in the spectrum of *Figure 5b* so that the 1375 cm^{-1} appears as a shoulder on the 1356 cm^{-1} band. In the 3:1 complex the bands are at 1356 and 1311 cm^{-1}. The 1375 cm^{-1} mode has lost intensity and appears as a very weak band in the spectrum of *Figure 5c*. In the 4:1 complex (*Figure 3b*) the 1375 cm^{-1} band is very weak and the two adjacent bands are at 1356 and 1311 cm^{-1}. The 1238 cm^{-1} skeletal mode and phenyl C–H bending modes (1147, 880 and 812 cm^{-1}) of BBB are affected very little by complexation with $GaCl_3$. None shifts more than 4 cm^{-1} in the spectra of *Figure 5* and *Figure 3b*. As the stoichiometry of $GaCl_3$ is increased, the 993 cm^{-1} skeletal mode of BBB shifts gradually to 999 cm^{-1} in the 4:1 complex. The 754 cm^{-1} out-of-plane C–H bending of the naphthalene ring of BBB shifts to 758 cm^{-1} in the spectrum of the 4:1 complex (*Figure 3b*) and increases noticeably in intensity, relative to adjacent bands. The hydrogens in question are very close to the sites of Lewis acid coordination, namely the carbonyl oxygens and imine nitrogens. The steric influence of nearby Lewis acids causes the observed effect of complexation on this C–H mode.

The 4:1 $AlCl_3$:BBB complex had an *FT*i.r. spectrum (not shown) which was similar to that of the 4:1 $GaCl_3$:BBB complex of *Figure 3b*. The ν(C=O) band was at 1735 cm^{-1} and the amide carbon–nitrogen stretch was at 1478 cm^{-1}. This indicates coordination of $AlCl_3$ to the carbonyl oxygens, as before. The ν(C=O) shift relative to BBB is 23 cm^{-1} which is slightly less than the 27 cm^{-1} shift observed for the $GaCl_3$ complex. The ν(C=N) band was at 1590 cm^{-1} and by comparison with the 1592 cm^{-1} band of the $GaCl_3$ complex this also indicates coordination of $AlCl_3$ to the imine nitrogens. Other bands associated with ν(C–N) modes, skeletal modes and (C–H) deformations were within 3 cm^{-1} of those observed for the 4:1 $GaCl_3$:BBB complex of *Figure 3b*.

In summary, the preceding results indicate that the 4:1 Lewis acid:BBB stoichiometry found in the solution studies is accounted for by coordination of the Lewis acids ($AlCl_3$ or $GaCl_3$) to specific sites in the polymer backbone. These sites are the two carbonyl oxygens and two imine nitrogens. Coordination of the Lewis acids involves withdrawal of the lone pair electrons of these heteroatoms and resonance stabilization in adjacent bonds.

The effects of complexation on the absorption bands of BBL are analogous to the effects observed in complexes of BBB. Coordination of $GaCl_3$ to the carbonyl oxygens of BBL effects a shift of the ν(C=O) band from 1702 cm^{-1} in *Figure 4a* to 1740 cm^{-1} in *Figure 4b*. The amide carbon–nitrogen bands at 1458 and 1414 cm^{-1} in BBL merge into a broader band at 1440 cm^{-1} on complexation. The imine ν(C=N) band of BBL at 1582 cm^{-1} shifts to 1604 cm^{-1} in the BBL/$GaCl_3$ complex spectrum of *Figure 4b*. This band is very intense compared to the uncomplexed ν(C=N) mode of BBL. The blue shift of 22 cm^{-1} indicates an increase in C=N bond order and coordination of the Lewis acid to the imine nitrogens as in BBB. The ν(C–N) modes at 1375, 1324 and 1307 cm^{-1} of BBL shift to 1398, 1356 and 1294 cm^{-1}, respectively, on complexation with $GaCl_3$. The various other skeletal modes of BBL are affected by complexation in an analogous fashion to bands of BBB discussed earlier. Most notably, the 1239 cm^{-1} band shifts to 1249 cm^{-1} and the 995 cm^{-1} band shifts to 1000 cm^{-1}. The 754 cm^{-1} out-of-plane C–H deformation of the naphthalene ring of BBL shifts to 756 cm^{-1} and has greater intensity in *Figure 4b* relative to adjacent bands than in the BBL spectrum of *Figure 4a*.

Electronic structures of BBB and BBL complexes

The wavelengths of maximum absorption (λ_{max}) and the low energy band edges or optical bandgaps (E_g) of BBB, BBL and their complexes are given in *Table 2*. The optical absorption spectrum of 10^{-4} M BBB in $GaCl_3$/nitromethane is shown in *Figure 6*. The absorption spectrum of 10^{-4} M BBB in $AlCl_3$/nitromethane is similar to that of BBB in $GaCl_3$/nitromethane and has been reported earlier[32]. The λ_{max} and E_g of BBB in both solutions are very close, as seen in *Table 2*. Thus BBB/$GaCl_3$ complex has essentially the same electronic structure in solution as its $AlCl_3$ or $GaCl_3$ complex. The optical absorption spectrum of BBL in $GaCl_3$/nitromethane (10^{-4} M) is shown in *Figure 6* and was almost indistinguishable from that of BBL in $AlCl_3$/nitromethane. The data in *Table 2* show that the λ_{max} and E_g values are practically the same for these solutions. Therefore the BBL/$GaCl_3$ and BBL/$AlCl_3$ complexes have very similar electronic structures in solution. The spectra of *Figure 6* show that there is considerable overlap of the lowest energy absorption bands of BBB and BBL complexes in solution. The λ_{max} of BBB complexes are blue-shifted by

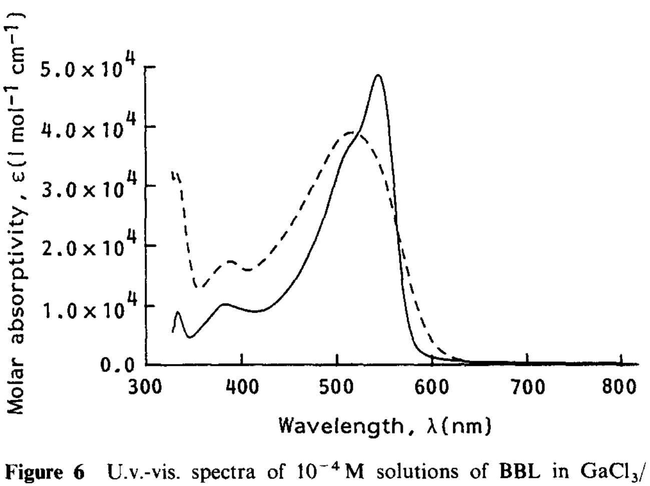

Figure 6 U.v.-vis. spectra of 10^{-4} M solutions of BBL in $GaCl_3$/nitromethane (——) and BBB in $GaCl_3$/nitromethane (– – –)

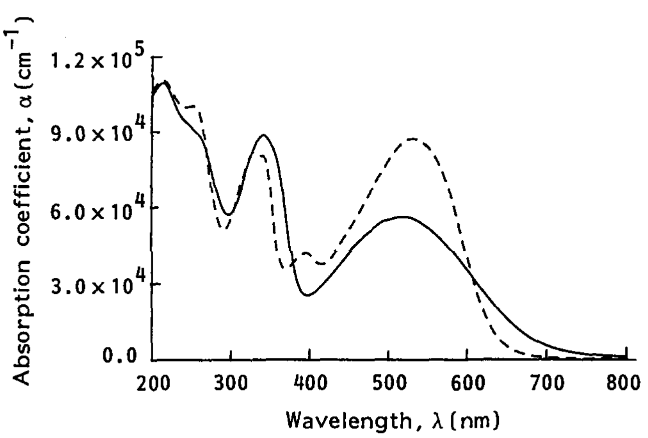

Figure 7 U.v.-vis. spectra of thin films of BBB (—) and the 4:1 $GaCl_3$:BBB complex (- - -)

25–29 nm relative to the BBL complexes. However, the sharp decrease in absorption at wavelengths above λ_{max} for BBL complexes results in a bandgap of higher energy than for BBB complexes. This lower bandgap of BBB complexes in solution implies better conjugation in BBB, which suggests that BBB complexes have an extended chain conformation in solution since this is the necessary chain geometry to achieve better conjugation than BBL whose molecules are rigid and rod-like.

Figure 7 shows the absorption spectra of thin films of BBB and the solid BBB/$GaCl_3$ (1:4) complex. The λ_{max} and E_g values obtained from these spectra are given in *Table 2*. The λ_{max} and E_g values of the solid BBB/$AlCl_3$ complex are also given in *Table 2*, and the spectrum of this complex was exactly the same as that of the BBB/$GaCl_3$ complex in *Figure 7*. Thus, as in solution the BBB/$AlCl_3$ and BBB/$GaCl_3$ solid complexes have similar electronic structures. The absorption coefficient, α, of the BBB/$GaCl_3$ complex of *Figure 7* was estimated by dividing absorbance by the thickness of the BBB film subsequently regenerated from the complex. This involves the assumption that complexation did not affect film thickness. However, the absorption coefficient calculated in this way represents the absorption per unit thickness of pure BBB and therefore gives insight into the effect of complexation on the absorption coefficients of the BBB chromophore. Comparison of the spectra of *Figure 7* shows that complexation causes a 55% increase in absorption coefficient at λ_{max}. This indicates that complexation increases the transition dipole moment of BBB. There is also an increase of 13 nm in λ_{max} while the band edge decreases by 65 nm. The effect of coordination of Lewis acid to the BBB chains is therefore to decrease conjugation due to the effect of electron withdrawal on the delocalized π-electron cloud in BBB molecules.

Figure 8 shows the absorption spectra of thin films of BBL, BBL/$AlCl_3$ complex and BBL/$GaCl_3$ complex. The λ_{max} and E_g values from these spectra are given in *Table 2*. In this case the $AlCl_3$ and $GaCl_3$ complexes exhibit some discernible differences although they are qualitatively similar in terms of the effects of complexation on the BBL spectrum. About 50% increases of the absorption coefficient at λ_{max} are observed for both complexes. The lowest energy absorption band of both complexes is blue-shifted relative to that of BBL. Thus the effect of complexation is to decrease conjugation and increase the transition dipole moment of BBL. The reasons for the differences between the BBL/$AlCl_3$ and BBL/$GaCl_3$ spectra are not obvious and probably arise from differences in the morphology of the complexes.

In the solid state BBL is known to be highly crystalline[15,16] whereas random-coil BBB molecules form amorphous polymer films[12–14]. This is in contrast to the solution phase where BBB molecules are chain extended. The effect of coiling of the BBB molecules when the polymer aggregates is evident in the optical spectra presented here. As discussed earlier, BBB complexes are more highly conjugated than BBL complexes in solution, as evidenced by the differences in their optical absorption edges. However, when these complexes are aggregated into solid films or precipitated as films of pure BBB or BBL, increased intermolecular interactions cause red shifts of λ_{max} and E_g compared to the solution values. The effect is, however, greater for BBL. The band edge of solid BBL is red-shifted by 18 nm from that of BBB. Therefore, although BBB is more highly conjugated than BBL in solution, coiling of the BBB molecules on aggregation results in decreased π-electron delocalization between the repeat units, and BBL which retains its rigid-rod conformation on aggregation is the more conjugated structure of the two in the solid state. The band edges of the solid BBL complexes are also red-shifted from those of the BBB complexes and hence it appears that the solid BBB complexes have contracted coil structures in which there is poorer π-electron delocalization than in BBL complexes.

Solution properties of BBB and BBL complexes

Dilute solutions. The intrinsic viscosities of BBB and BBL in various solvents are listed in *Table 3*. In these experiments the minimum amount of Lewis acid was used in the Lewis acid/nitromethane solvents to prevent precipitation of polymer during the experiments. It proved impractical to use just the stoichiometric requirement of Lewis acid (i.e. $r = 4$ in equation (1)) due to tendency of BBB and BBL to precipitate under the influence of atmospheric moisture, and therefore an excess of ~20% Lewis acid ($r \approx 4.8$) was used to prevent precipitation from occurring.

A large variation in intrinsic viscosity of BBB with solvent was observed. Berry *et al.*[12,19] have proposed that BBB can be modelled as a non-draining coil polymer

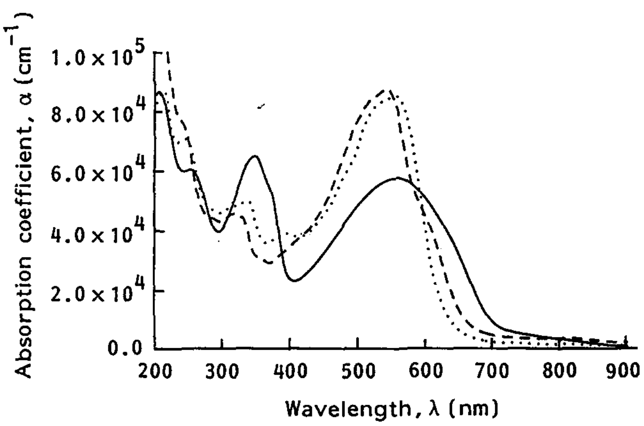

Figure 8 U.v.-vis. spectra of thin films of BBL (—), the 4:1 $AlCl_3$:BBL complex (- - -) and the 4:1 $GaCl_3$:BBL complex (···)

Table 3 Intrinsic viscosity $[\eta]$ of BBB and BBL in various solvents at 30°C

Polymer	Solvent	$[\eta]$ (dl g^{-1})
BBB	97% sulfuric acid	2.64
	99%MSA	5.65
	1 wt% $AlCl_3$ in NM	6.10
	1 wt% $GaCl_3$ in NM	4.90
BBL	99% MSA	8.20
	1 wt% $AlCl_3$ in NM	8.20
	1 wt% $GaCl_3$ in NM	8.30

and the intrinsic viscosity may be given by the relation:

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

where Φ_0 is the universal constant, M is the molecular weight, $(\langle s^2\rangle_0)^{1/2}$ is the root-mean-square radius of gyration of the unperturbed coil and α is the coil expansion factor. The factor α^3 is proportional to the hydrodynamic volume of the coils and hence $[\eta]$ is directly related to coil volume. The data in *Table 3* show that $[\eta]$ of BBB is lowest in sulfuric acid, which implies that the BBB chains are highly contracted in this solvent. Berry and co-workers have observed that as the concentration of sulfuric acid is decreased from 100 to 92%, the BBB coils contract and may even aggregate[12,19]. In MSA, $AlCl_3$/nitromethane and $GaCl_3$/nitromethane the BBB chains are expanded by factors of 2.14, 2.31 and 1.86, respectively, relative to their volume in 97% sulfuric acid. This concurs with our interpretation of the u.v.-vis. absorption spectra, namely, that the BBB coils are highly chain-extended in the Lewis acid/nitromethane solvents, compared to the solid state.

Berry's study[22] of the intrinsic viscosity behaviour of BBL proved inconclusive as to the quantitative form of the relationship between $[\eta]$ and the molecular parameters persistence length ρ, contour length L, equivalent segment length b, and mass per unit chain length M_L. This was attributed[22] to the need to know too many parameters to apply the worm-like chain theory and to aggregation of BBL in solution. Whatever the exact functional form of this relationship is, i.e. the form of the function f in equation (3)[22]:

$$[\eta]=\frac{\pi N_A d^2}{100M_L}\left(\frac{L}{d}\right)^2 f\left(\frac{L}{d},\frac{\rho}{d},\frac{b}{d}\right) \tag{3}$$

where N_A is Avogadro's number and d is the hydrodynamic diameter, the data in *Table 3* clearly show that complexes of BBL with Lewis acids exhibit the same rigid-rod behaviour as BBL exhibits in MSA, since the measured intrinsic viscosity is almost the same in all three solvents. This contrasts with the flexible-chain behaviour of BBB and its complexes.

Concentrated solutions. The different chain topologies of BBB and BBL are also expected to lead to quite different phase behaviour of the two polymers in concentrated solutions. According to the molecular theory of liquid crystals[49], BBL, by virtue of its rigid-rod topology should exhibit lyotropic liquid crystallinity. BBB on the other hand, being a flexible or at least a semiflexible chain polymer due to its semiladder structure and the inherent non-linearity of the chains is not expected to show liquid crystallinity.

Extensive studies of the concentrated solution behaviour of BBB have revealed no evidence of liquid crystallinity in protonic acids[19,23,24]. Jenekhe and Johnson[32] reported shear thinning of solutions of BBB in $AlCl_3$/nitromethane and $GaCl_3$/nitromethane at concentrations of > ~5 wt% polymer, which may indicate shear induced alignment of the repeat units. We have investigated solutions of up to 10 wt% BBB in $AlCl_3$/nitromethane and $GaCl_3$/nitromethane. Optical microscope study of these solutions revealed that they were isotropic.

Despite the rigid-rod nature of BBL, there have been no reports of liquid crystallinity in its protonic acid solutions, to the best of our knowledge. Attempts[24] to observe liquid crystallinity in protonic acid solutions of BBL were hampered by the poor solubility of BBL in these media. However BBL does exhibit liquid crystallinity in Lewis acid/nitromethane solutions[32]. We prepared solutions up to 12 wt% BBL in $AlCl_3$/nitromethane and in $GaCl_3$/nitromethane. A liquid crystalline phase with a typical nematic mesophase texture was evident above the critical concentration in both solvents. This texture was bright red in colour and is shown in *Figure 9*. The nematic regions were evident to the naked eye as cloudy areas in surrounding deep purple isotropic solution.

The critical concentration of BBL in $AlCl_3$/nitromethane, defined as the highest polymer concentration above which there is evidence of liquid crystallinity[49] and measured under zero shear conditions, is 8 wt%. Samples of 8 wt% solutions prepared for optical microscopy, as described in the Experimental section, exhibited shear alignment when prepared. The samples, which were prepared by compression and therefore shearing of the solutions, were bright red and virtually textureless as viewed through the crossed polarizers of the optical microscope, immediately after preparation. After a period of ~10 min the alignment relaxed and the solutions became isotropic, losing the bright red colour transmitted through the crossed polarizers of the optical microscope. Solutions of concentrations between 4 wt% and 8 wt% BBL in $AlCl_3$/nitromethane showed such temporary alignment. Below 4 wt% the solutions were isotropic and showed no visible tendency towards shear alignment even when repeatedly sheared. At concentrations above 8 wt% the phase equilibria were quite different. Small islands of liquid crystalline regions were apparent in an 8.25 wt% solution even after allowing several hours for relaxation of shear alignment. A 9 wt% solution exhibited nematic liquid crystallinity with the anisotropic phase constituting about 30 vol% of the solution. A 10 wt% solution was ~90% anisotropic and a 12 wt% solution was gel-like and completely anisotropic. The critical concentration of BBL in $GaCl_3$/nitromethane is between 9 wt% and 9.5 wt% polymer. Solutions in $GaCl_3$/nitromethane of > ~5 wt% showed evidence of temporary shear alignment when prepared.

Flory's molecular theory[49] can be used to gain some insight into the nature of these liquid crystalline solutions. The axial ratio, x, of a rigid-rod molecule may be estimated using the formula[49]:

$$x=\left(\frac{M}{M_u}\right)\left(\frac{l_u}{d}\right) \tag{4}$$

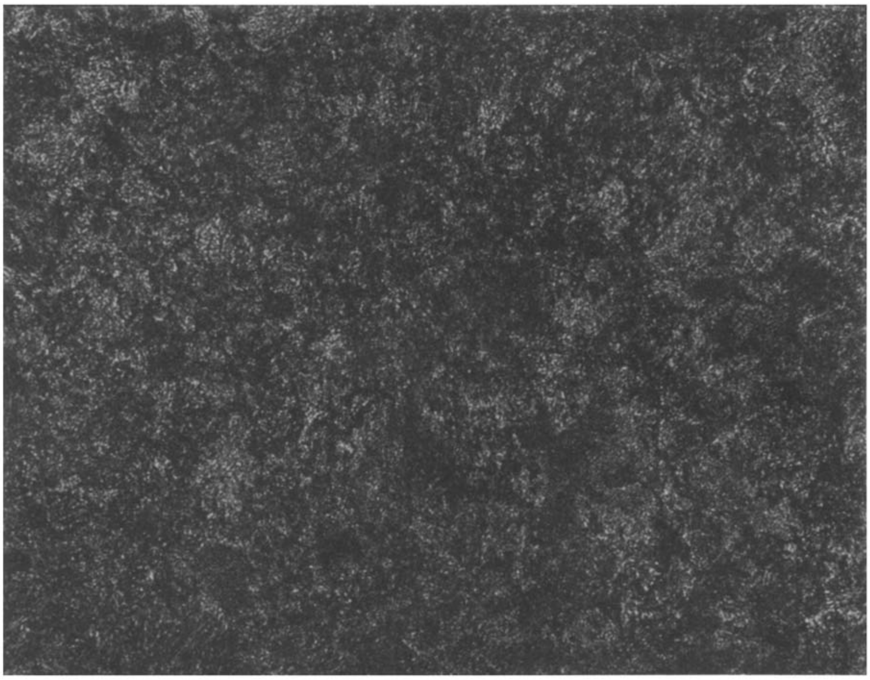

Figure 9 Photomicrograph of liquid crystalline regions of a 10.2 wt% BBL solution in $GaCl_3$/nitromethane viewed through crossed polarizers (×200)

where M is the molecular weight, M_u is the molecular weight of the repeat unit, l_u is the length of the repeat unit and d is the average chain diameter. We estimated the molecular weight of our BBL sample to be 75 000 in the Experimental section. This estimate was based on an assumed hydrodynamic chain diameter of 12 Å which we equate with d. M_u is 334. In an earlier paper[37] an l_u of 12.5 Å was found for PBZT. Comparison of the molecular structures of BBL and PBZT shows that l_u of BBL is very close to that of PBZT and therefore we use the value of 12.5 Å as an estimate. From equation (4), x is then 234 for BBL. Flory predicted that x is the sole factor which determines the critical concentration by[49]:

$$\phi^* = \frac{8}{x}\left(1 - \frac{2}{x}\right) \tag{5}$$

where ϕ^* is the critical concentration in volume fraction. Equation (5) predicts ϕ^* for BBL to be 3.4 vol%. The measurements we obtained show that the critical concentration of BBL is 8 wt% in $AlCl_3$/nitromethane and 9–9.5 wt% in $GaCl_3$/nitromethane. To convert these values to vol% the following densities are used: 1.31 g cm^{-3} for BBL[18], 1.35 g cm^{-3} for $AlCl_3$/nitromethane and 1.43 g cm^{-3} for $GaCl_3$/nitromethane at the Lewis acid concentrations used[37]. The ϕ^* values are 8.2 vol% in $AlCl_3$/nitromethane and 9.7–10.3 vol% in $GaCl_3$/nitromethane. The corresponding respective axial ratios are 96 and 78–82 from equation (5). Obviously these ϕ^* values are much higher and the axial ratios are much lower than for pure BBL calculated above. This is evidence that the pendent Lewis acid and any associated solvent act as bulky side groups to BBL in solution, effectively increasing the chain diameter and so decreasing the axial ratio. Using equation (4), the effective hydrodynamic diameter of BBL in $AlCl_3$/nitromethane is 29 Å and that of BBL in $GaCl_3$/nitromethane is ~35 Å. These values are much larger than the assumed d of 12 Å for uncomplexed BBL. Our view is that nitromethane may be weakly associated with the BBL complex chains, forming solvated species of approximately elliptical cross-section, the cross-sectional areas being much larger than that of the BBL chain.

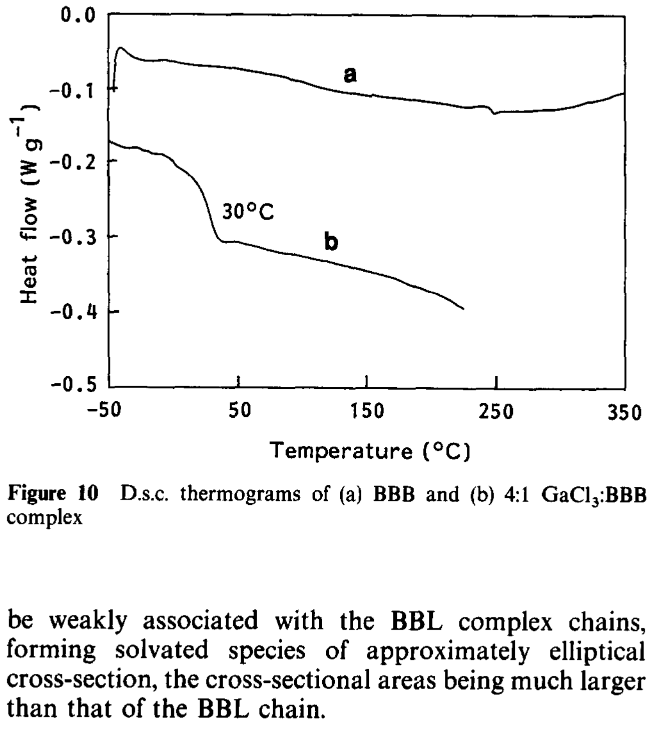

Figure 10 D.s.c. thermograms of (a) BBB and (b) 4:1 $GaCl_3$:BBB complex

Thermal properties of BBB and BBL complexes

Figure 10a shows a d.s.c. thermogram of BBB. There are no transitions up to 350°C. Others[12–14] have studied BBB by using X-ray diffraction techniques and shown that there are no thermal transitions in the range 30–500°C. *Figure 10b* shows a d.s.c. thermogram of the 4:1 $GaCl_3$:BBB complex. In contrast to BBB this complex has a glass transition with a midpoint (T_g) at 30°C. Onset and endpoint values for this transition are given in *Table 4*. The d.s.c. data were reproducible on repeated thermal cycling up to ~175°C, above which there is decomposition of the complex. The measured value of T_g was found to vary by up to 7°C from sample to sample and

Table 4 Temperatures (°C) relevant to the glass transitions of the 4:1 $GaCl_3$:BBB and $GaCl_3$:BBL solid complexes

	BBB/$GaCl_3$ complex	BBL/$GaCl_3$ complex
By d.s.c.		
Onset	19	12
Midpoint (T_g)	30	15
Endpoint	36	20
By d.m.a.		
T_g(0.16 Hz)	12	29
$T_{g,onset}$(0.16 Hz)	−14	−18
T_g(1.6 Hz)	18	33
$T_{g,onset}$(1.6 Hz)	−11	−15
T_g(16 Hz)	24	37
$T_{g,onset}$(16 Hz)	−7	−12
Activation energy (kJ mol^{-1})	293	448

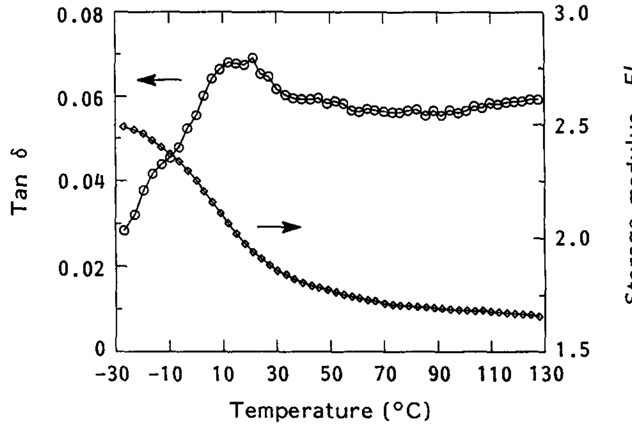

Figure 11 Loss tangent (tan δ) and storage modulus (E') plots for the 4:1 $GaCl_3$:BBB complex obtained at a frequency of 0.16 Hz. Units of E' are arbitrary due to the sample geometry employed

for repeated runs on a given sample. *Figure 11* shows the temperature dependent dynamic mechanical properties of the 4:1 $GaCl_3$:BBB complex. The glass transition of the complex is evident from the characteristic loss tangent peak and step decrease in modulus[50]. The temperature at which the loss tangent is a maximum, T_g, is normally regarded as the glass transition temperature. Such a T_g and the temperature at which the storage modulus begins to decrease, $T_{g,onset}$, are given in *Table 4*. Measurements similar to those of *Figure 12* were also made at frequencies of 1.6 and 16 Hz. T_g and $T_{g,onset}$ values obtained from these measurements are presented in *Table 4*. These temperatures vary with frequency, as expected for a glass transition[49,50]. The variability may be described by defining the activation energy, E_A, of process according to:

$$f = f_0 \exp\left(\frac{-E_A}{RT}\right) \qquad (6)$$

where f is frequency (in Hz), R is the gas constant and T is the temperature (in K). From plots of 1/T *versus* ln f of the T_g and $T_{g,onset}$ data of *Table 4*, the activation energy is found to be 293 kJ mol^{-1}, which is typical for a polymeric material[51].

Figure 12a shows a d.s.c. thermogram of BBL. As has been seen by others[12–14,17] there are no observable thermal transitions. *Figure 12b* shows a d.s.c. thermogram of the 4:1 $GaCl_3$:BBL complex. There is a glass transition with a T_g at 15°C. This transition is reproducible on repeated thermal cycling below ~150°C. The onset and endpoint temperatures are tabulated in *Table 4*. Dynamic mechanical measurements on this complex taken at a frequency of 0.16 Hz are shown in *Figure 13*. The loss tangent peak and step decrease of the storage modulus signifying the glass transition are evident in the data. The T_g and $T_{g,onset}$ values are given in *Table 4* for this frequency and for measurements taken at frequencies of 1.6 and 16 Hz. An activation energy of 448 kJ mol^{-1} for the transition is found from these data.

The appearance of glass transitions in the BBB and BBL complexes with $GaCl_3$ arises from the dramatic reduction in intermolecular forces which occurs when the complexes are formed. We have observed glass transitions for the complexes of several other polymers with Lewis acids such as PBZT[37] and polyamides[39,40]. Molecular modelling of the complexes of PBZT showed[38] that complexation results in amorphous aggregate structures with lower cohesive energy densities (*CEDs*) than PBZT. This accounts for the high solubility and low T_gs of the complexes compared to the pure polymers. The present results show that the effect also holds for the complexes of BBB and BBL. One way to estimate the *CED* of

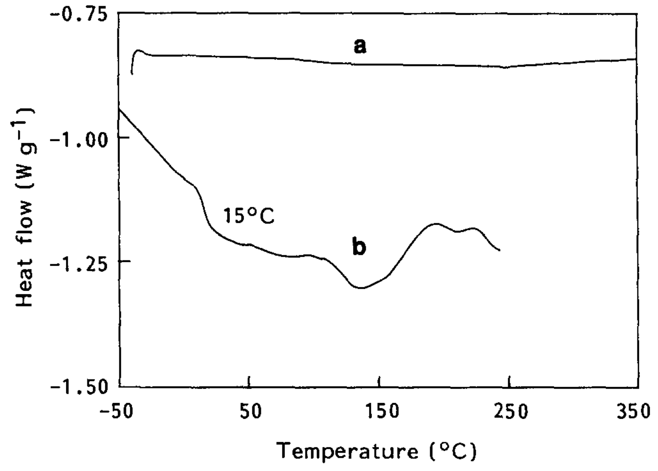

Figure 12 D.s.c. thermograms of (a) BBL and (b) 4:1 $GaCl_3$:BBL complex

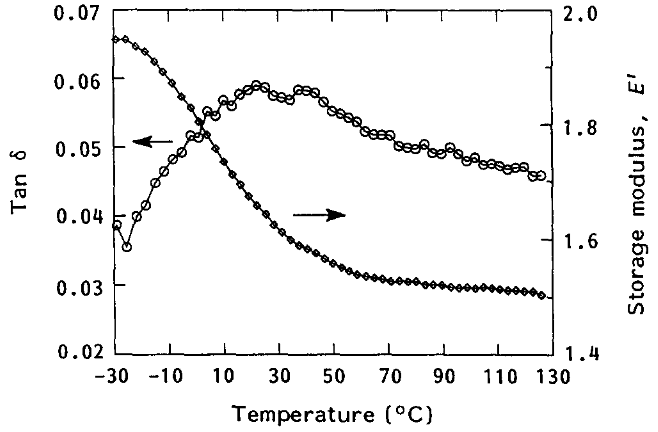

Figure 13 Loss tangent (tan δ) and storage modulus (E') plots for the 4:1 $GaCl_3$:BBL complex obtained at a frequency of 0.16 Hz. Units of E' are arbitrary due to the sample geometry employed

polymers is to use the group contribution method described by Van Krevelen[52]. To calculate *CED*s for aluminium- and gallium-containing molecules, the Fedors type contributions[53] are appropriate. By this method the *CED* of BBB is 2251 J cm^{-3} and that of BBL is 3279 J cm^{-3}. The *CED*s of fully complexed (4:1 Lewis acid:polymer) BBB and BBL are 916 and 929 J cm^{-3}, respectively. Complexation with Lewis acids is therefore predicted to lower the *CED* of BBB and BBL by 59 and 72%, respectively. This supports our contention that the very low T_gs of BBB and BBL complexes arise from reduced intermolecular interactions compared to the pure polymers. Furthermore, the solubility parameters (δ, the square root of *CED*[53]) of BBB and BBL complexes are 30.2 and 30.5 J$^{1/2}$ cm$^{-3/2}$, respectively. These values are reasonably close to that of nitromethane[52] (25.6 J$^{1/2}$ cm$^{-3/2}$), whereas the δ values of the pure polymers are much higher (47.4 and 57.3 J$^{1/2}$ cm$^{-3/2}$, respectively) and preclude solubility in nitromethane.

The glass transition of the BBL/GaCl$_3$ complex has a higher activation energy than that of the BBB/GaCl$_3$ complex. The lower value for the BBB/GaCl$_3$ complex is due to the flexibility of the BBB chains arising from the flexible linkages between repeat units. The stiffer BBL chains do not have such rotational freedom. The d.s.c. data indicate that the BBB/GaCl$_3$ complex has a higher T_g than the BBL/GaCl$_3$ complex. However, there was significant variability of the broadness and midpoint value from sample to sample for these complexes. For example T_g values as low as 23°C were observed for the BBB/GaCl$_3$ complex and as high as 25°C for the BBL/GaCl$_3$ complex. On the other hand the dynamic mechanical data consistently show that the T_g of the BBB/GaCl$_3$ complex is lower at any frequency than the T_g of the BBL/GaCl$_3$ complex. This we also attribute to the added flexibility of the BBB chains compared to BBL since chain flexibility is a structural factor which is well known to lower the T_g[53]. The data of *Table 4* and *Figure 13* also show that the glass transition of the BBL/GaCl$_3$ complex occurs over a wider temperature range than the glass transition of the BBB/GaCl$_3$ complex, i.e. although the T_g of the BBL/GaCl$_3$ complex is always the higher of the two, the $T_{g,\mathrm{onset}}$ of the BBL/GaCl$_3$ complex is lower at each frequency.

CONCLUSIONS

BBB and BBL form electron donor–acceptor complexes with the Lewis acids AlCl$_3$ and GaCl$_3$. These complexes are highly soluble in organic solvents at ratios of 4:1 or greater of Lewis acid:polymer repeat unit. At the 4:1 stoichiometry the metal atoms of the Lewis acids are coordinated to the polymers, one to each of four electron-rich heteroatoms in the polymer repeat units, namely the carbonyl oxygens and imine nitrogens.

Despite the similarity of the chemical structures of BBB and BBL, several important differences arise in the structures and properties of their complexes due to the differences in the polymer chain topologies. BBB is a semiladder polymer and as such has rotatable bonds between repeat units which give the polymer chains a degree of flexibility. As a result BBB chains are chain extended in solution to a degree which depends on the solvent employed, whereas in the solid state the coils are highly contracted and consequently π-conjugation is poorer. BBL and its complexes are by contrast ladder structures with inflexible chains, exhibiting rigid-rod conformations in solution and in the solid state. The flexibility of the BBB chains also results in lower activation energy of glass transition, and T_gs for the BBB/GaCl$_3$ complex compared to the BBL/GaCl$_3$ complex. These differences in chain topologies are also manifested in the physical properties of BBB and BBL. For example, the third-order non-linear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of thin films of both polymers, prepared from solutions of their complexes, measured by third harmonic generation spectroscopy, was found to be lower for BBB by a factor of 2 than BBL over the entire wavelength range from 1.0 to 2.4 μm (ref. 30).

The observed properties of the BBB and BBL complexes have broad implications for the processability and tractability of these polymers. The pure polymers can easily be regenerated from the complexes by washing with a suitable non-solvent such as water[31,32]. Thus in one sense the complexes may be viewed as processing intermediates for the pure polymers, to which they may easily be converted after processing to the desired form. The feasibility of this method has already been amply demonstrated by the preparation of good quality films and coatings for electronics[28,54], photoconductivity[55], non-linear optics[30], and electroluminescence[56,57]. The liquid crystalline solutions of BBL complexes are ideal for preparing films and fibres of high strength and stiffness and the mechanical properties of BBB may also be optimized by processing from concentrated solutions of its complexes. The low T_gs of the solid BBB/GaCl$_3$ and BBL/GaCl$_3$ complexes also offer the possibility of 'melt' processing of the polymers.

ACKNOWLEDGEMENTS

We thank John Osaheni and Ashwini Agrawal for synthesis of the BBL and BBB polymers, respectively. This research was supported in part by the National Science Foundation (CTS 9311741), the NSF Center for Photoinduced Charge Transfer (Grant CHE 912-0001), and an Elon Huntington Hooker fellowship to MFR.

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