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Melt-Processable Poly(ether imide)s Based on Catechol Bis(ether anhydride)

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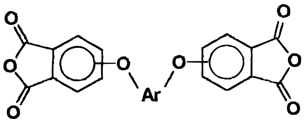
ABSTRACT: Having previously demonstrated the possibility of synthesizing high molecular weight poly(ether imide)s with *ortho*-linked main-chain units from bis(ether anhydride)s derived from catechol or its derivatives, we now provide a preliminary assessment of the properties of the polymers prepared from the catechol bis(ether anhydride) and a variety of diamines. The polymers have low color, are soluble in a variety of solvents, and are thermally stable to temperatures in excess of 470 °C. Glass transition temperatures are comparable with or higher than that of the commercial poly(ether imide) Ultem. Solvent-cast films have high modului and strengths. Extensions to break are relatively low, except for the polymer based on 4,4′-bis(4-aminophenoxy)biphenyl, which has an extension of 170%. All the polymers can be drawn to produce materials with higher moduli and strengths and, in most cases, higher extensions to break. Thus the polymers can be processed from the melt or from solution.

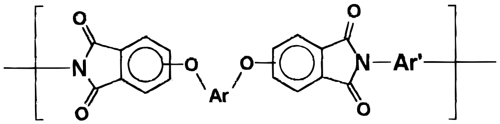
Because of their insolubility and nonmelting character, most aromatic polyimides must be fabricated into fibers and films as organosoluble poly(amic acid) precursors prior to cycloimidization. A key reason for this behavior is lack of chain flexibility in the polyimide. Judicious incorporation of ether links into polyimide structures can increase flexibility and significantly lower melting points to provide thermoplastic, moldable polyimides. Nevertheless, high molecular weight homopolyimides having sufficient melt fluidity to permit fiber spinning below their decomposition temperatures remain rare. A notable example of this type is the polypyromellitimide of 4,4′-bis(3-aminophenoxy)biphenyl recently introduced commercially in Japan.[1] This polymer may be melt spun at about 380−420 °C. We now examine the efficacy of *ortho*-phenylenedioxy components in the dianhydride for lowering polyimide melt temperatures to permit melt spinning. This may also be expected to allow solution processing as an alternative.

Over the years there have been many attempts to produce soluble, processable polyimides by incorporating different moieties into their structures.[2] Apart from the use of fluorinated monomers, these variants have often involved the incorporation of bulky substituents[3] and many workers have concentrated on the use or synthesis of new, often exotic, diamines with flexible linkages or structural irregularities.[4]

A major advance was the development of bis(ether anhydride)s **I** which, by reaction with a diamine, could be incorporated into poly(ether imide)s **II**; Ar and Ar′ are aromatic residues derived from a diol and a diamine, respectively. In this way, General Electric introduced the relatively inexpensive, commercial product Ultem in which Ar is derived from Bisphenol A and Ar′ is a *meta* phenylene unit.[5] Even so, many polymers with structure **II** are unprocessable or are difficult or expensive to process; there is a potential need for alternatives of similar or less cost that are more processable. Polymers **II** where Ar is *p*- or *m*-phenylene have limited solubility; the relevant bis(ether anhydride)s **I** prepared from hydroquinone and resorcinol are here referred to as HBA and RBA, respectively.



(I)



(II)

We recently disclosed the synthesis of polymers **II** in which Ar is *o*-phenylene.[6] These polymers were prepared from the corresponding anhydride **III** (catechol bis(ether anhydride, CBA) and are derived from catechol; related materials can be prepared from catechol derivatives. We demonstrated that catechol and its derivatives will undergo nitrodisplacement with 3- or 4-nitrophthalodinitrile to form bis(phthalodinitrile ether)s, which can then be converted to bis(ether anhydride)s.[7,8] Ultimately the anhydrides can be used in the synthesis of poly(ether imide)s.

The synthesis of thermally stable high molecular weight polymers having *ortho*-linked residues is relatively unusual. Polyesters based on *o*-hydroxybenzoic acid are known to be thermally unstable,[9−11] and other copolyesters based on catechol often have relatively low molecular weights.[12] In polyamides, the substitution of *m*- or *p*-phenylenediamine by the *ortho* isomer,[13] or the corresponding substitution of phthalic acid for its isomers,[14] produces such large reductions in softening and melting temperatures that utility is frequently compromised. Yang and Chen recently reported the synthesis of polyimides with *ortho*-linked bis(phenoxy)naphthalene units in the diamine moiety.[15] Kasashima *et al.* have also very recently reported the synthesis of thermally stable polyimides based on the *ortho*-linked diamine 4,4′-diamino-*o*-terphenyl, i.e., with an *ortho*-linked unit without ether linkage, and found they had low solubility.[16] Previously, the same group had reported the synthesis of soluble polyimides having 2,3-quinoxalilnediyl units in the diamine moiety.[17] St.Clair

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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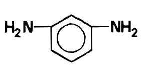
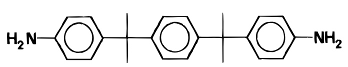
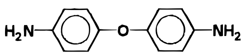
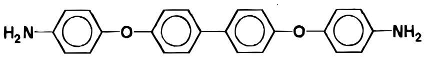
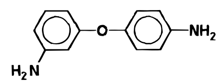
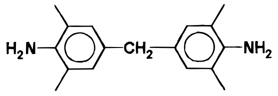
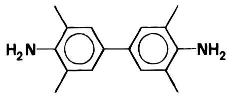
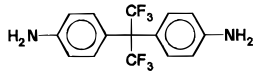
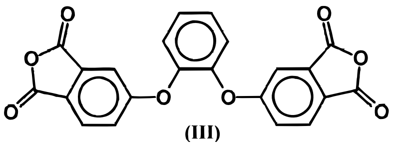
Table 1. Structures of Diamines IV Used in Polymer Syntheses

Code	Structure	Code	Structure
MPD		BAP	
ODA		BAPB	
3,4-ODA		MBXD	
TMBD		BAAF	

et al. previously reported the use of unsymmetrical diamines in which one amine group is *ortho* to a bridging group.[4]

In a preliminary communication we reported that high molecular weight poly(ether imide)s based on the catechol-derived bis(ether anhydride) **III** (CBA) and any of several diamines **IV** can be synthesized, and where investigated, the polymers had good thermal stability.[7] More recently we reported the synthesis of a series of polymers based on bis(ether anhydride)s derived from catechol derivatives and 4,4′-oxydianiline (ODA) as diamine.[8]



(III)

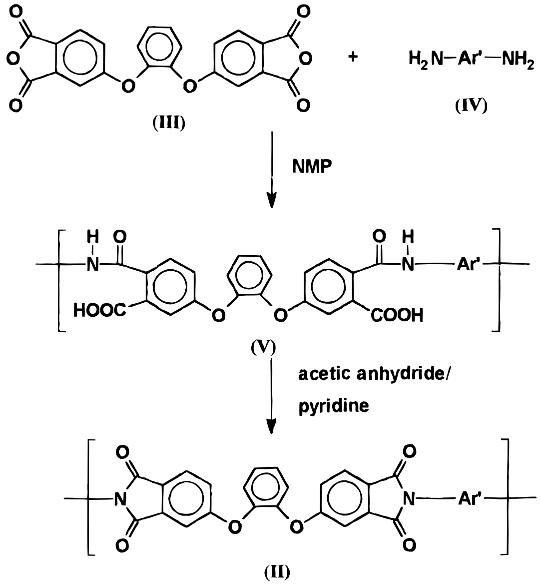
$H_2N—Ar'—NH_2$

(IV)

In this paper, we now extend the series of polymers based on CBA to additional diamines; the polymers prepared were characterized in terms of molecular weight and glass transition temperature. We also report in more detail on the nature and properties of a series of poly(ether imide)s based on CBA and diamines **IV** (Table 1). This paper also explores the major features of the mechanical properties of the polymers. We thus provide more information on the thermal and mechanical properties of the materials, as films, and on their processability and properties when drawn. These data add further to an appreciation of the nature and behavior of poly(ether imide)s containing *ortho*-linked, *vis à vis meta*- and *para*-linked, phenylene units, and we briefly consider the origins of the different patterns of behavior observed.

All members of this new class of poly(ether imide)s so far prepared are far more processable (from melt or solution) than the corresponding polymers, where known, based on the bis(ether anhydride)s HBA and RBA derived from hydroquinone and resorcinol, respectively. Previous use of unsymmetrical diamines where one amine is *ortho* to a bridging group enhances solubility to some extent in aprotic solvents and *m*-cresol, compared to their symmetrical *all*-*para*-linked isomers,[4] but the irregularity of those structures will almost certainly preclude crystallinity and may detract from properties.

Scheme 1



The polymers so far prepared from bis(ether anhydride)s derived from catechols are totally amorphous, but while this fact may reduce the potential ultimate upper working temperature of the polymers, it has the advantage that the polymers are less subject to time dependence of properties than are semicrystalline materials. The structural regularity of polymers based on catechol itself, or a symmetrical derivative, however, means that it may be possible to establish processing conditions that induce crystallinity and raise ultimate properties. These polymers have the additional advantage that they can be prepared from simple inexpensive diols and diamines and may provide an alternative series of relatively inexpensive, processable poly(ether imide)s.

Experimental Section

Materials. The synthesis of CBA **III** and other bis(ether anhydride)s based on catechol and its derivatives have been described elsewhere in recent publications.[7,8] Poly(ether imide)s **II** prepared in this work were synthesized in NMP solution according to a conventional two-stage procedure (Scheme 1) in which the bis(ether anhydride) **III** and a diamine

Table 2. Characterization of Poly(ether imide)s

		gel permeation chromatography			
			poly(ethylene oxide) stds		
amine	appearance	polystyrene stds M_p (kg mol^{-1})	$\bar{M}_w$ (kg mol^{-1})	$\bar{M}_n$ (kg mol^{-1})	IV[a] (dL g^{-1})
MPD	colorless	112	67.9	5.2	0.96
ODA	pale yellow	287	124	8.93	1.63
3,4′-ODA	pale yellow	151	64.2	6.42	1.04
BAPB	pale yellow	476	207	18	1.87
BAP	pale yellow	422	187.5	8.99	1.54
MBXD	pale yellow	214	81.7	9.34	1.15
TMBD	pale yellow		59	8.42	1.00
BAAF	colorless	62	39.1	9.24	

[a] Inherent viscosities.

IV, identified in Table 1, were reacted together in exactly equimolar proportions to form a poly(amic acid) intermediate **V** which was then chemically imidized to poly(ether imide) **II**; the anhydride was added in one portion to a solution of diamine. Polymers are defined according to the anhydride and diamine from which they are prepared (Table 2), thus the polymer derived from CBA and MPD is defined as CBA/MPD. The sources of diamines other than MBXD (Kennedy and Klim) and BAAF (Aldrich Chemicals) have been identified previously.[7] Polymers were isolated by precipitation into methanol and dried in a vacuum oven. Details of the procedures have been presented elsewhere.[7,8]

Sample Preparation. For the purposes of mechanical testing, samples of the polymers were cast from homogeneous solution in chloroform by slow evaporation in flat-bottomed (Anumbra) petri dishes. The films were dried from residual solvent by heating under vacuum at room temperature for 4−5 h and then at 10−20 °C below the glass transition temperature for 7 h.

Characterization. Molecular weights were determined by gel permeation chromatography using different procedures. One instrument, used in our earlier study, was based on columns packed with 5μ-PL gel (polystyrene) and a refractive index detector. DMF with 1 M LiCl (90 °C) was used as eluant with a flow rate of 1 mL min^{-1}, and the system was calibrated with polystyrene (Polymer Laboratories) standards. A second instrument (at RAPRA Technology) used DMF with 1 M LiBr as eluant (80 °C) and was calibrated with poly(ethylene oxide) standards. For both instruments, samples were filtered through PTFE membranes with 0.45 μm pores prior to injection.

Glass transition temperatures (T_gs) were measured using a Perkin-Elmer DSC2 (University of Liverpool) and a TA Instruments Model 2910 differential scanning calorimeter (Du Pont); evidence for crystallinity was also assessed on the same instruments. Heating rates to 420 °C (Liverpool) and 500 °C (Du Pont) were 10 °C min^{-1} under a nitrogen atmosphere. Onset values of T_g are recorded in Table 3. These measurements provided preliminary information on thermal decomposition. Thermogravimetric analysis (TGA), using a TA Instruments Model 2950, at a specimen heating rate of 10 °C min^{-1} to 600 °C in nitrogen, showed the temperatures of thermolytic weight loss, both incipient and maximal, as well as weight percent residue; these measurements also monitored the presence, if any, of residual solvent.

For the determination of mechanical properties, cast films were cut into 0.25 in. wide strips with a sharp blade. Some strips were stretched maximally, short of breaking, by hand while in brief contact with a heated pin (1.0 in. diameter) at various selected temperatures. Linear densities of fiber strips, drawn and undrawn, were determined using a vibrascope according to ASTM method D1577 and applied to the determination of a longtitudinal stress−strain curve with the aid of an Instron tensile tester type 1122 according to ASTM method 2101. Specimens of 1.0 in. gauge length were clamped between the jaws of the instrument and elongated at a constant rate of 0.6 in. min^{-1}, i.e., 60% per minute at room temperature. Force−elongation data were used to determine tenacity (force just prior to break), percentage elongation at break, initial modulus, and work to break (proportional to the area under the stress−strain curve). Reported data (Table 4) are averages of at least two replica tests.

Results and Discussion

The polymers described in this paper represent a selection from a new series of materials with, unusually, 1,2-linked main-chain units. The data presented in this paper constitute the results of a preliminary assessment of the nature and properties of the materials. The polymers described are based on the bis(ether anhydride) CBA **III** and one of several diamines (Table 1).

1. Appearance. Polyimides and poly(ether imide)s are normally colored as a result of interchain interactions and many are deep yellow.[18] It is recognized that the color depends on molecular structure and, for a particular anhydride, on the structure of the diamine. Colors of poly(ether imide)s based on CBA were found to be generally pale yellow and paler than corresponding polymers prepared from the same diamine with other anhydrides (Table 2). Usually polymers prepared from MPD or diamines having trifluoromethyl substituents are paler than polymers prepared with other diamines. In this case the polymers prepared from MPD and BAAF were colorless.

2. Molecular Characterization. Mechanical properties of polymers can be influenced by molecular weight unless the molecular weight exceeds some critical value. In this preliminary study, the molecular weights of the poly(ether imide)s were not optimized and it is therefore necessary to have an assessment of molecular weight in order to put property data into perspective. Previously we reported molecular weight data for some of these polymers determined by gel permeation chromotography (GPC) in DMF−LiCl (1 M) based on polystyrene standards; M_p values, molecular weights at the peaks of the chromatograms, were reported for the several polymers prepared (Table 2); data for additional polymers are also included in Table 2. Peak molecular weights were quoted because they allow comparison of relative values for a given polymer and are not sensitive to errors caused by irreproducibility or contamination in the wings of the chromatograms (especially at low molecular weight) and uncertainty in drawing baselines and, hence, in calculated averages. It is known that molecular weights determined by GPC are not absolute. It has also been reported that polystyrene standards are abnormally retained on polystyrene-based columns when DMF is used as eluant.[19] A comparable set of chromatograms were, therefore, obtained from an instrument calibrated with poly(ethylene oxide) standards and these data ($\bar{M}_w$ and $\bar{M}_n$; average of two values) are also reported in Table 2. A comparison of these results is consistent with the original molecular weights being overestimates and values of $\bar{M}_w$ found are about half the values of M_p determined using polystyrene standards. This finding is consistent with our previous study in which we compared molecular weights determined by GPC using polystyrene standards with number-average

Table 3. Thermal Properties of Catechol-Based Poly(ether imide)s

	T_g (°C)		thermogravimetric analysis			
amine	Du Pont	Liverpool	init dec T (°C)	T (°C) for wt loss max rate	breadth of peak (°C)	wt loss (%)
MPD	216	220	440	545	100	26
ODA	207	208	450	560	75	29
3,4′-ODA	180	190	460	560	100	30
BAPB	184	204	440	560	120	29
BAP		211	470	525	60	49
MBXD		243.5	420	485	80	28
TMBD			450	490	80	23
BAAF			420	550	80	49
HBA/MPD		244,[a] 255,[b] 242[c]				
RBA/MPD		224[b]				

[a] Reference 7. [b] Reference 21. [c] Reference 22.

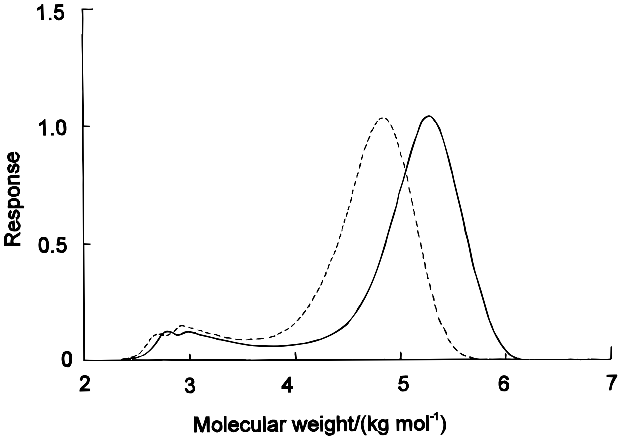


Figure 1. Molecular weight distributions, determined by gel permeation chromatography, for polymers CBA/MPD (- - - - - -) and CAB/BAP (—).

molecular weights determined by membrane osmometry, when we found that number-average molecular weights determined by GPC were a factor of 2−4 greater than those determined by osmometry.[20]

Both sets of chromatograms show the presence of a major high molecular weight peak and a small low molecular weight peak. The polydispersities from the chromatograms in the second instrument are extraordinarily high (4−20). They are possibly exacerbated by the presence of the small content of low molecular weight polymer which is oligomeric and correponds to up to about two to four anhydride units; two typical chromatograms are shown in Figure 1. Deleting the low molecular weight peaks greatly increases $\bar{M}_n$ and increases $\bar{M}_w$ slightly and decreases the polydispersity to $\sim$2, which is consistent with a high molecular weight polymer produced by step polymerization. We are currently investigating the origin of the apparently very large low molecular weight peak to determine whether it arises from a large weight fraction of oligomer (possibly cyclic) or is due to a high refractive index increment for end groups.

Frequently, for high-performance polymers it is usual to quote inherent viscosities rather than molecular weights, and for comparison, inherent viscosoities of the several polymers determined in NMP solution are quoted in Table 2. The values, which range from about 1 to 1.9 dL g^{-1} are comparable with that for Kapton polyimide film and confirm that the polymers are indeed high molecular weight materials.

3. Thermal Properties. Poly(ether imide)s are generally amorphous and their upper-use temperatures and potential melt processabilities depend on their glass transition temperatures. Glass transition temperatures of poly(ether imide)s cover a wide range and vary with molecular structure according to well-established principles. Low T_gs are found for polymers with ether or other flexible linkages (CH_2) in the diamine moieties (i.e., in the Ar′ residues in **II**, e.g., CBA/ODA and CBA/3,4-ODA), and for polymers with groupings that hinder chain packing (e.g., the unsymmetrical 3,4′-ODA). Residues that hinder bond rotation raise T_g (hindering methyl groups in *ortho* positions in the diamines of CBA/MBXD) and rigid units, especially with hindering groups, may render T_g nonobservable below 420 °C [CBA/TMBD and TMBD in a series of isomeric poly(ether imide)s studied previously[20]]. But the ether-linked catechol unit, while having some sterically forbidden conformations, is generally flexible and allows considerable changes in chain conformation through rotation about the ether linkages. These conformational changes might be expected to keep T_g low, compared with the equivalent polymers based on HBA because the *para*-linked unit is usually considered to enhance chain rigidity; the central phenylene unit is a simple rigid rotor. Previously we discussed briefly the conformations in diphenoxyphenylene units and concluded that the probable preferred conformations in catechol-based poly(ether imide)s may well reduce interchain packing and interchain interactions and hence help to keep T_g relatively low, possibly by reducing the concentration of interchain interactions responsible for color. However, observed T_gs for the polymers prepared in this study are not unusually low (Table 3) and the polymers are potentially useful for some practical purposes; the commercial polymer Ultem has a T_g of $\sim$220 °C[5] while for CBA/TMBD T_g is in excess of 420 °C, if a T_g exists at all (see comments on melt drawing to fiber later). We noted previously, in a study of other poly(ether imide)s, that TMBD is responsible for high T_gs; the *o*-methyl groups in TMBD restrict bond rotations and generate a very large, rigid, main-chain unit.[20] Similar considerations are also applicable in this context. We also failed to identify a thermal transition in CBA/BAAF below 420 °C. While BAAF does not have *o*-methyl groups to restrict bond rotations between its aromatic rings and the adjacent phthlimide moieties, it does constitute a very stiff main-chain unit; the CF_3 groups restrict rotation within the BAAF unit.

In DSC traces there was no evidence of crystallinity or melting endotherms for any sample, even after melt drawing (see later).

4. Thermal Stability. Many polymers containing 1,2-linked units are relatively unstable to thermal decomposition.[9,10] Therefore, it is of interest to learn the influence of incorporating the ether-linked, 1,2-units into structures that otherwise are well-known for their thermal stability. We reported previously that poly(ether imide)s based on CBA with diamines MPD and BAPB are thermally stable in air to temperatures in excess of 450 °C and lost 98.5 and 95% of their weight in the temperature ranges 477−670 and 520−676 °C,

Table 4. Tensile Data for Poly(ether imide)s and Related Polymers

	as-cast			drawn samples					
				draw conditions					
amine	init mod (MPa)	UTS[a] (MPa)	% elong at break	*T* (°C)	ratio	init mod (MPa)	UTS (MPa)	% elong at break	toughness (MPa)
MPD	1334	64	3.3	180	4.4	2223	136	4.5	2
				205	4.6	2470	185	6.7	6
				219	4.2	5433	185	43.2	67
				245	8.8	3210	173	35.1	47
ODA	1704	81	6.4	180	3.8	2840	247	14.4	21
				205	4.8	6421	630	12.7	43
				220	4	2964	346	47.9	100
3,4-ODA	1667	104	5.3	180	5.4	3087	198	10.9	14
				205	5.5	3457	198	16.5	23
				219	5.5	2099	148	29.7	28
BAPB	2161	115	170	180	4	3951	321	14.9	28
				205	3.8	4075	272	17.6	32
				220	3.7	3334	407	60.4	151
BAP	2383	93	4.8	180	4.0	3951	284	17.9	32
				205	5.6	4075	247	2	12
				219	4.3	3951	296	24.6	52
MBXD	2136	109	7.9	205	3	2964	296	11.7	19
				220	4	3087	185	9.3	10
				245	5.8	3210	148	6.6	6
TMBD	2396	123	8.9	245	2.3	4198	173	5.2	5
				282	7.8	3704	259	20.7	36
BAAF	1581	79	4.8	205	3.0	2717	99	4.6	2
				219	5.5	2470	111	11.6	10
Kapton	2960	172	70						
Ultem	2960	105	60						

[a] UTS (MPa) converted from tenacity/gpd with a conversion factor of 1 gpd = 123.5 MPa.

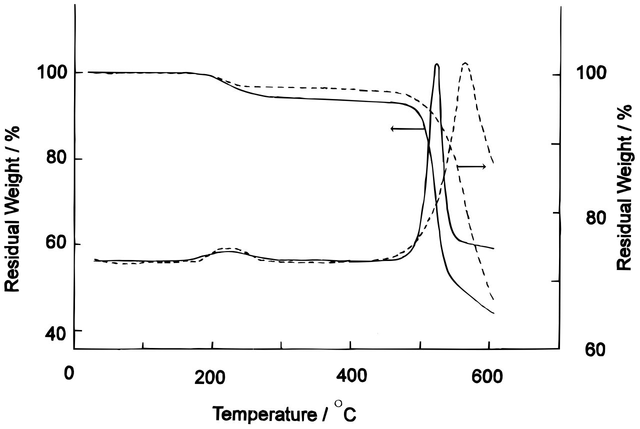


Figure 2. Thermogravimetric analysis data showing weight losses and differential weight losses for polymers CBA/BAP (—) and CAB/BAAP (- - - - - -).

respectively.[7] When examined by TGA, under a nitrogen atmosphere, all the polymers showed a small weight loss, normally less than 5 wt %, between about 200 and 250 °C (Table 3). These small weight losses are almost certainly attributable to loss of residual solvent since, prior to testing, the solvent-cast samples were only heated under vacuum to ~10 °C below their respective T_gs; there was no visual sign of decomposition when samples were heated to these temperatures in air. These small weight losses occurred at or just above the T_gs of the individual polymers, as determined by differential scanning calorimetry (Table 3), where enhanced molecular mobility would allow residual solvent to diffuse out of the polymer. None of the polymers studied showed signs of thermal degradation below 420 °C, and this lowest temperature for the onset of degradation was for a polymer with a bridging methylene unit in the diamine residue; this unit might be a source of thermal instability. Other polymers showed greater stability.

The nature of the thermograms for thermal decomposition in a nitrogen atmosphere was that the polymers showed a significant loss of weight over a temperature range of about 70−100 °C above the initial decomposition temperature. Weight losses associated with the peaks, and the breadths of the peaks in the differential thermograms, are listed in Table 3. Weight continued to be lost at higher temperatures, but rates of weight loss were lower. Two typical thermogram are shown in Figure 2 along with the corresponding differential curves.

The data demonstrate that, in general, these catechol-based poly(ether imide)s have good stability toward thermal decomposition above their T_gs, a factor that makes them potentially attractive for melt processing.

5. Tensile Properties. Tensile data recorded in Table 4 for cast films were determined on two sample strips, and the average result is recorded. Test data, recorded as gram per denier, were converted to MPa by the relation 1 g denier^{-1} = 88.2ρ MPa with a nominal value of 1.4 for the density (ρ) of poly(ether imide). These preliminary samples were not optimum, but ultimately, data for polyimides and poly(ether imide)s are inevitably compared with those of the commercial polyimide Kapton[23] and poly(ether imide) Ultem.[5] Data for these two polymers are also recorded in Table 4.

The properties of the new polymers, as cast, vary quite markedly from one to another. While none of the polymers have strengths or modulus equal to those of Kapton (172 MPa, 2.96 Gpa, respectively), the strengths of some of some films were superior to those of Ultem (105 MPa), although the initial moduli were lower than that for Ultem (2.96 GPa). In most cases, the elongation to break of the films were much less than those of Kapton (70%) or Ultem (60%) and much lower than we have observed in other poly(ether imide)s of high molecular weight. Sample CBA/BAPB, however, exhibited 170% extension to break; it also had a higher ultimate tensile strength and modulus than observed for most other films examined in this study. We are unaware of any other studies that identify the BAPB unit as conferring superior extensibility, and at first sight, there are no obvious structural reasons why this polymer should have superior properties. However, we now have other evidence that the high extensibility is a genuine phenomenon associated with the presence of BAPB in poly(ether imide)s.[24] We suggest that, in the polymer film as cast, the BAPB unit adopts a conformation that causes the polymer chain to coil strongly, through the disposition of the aromatic rings adjacent to the ether linkages, but that under stress these conformations are modified to give a more linear in-chain unit; the effective uncoiling of the long BAPB unit about its ether linkages could provide a mechanism for considerable chain extension.

The stress–strain curves and low elongations to break are indicative of brittle fracture which, in poly(ether imide)s, is frequently associated with low molecular weights; the polymer films, however, were creasable without cracking. Despite the low values of $\bar{M}_n$ recorded in Table 2, the bulk of each sample was of high molecular weight. It is possible that the lack of yield in these samples was due to the presence of the low molecular weight component. However, some films were subsequently found to contain microscopic heterogeneities which, if present in the samples tested, could have led to premature fracture and properties less than optimum. The data recorded here are similar to, and in many cases superior to, those reported by Yang and Chen for the polyimides based on pyromellitic dianhydride and the *ortho*-linked diamine 2,3-bis(4-aminophenoxy)naphthalene; these workers also reported small extensions to break.[15]

It is noticeable that, in general, the properties of the polymers improved with increasing molecular weight even though different polymer structures were involved and degrees of polymerization calculated from values of $\bar{M}_w$ of most samples were very similar.

6. Drawing Studies. Ultimate mechanical properties of polymers are often only achieved through appropriate processing. The polymers synthesized in this study were prepared in order to explore whether they might be solution or melt processable and potentially usable as high-temperature fibers. We therefore undertook preliminary drawing studies and determined the room-temperature properties of the drawn fibers. Data recorded in Table 4 are from measurements on single samples. In all cases fibers could be drawn from pools of molten polymer and some very long, nonbrittle fibers were obtained in this way.

None of the polymers films investigated could be drawn at temperatures below 180 °C, which is below the glass transition temperatures, as measured by DSC, of all the polymers studied, although some could be drawn to some extent at 180 °C (Table 4).

All polymers involved in this study showed increases in tenacity and modulus when drawn and, in most cases, an increase in elongation to break. In many cases the improvements in properties were modest although significant increases in these properties might have been expected (to moduli of, say, 860 MPa, 70 g denier^{-1}). The lack of improvement in properties may be due to plastic flow rather than to molecular orientation. However, there are indications that molecular alignment may be induced, giving rise to increased elongation to break, modulus, and an increase in toughness (work to fracture). Samples surviving extension beyond 5% showed distinct yield points. CBA/ODA yielded and strain hardened after drawing at 180 °C and similar, but more marked behavior, when drawn at 220 °C. CBA/BAPB did not show a yield point when extended at 180 °C but also yielded and strain hardened after drawing at 220 °C.

There were other marked variations in properties with draw temperature. For example, CBA/MPD does not align well when drawn at temperatures below its T_g and low values of work to fracture (toughness) and extensions to break were recorded. But, when drawn above T_g, the toughness and extension to break increased significantly. CBA/ODA, when drawn above 200 °C, probably achieved the best combinations of modulus and strength (when drawn at 205 °C), with good extensions to break when drawn at 220 °C. CBA/BAPB shows an increase in tenacity on drawing and a modest increase in modulus, but the elongation to break is considerably reduced relative to the very high value for the undrawn film. This observation might be consistent with establishing extended conformations on drawing.

For polymers with higher glass transition temperatures, e.g., CBA/TMBD and CBA/BAAF where no T_g was observed, it was necessary to heat to higher temperatures in order to draw the films. CBA/MBXD (T_g 244 °C) and CBA/BAAF could not be drawn below 205 °C, and CBA/TMBD could not be drawn below 220 °C. The facts that fibers could be readily drawn with ease from molten pools of polymer of CBA/TMBD and CBA/BAAF and that their films could be drawn indicates that, although no T_g was observed for these polymers by DSC, there must be sufficient increase in thermal mobility above 200 °C. There may be a very weak glass transition due to the rigidity of the unit consisting of the rigid diamine residue and its flanking phthalimde moieties.

Most polymers broke when attempts were made to draw them at temperatures in excess of 250 °C, at 300 °C for CBA/TMBD, indicating a rather narrow processing window for melt processability by drawing.

In general, the tensile properties increased with the temperature of draw. However, in most cases, properties went through a maximum and decreased at the highest draw ratios. This effect may be caused by an increase in molecular mobility at the highest temperatures with some relaxation while drawing at the draw rates used. Although the data for individual polymers show different patterns, there is, except for CBA/MBXD, an increase in work to fracture on drawing at higher temperature. It is difficult to draw general conclusions about the potential ultimate properties of this series of polymers from these preliminary data. Further work would be required to obtain a full appreciation of the variations in properties and their dependences on draw conditions.Nevertheless the data do indicate that interesting, good mechanical properties may be achievable in this novel series of polymers.

It is interesting to consider the behavior of the isomeric poly(ether imide)s in terms of the relative flexibilities and conformations of the moieties incorporating *o*-, *m*-, and *p*-phenylenedioxy units (Figure 3).

It is difficult to visualize exactly the conformational consequences of the different units on paper because, while in these several structures rotation about the ether linkages is not severely restricted, the aromatic rings in none of the structures can be coplanar, as depicted. It is usually considered that *para*-linked units impart a certain linearity and often rigidity to polymer chains; rotations about the several main-chain bonds indicated allow changes in molecular shape. Although the most likely conformations (based on consideration of space-filling models) are relatively extended, the unit very easily undergoes a 180° bend, as in a chain-folded conformation. *Meta*-linked units reduce chain linearity and provide more strongly coiled conformations, as can be visualized by considering the possibilities arising

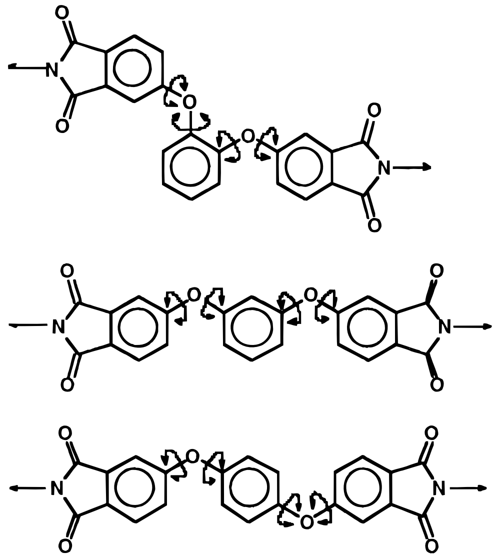


Figure 3. Structures of main-chain units based on isomeric structures with variously substituted phenylene units.

from rotation about the several C−O bonds; enhanced processability of *meta*- over *para*-linked units is exemplified in aromatic polyamides by comparing, for example, Kevlar (*para*-linked) and Nomex (*meta*-linked). Incorporation of *ortho* units further reduces linearity, and most conformations impart strong coiling on the polymer chain; there are more hindrences to rotation in these units in consequence of steric factors between the nonadjacent aromatic rings. The other outcome of considering space-filling models is that the *para*- and *meta*-linked units can easily form extended units which are fairly open and unhindered laterally. These conformations provide excellent opportunities for neighboring chains to pack and develop interchain interactions. In contrast, the *ortho* unit can also produce an overall approximately linear unit, but in this case, the central phenylenedioxy ring protrudes laterally and must hinder packing; this conformation, which is a low-energy conformation, is depicted in our previous paper.[8] Thus we propose that the enhanced solubility and high melt processability of poly(ether imide)s with *ortho*-linked units, demonstrated previously,[7,8] is a result of poorer packing and reduced density of interchain interactions. Such less well-developed packing may also reduce interchain interactions and be responsible for the reduced color found in these materials.

Conclusions

To further the development of new poly(ether imide)s based on catechol, we have now extended the range of polymers prepared using different diamines. The poly(ether imide)s based on CBA are all soluble in a range of organic solvents, including some simple halogenated solvents, and are less colored than other poly(ether imide)s; two are colorless. The molecular weight distributions of the polymers have been determined and show a major high molecular weight peak and a small amount of oligomeric material corresponding to dimer to tetramer.

Glass transition temperatures are generally in excess of 250 °C and are unobservable for polymers with rigid or inflexible diamine residues. The polymers exhibit good stability to thermal degradation under a nitrogen atmosphere and mostly only lose less than 30% of their weight at temperatures between 500 and 560 °C.

The tensile properties of the preliminary samples show good but not outstanding values. Elongations to break are generally between 3 and 9%, although the undrawn polymer based on BAPB as diamine has an extension to break of 170%. The polymers can all be drawn at temperatures in excess of 180 °C and up to 220 °C (up to 280 °C for the polymer based on TMBD), and drawn samples show improved mechanical properties.

Thus this series of polymers demonstrates a good combination of properties and processability, either by solution or melt processing. The temperature ranges over which the polymers may be drawn without break are small, which might represent a very narrow processing window for drawing just above T_g. The viscosities of the polymers under these conditions may be too high for efficient melt spinning. Solution spinning might be a viable alternative. Differences between T_g and degradation temperatures may provide a good window for other forms of melt processing.

This new series of polymers based on CBA has a high concentration of imide residues; they are structurally regular and may be crystallizable under suitable processing conditions. They are prepared from relatively inexpensive diol and diamines and could provide a source of alternative, highly processable, and inexpensive poly(ether imide)s by a process comparable to that used for Ultem.

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