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The influence of multiple *ortho*-substituted phenylenes on the nature of poly(ether imide)s

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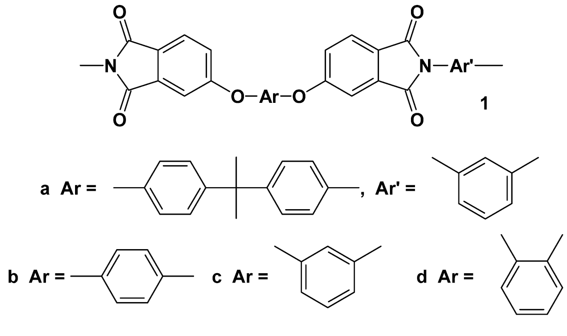
Abstract

The new *ortho*-aminophenyl diamine 1,2-bis(2′-aminophenoxy)benzene has been synthesized and polymerized with 1,2-bis(3′,4′dicarboxyphenoxy)benzene dianhydride to yield a poly(ether imide) with four *ortho*-catenated phenylenes per structural repeat unit. The polymer has been characterized by gel permeation chromatography and MALDI-TOF mass spectrometry and shown to contain a large proportion of oligomers. The oligomers have been found to be primarily macrocyclic oligomers with two to 10 repeat units. The results are contrasted with the high-molecular-weight polyimides formed from corresponding *para*-aminophenoxy diamines. It is concluded that either the *ortho*-aminophenoxy moiety or the large sequence of *ortho*-catenated phenylene rings gives a high propensity for ring closure and macrocycle formation in competition with propagation.

Keywords: Poly(ether imide); Macrocycle; *ortho*-Aminophenoxy diamine

1. Introduction

Since General Electric introduced the poly(ether imide) Ultem® **1a** as a processable polyimide [1], there have been numerous reports of attempts to produce solution or melt-processable polyimides. The majority of these reports describe the syntheses of poly(ether imide)s based on dianhydrides with ether linkages, as in **1**, i.e. prepared from bis(ether anhydride)s. It is equally feasible to introduce ether linkages into the diamine moiety of polyimides. Apart from the use of a few commercial diamines containing ether linkages, there have been relatively few reports of effort in this direction. Nevertheless, bis(ether amine)s are as easily prepared as bis(ether anhydride)s; we have reported the synthesis of several such diamines [2]. A number of these bis(ether amine)s have been used by us and others in studies of poly(ether amide)s [3] and poly(ether imide)s [4,5]. One active line of research is to establish the influence of aromatic substitution patterns on the nature of polyimides.



For bis(aminophenoxy)benzenes **5**, Scheme 1, there are nine possible structures; it is assumed that the terminal units have the same substitution pattern and the products are symmetrical. Evers introduced a nomenclature for such compounds based on the substitution pattern at each ring, e.g. *ppp*, *pmp*, etc. and the nature of the functional group [6]. Accordingly, the dinitro compound **4** formed from **2**, where **X** and the nitro group are *para* to each other, and **3** is catechol is designated *pop*$(NO_2)_2$. We have adopted this nomenclature and adapted it for the presence of substituents [2,3].

Ether linkages in **4** are conveniently prepared by aromatic nucleophilic displacement reactions (S_NAr) in

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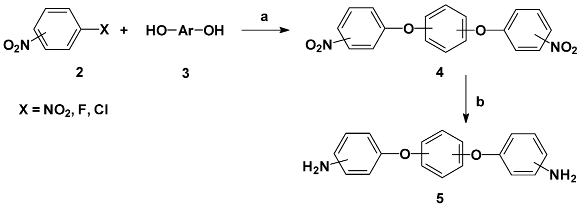
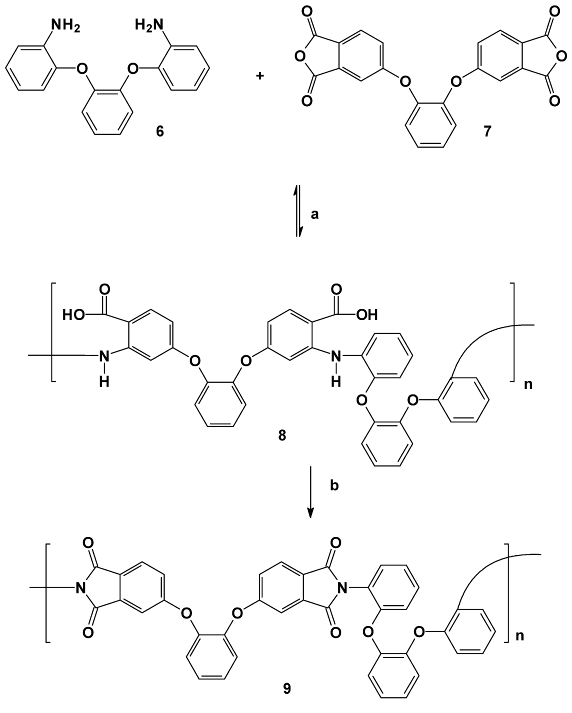


Scheme 1.

which a nitro-, fluoro- or chloro- leaving group **X** is activated by a nitro group, as in Scheme 1. We and others have demonstrated that *pxp*$(NH_2)_2$-type ($x = p$, m, or o) diamines lead to high-molecular-weight polyimides when reacted with various dianhydrides. It has thus been demonstrated that polyimides formed from diamines with *ortho*-catenated phenylenes, such as *pop*$(NH_2)_2$ and its derivatives, have enhanced solubility while retaining other favourable properties. We have also demonstrated that polyimides **1d**, which have an *ortho*-catenated phenylene unit, have enhanced solubility compared with corresponding polyimides **1b** and **1c**, while retaining good mechanical and thermal properties [7,8]. Similarly, the solubility of aramids is enhanced by incorporating *ortho*-catenated phenylene units [3]. We therefore decided to extend our studies on the influence of substitution patterns on polyimide properties by preparaing new diamines such as *oxo*$(NH_2)_2$ and its derivatives. Here we describe the synthesis of *ooo*$(NH_2)_2$ **6** and the consequences of its use in the synthesis of polyimides in which the dianhydride also has an *ortho*-catenated phenylene, viz. **7** in Scheme 2, to give poly(ether imide) **9** which has four *ortho*-linked phenylenes per repeat unit.



Scheme 2.

2. Experimental

2.1. General

1-Fluoro-2-nitrobenzene was obtained from Fluorochem. Dianhydride **7** was synthesized as described previously [7]. Other reagents and solvents were obtained from Aldrich or were general laboratory reagents. Polymer molecular weights were determined by gel permeation chromatography using a Polymer Laboratories system fitted with an Knauer refractive index detector. Molecular weight calibration was against polystyrene standards, the eluant was NMP/LiCl(0.1 M) with a flow rate of 1 ml min^{-1} through PLgel polystyrene columns. The polyimide was examined by MALDI-TOF mass spectrometry using a Micromass TofSpec spectrometer. The sample was dispersed in dithranol as matrix and with or without added silver trifluoroacetate (AgTFA).

2.2. Synthesis of 1,2-bis(2′-aminophenoxy)benzene 6

Diamine **6** was prepared by the same procedure as used for *pop*$(NH_2)_2$ and related diamines [9]. In the first stage (Scheme 1, step **a**) the *ooo*$(NO_2)_2$ precursor was prepared by reacting 1-fluoro-2-nitrobenzene **2** with catechol **3** under anhydrous conditions in the presence of potassium carbonate in *N*,*N*-dimethyl formamide (DMF)/xylene mixture while refluxing at 130–135 °C under a nitrogen atmosphere. The fluorodisplacement reaction proceeded readily to give *ooo*$(NO_2)_2$ in 89% yield of pure white product, melting point 110 °C. The dinitro compound was then converted to diamine (Scheme 1, step **b**) by reduction with hydrazine monohydrate in the presence of 10% Pd/C in ethanol under reflux. Diamine **6** was extracted by addition of water, filtering and recrystallization. The yield of **6** was 83% of pure white product with a melting point of 109–110 °C. Elemental analysis for **6** was: calculated for $C_{18}H_{16}N_2O_2$ C 73.99%, H 5.52%, N 9.58%; found C 74.00%, H 5.52%, N 9.56%; NMR spectroscopic data will be presented with the synthesis of related compounds in a subsequent publication.

2.3. Synthesis of poly(ether imide)s

Polyimide syntheses are exemplified by the specific synthesis of **9** from **6** and **7**; other polyimides were prepared similarly. Using the normal conditions to produce high-molecular-weight polyimides [9,10], diamine **6** was reacted with an exactly equimolar amount of the catechol-derived dianhydride **7** (15 wt% total monomers) in *N*-methylpyrrolidinone (NMP) at room temperature to form the intermediate poly(amic acid) **8** (Scheme 2, step **a**). Unlike syntheses using *pop*$(NH_2)_2$ and other diamines which led to high-molecular-weight polymers, the reaction mixture did not go viscous rapidly but remained non-viscous over extended periods of time. Chemical imidization, after 7 days reaction, to convert **8** to the corresponding poly(ether imide) **9** was achieved with an equi-volume mixture of acetic anhydride and pyridine at room temperature (Scheme 2, step **b**). The product was isolated by precipitation into methanol to give a fine powder, in contrast to the usual fibrous or bead-like precipitate.

3. Results

Examination of polyimide **9** by gel permeation chromatography (Fig. 1) showed it to be of low average molecular weight and to consist of a higher-molecular-weight component (with a peak molecular weight, identified as M_p, of 38 kg mol^{-1}) and a series of low-molecular-weight oligomers with molecular weights mainly below 5 kg mol^{-1}; the nominal number-average molecular weight, identified as $\bar{M}_n$ in Fig. 1, is 3.4 kg mol^{-1} and $\bar{M}_w/\bar{M}_n$ was 6.5. Occasionally, gel permeation chromatograms of high-molecular-weight polyimides show the presence of a small low-molecular-weight peak [8], which might arise from a low concentration of oligomers alongside a major high-molecular-weight peak of molecular weight 60–250 kg mol^{-1}, based on polystyrene calibration. However, in this case the oligomers clearly constitute a large fraction of the reaction product.

When the product was examined by MALDI-TOF mass spectrometry the only peaks of any magnitude observed corresponded to a series of cyclic oligomers **10** decreasing in intensity with increasing *n*. In the presence of AgTFA, Fig. 2, cyclic oligomers corresponding to $[M_n + \mathrm{Ag}]^+$ with $n = 2–7$ (M is the repeat unit mass) were readily identifiable. Relative intensities of oligomeric peaks with different values of *n* are presented in Table 1. In the absence of added AgTFA peaks corresponding to cyclic oligomers $[M_n + H]^+$ with $n = 1–10$ were visible.

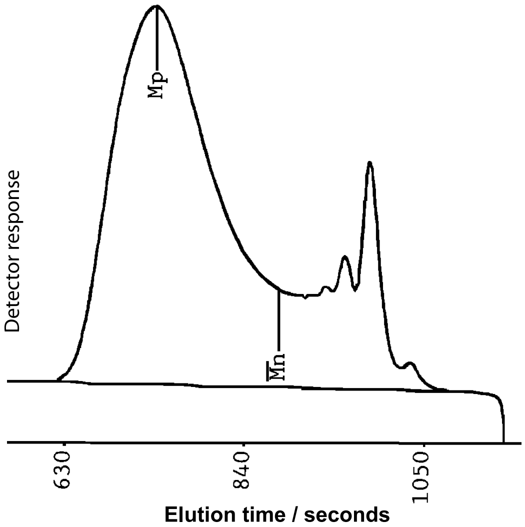


Fig. 1. Gel permeation chromatogram of poly(ether imide) prepared from diamine **6** and dianhydride **7**.

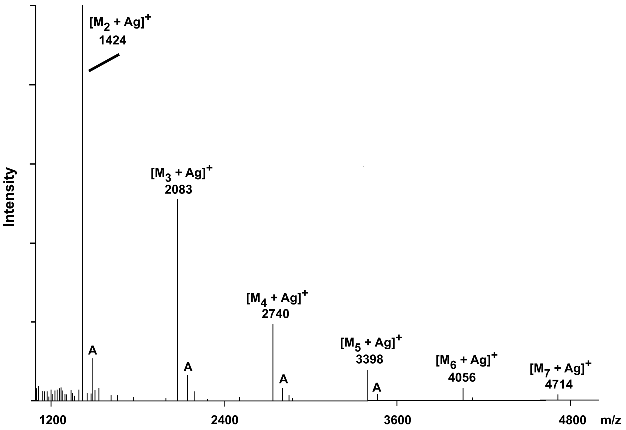
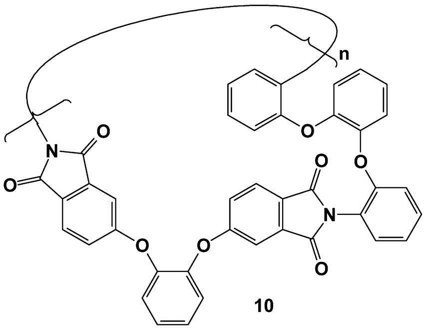


Fig. 2. MALDI-TOF mass spectrum of polyimide **9** in the presence of silver trifluoroacetate.



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The only minor peaks, separated by the mass of the repeat structure, observed in the presence of AgTFA (marked A in Fig. 2) had masses 67 or 68 mass units greater than those of the cyclics with $n = 2–6$. The nearest match between these very small peaks and linear species with any conceivable endgroups was with linear oligomers with one unacetylated amine end and one diesterified anhydride end. This combination seems highly unlikely in view of the conditions used for chemical imidization and polyimide isolation, and the peaks were at masses 3 or 4 Da higher than those calculated. In the absence of added AgTFA there were no corresponding small peaks or other minor peaks. We do not attribute the tiny extraneous peaks in the presence of AgTFA to linear oligomers but to some adduct or artifact.

ortho-Linked units are frequently incorporated into liquid crystalline polyesters where their highly bent configuration can aid the alignment of neighbouring mesogens [10]. In contrast, incorporation of *ortho*-linked units into potentially high-performance aromatic polymers is relatively unusual; Feasey demonstrated that polyesters derived from *ortho*-hydroxybenzoic acid were prone to thermal degradation [11]. Our research on poly(ether imide)s and aramids with 1,2-phenylene units incorporated into the polymer backbones through ether linkages in the dianhydride and diacid moieties, respectively, established

Table 1
Relative intensities of peaks for cyclic oligomers observable by MALDI-TOF mass spectrometry in the presence or absence of AgTFA

n	2	3	4	5	6	7	8	9	10
$[M_n + \mathrm{Ag}]^+$	100	52	19	8	3	1			
$[M_n + \mathrm{H}]^+$	98	45	22	12	7	3	2	1	0.5

that such 1,2-phenylene units do not impart thermal instability [3,8]. In the present case, although the molecular weight of polymer **9** was low, long threads could be drawn from the melt above 300 °C and the gel permeation chromatogram of a sample heated for 5 h at 300 °C was identical with that for an unheated sample. Thus, 1,2-phenylene units between either ether linkages or ether and imide groups are thermally stable.

The main features of polymer **9** are its low molecular weight, compared with those of other poly(ether imide)s, and its extremely brittle nature as a cast film. The peak of the high-molecular-weight component in the gel permeation chromatogram at 38 kg mol^{-1} contrasts with that for the corresponding poly(ether imide)s prepared from *ppp*$(NH_2)_2$, *pmp*$(NH_2)_2$ and *pop*$(NH_2)_2$ and the same dianhydride, i.e. where the NH_2 groups are *para* to the ether linkages. Those polymers, prepared under identical conditions, had peak molecular weights of 245, 160 and 214 kg mol^{-1}, respectively, measured against the same polystyrene standards; the chromatograms showed very little or no weight fraction of oligomers [4]. These three isomeric polymers, with one or two *ortho*-linked units per repeat unit, could all be cast from solution to form strong films with good mechanical properties [4]; details of their properties will be reported as part of a larger comparative study.

One potential reason for the formation of low-molecular-weight polymers in any step polymerizations is deviation from exact stoichiometry, possibly through the use of impure reagents, i.e diamine **6** might have been impure. This is an unlikely scenario since the diamine was probably the purest white of any diamine prepared in our extensive studies. More importantly, a sample of the same diamine, when reacted with equimolar quantities of terephthaloyl cloride or isophthaloyl chloride in *N*,*N*-dimethylacetamide solution, in the presence of calcium chloride and pyridine, rapidly (within 2 h) produced highly viscous solutions characteristic of high-molecular-weight polyamides, indicating that the diamine was both pure and inherently highly reactive. This was the same behaviour as observed when using *pxp*$(NH_2)_2$ diamines in the synthesis of poly(ether amide)s [3].

We conclude, therefore, that the low average molecular weight and the high content of cyclic oligomers are direct consequences of the substitution pattern of diamine **6** in combination with **7** in forming cylic oligomers of the intermediate poly(amic acid); there is no reason to believe that there is any change in distribution of species on imidization.

The original theory of step polymerisations by Carothers considered only the formation of linear polymer chains, where the number-average degree of polymerisation $\overline{\mathrm{DP}}$ is given by

$$\overline{\mathrm{DP}} = \frac{1}{1-p} \tag{1}$$

(p is the extent of reaction), and the frequency distribution of chains by

$$n_x = p^{x-1}(1-p) \tag{2}$$

(n_x is the mole fraction of chains of degree of polymerisation x) [12]. It has long been recognised that in polymers formed under either thermodynamic or kinetic control can and will form macrocyclic products. Jacobson and Stockmayer first analysed this problem (JS theory) [13]. Their and subsequent analyses assumed that all chains in the reaction are random-flight chains with free rotation and fixed bond angles and with a Gaussian distribution of end-to-end distances. There is then competition between cyclization and propagation in chains with mutually reactive ends and suitable end-to-end distances. Thus, and according to JS theory, the population of cyclic oligomers decreases with increasing ring size as $n^{-1.5}$ [13].

Later, Stepto and Waywell synthesized polyurethanes from hexamethylene disocyanate and long chain aliphatic diols, i.e. from long, flexible monomers [14]. Analysis of the products showed the formation of significant proportions of cyclic oligomers and extrapolation of their data indicated that such products increased to 100% at complete conversion; in general agreement with the predictions of JS theory. The products were analysed further in terms of the kinetics of ring formation in competition with chain growth by Gordon and Temple who analysed the system in terms of reaction kinetics [15], and subsequently by graph theory [16]. Later Stanford et al. adopted a statistical approach to rate theory [17]. These several approaches all reached the conclusion that step polymerisations with perfect stoichiometry of reactants inevitably lead to 100% cyclics at complete conversion, with the formation of cyclics favoured at intermediate conversions in dilute reaction systems. Only with a stoichiometric imbalance of reactants did calculations predict a predominance of linear species at complete conversion. The underlying model was perhaps more applicable to aliphatic reactants than aromatic monomers. Modification to theory to allow for stiff chains has been developed for ring-chain equilibria [18] and Kricheldorf et al. have presented a modified Eq. (1) to allow for different relative rates of propagation and cyclization in kinetically controlled polymerisations [19].

The polymer growth process (the formation of poly(amic acid) in this work), Scheme 2, step **a**, is an exothermic addition reaction; no condensation product is eliminated to limit formation of poly(amic acid) by a build-up in concentration and enhancing the back reaction of step **a**. Virtually all syntheses of polyimides via poly(amic acid) and subsequent chemical imidization lead to high-molecular-weight polymers; there is no reason to think that there is a major re-distribution of species on chemical imidization. That is, equlibrium constants for poly(amic acid) formation are large. These polymerisations are normally under kinetic control.

The peak molecular weights (normally close to weight-average molecular weights) of 245, 160 and 214 kg mol^{-1}, measured by GPC using polystyrene standards, for the poly(ether imide)s formed from the isomeric diamine with *para*-amino units correspond to degrees of polymerization of 372, 243 and 325, respectively. We are aware that molecular weights of poly(ether imide)s measured by GPC under our conditions exaggerate values of molecular weight. We previously compared absolute number-average molecular weights obtained by membrane osmometry with values obtained by GPC, results showed that the latter were too high by a factor of 2–3 [20]. Even assuming the molecular weights measured here were too high by a factor of 3; data still lead to degrees of polymerization of 124, 81 and 108, respectively, which are very high values and correspond to extents of reaction of 99.2, 98.8 and 99%, respectively, according to Eq. (1). Whether the polymer molecules responsible for the high-molecular-weight component are linear or cyclic, the extents of reaction are clearly high and the equilibrium constant for step **a** in Scheme 2 is high. Thus, as known, *para*-aminophenoxy units are highly reactive towards aromatic dianhydrides.

It is also to be expected that the *ortho*-aminophenoxy groups in the isomeric diamine **6** are highly reactive towards aromatic dianhydrides. While some conformations might be sterically restricted, it is anticipated that rotation about the ether linkages could leave amino groups able to react readily. This is supported by the rapid reactions with solutions of isophthalic and terephthalic acids to give viscous solutions of polyamides. Equally, reactivity with aromatic dianhydrides should be high. Although the reaction mixture with **6** did not develop high viscosity, consistent with the formation of high-molecular-weight polymer, the formation of a high content of cyclic products is, according to JS theory and subsequent developments, consistent with a high extent of reaction, and with high purity and good stoichiometry.

At this stage we do not claim that the polyimide **9** is wholly cyclic or that MALDI-TOF data accurately represent the population distribution of cyclics within the product; the distributions of species observed in the presence and absence of added AgTFA are slightly different and results might be sensitive to instrumental factors or factors involved with polymer isolation. Certainly, peak intensities for cyclics with $n \geq 3$ decrease with increasing n more rapidly than is consistent with cyclization of oligomers according to populations of species determined by random-flight statistics for long chains, i.e. than with $n^{-1.5}$. Populations of species observed are also inconsistent with Eq. (2) and for $n > 2$ they vary most consistently with $p \approx 0.4$ which is totally inconsistent with the observed peak molecular weight of about 38 kg mol^{-1}. The major distinction, therefore, between **6** and its *para*-aminophenoxy isomers is the low molecular weight of the poly(ether imide) **9**, coupled with a high content of cyclic oligomers.

Kricheldorf et al. prepared polyesters from aliphatic diacid chlorides or terephthaloyl chloride and dihydroxybenzenes. The products were all of low molecular weight and these workers found, by MALDI-TOF mass spectrometry, a strong tendency to form macrocyclic oligomers from all dihydroxybenzenes. When using aliphatic diacid chlorides there was little influence on the substitution pattern of the aromatic diol but with terephthaloyl chloride they found a stronger propensity for macrocycle formation, as evidenced by lower molecular weight products, when *ortho*-dihydroxybenzene (catechol) was used as a monomer [21].

In this work, we observed a dramatic difference between polymers prepared from *para*-aminophenoxy diamines or from the *ortho*-aminophenoxy diamine **6**. While all products contain a proportion of *ortho*-linked units in their structures, the high content of *ortho*-linkages, and especially the presence of *ortho*-aminophenoxy units, seems to impart an especially high propensity for macrocyle formation. Presumably, these units force the growing chains to adopt such conformations so as to raise the rate coefficient for cyclization relative to that for propagation. Space-filling models indicate that, while the incorporation of four *ortho*-linked units per repeat necessarily generates extremely contorted conformations, potentially reactive groups can be available for chain growth. Space-filling models also indicate that the $[1+1]$ cyclic ($n = 1$) of 10 might be feasible with a specific contorted conformation. Lack of observation of this species might be due to lack of formation or to loss of the species on isolation because of its solubility in the precipitant methanol. Cyclics in the poly(amic acid) form have more conformational flexibility than in the imidized form when rigid *N*-phenyl phthalimide units are created. The observation of cyclic imides by mass spectrometry clearly indicate that there is sufficient flexibility in structures with $n \geq 2$ for amic acid residues to be converted to phthalimides; no evidence was found for cyclic poly(amic acid)s in the reaction products.

The formation of cyclic oligomers in step polymerizations, especially polycarbonates, has received considerable attention in recent years [22] with interest in their conversion to super-high-molecular-weight polymers by ring-opening polymerization [23]. While JS theory predicts that formation of cyclic oligomers is favoured at low concentrations of reactive groups, positive efforts have been made, e.g. by use of phase transfer conditions to ensure pseudo-high-dilution conditions, to keep the concentration of active groups low and enhance formation of cyclic oligomers. In the present work, no attempt was made to reduce monomer concentrations; the reaction conditions employed were those used routinely to prepare high-molecular-weight polyimides with initial concentrations of amine and anhydride about $0.5\ \mathrm{mol\ l^{-1}}$. Presumably, if reaction conditions were modified to approximate to high-dilution conditions then even higher proportions of small cyclic oligomers might be achieved.

4. Conclusions

1,2-Bis(2′-nitrophenoxy)benzene can be prepared by S_NAr between *ortho*-nitrofluorobenzene and catechol, Scheme 1, and this compound can be readily reduced to 1,2-bis(2′-aminophenoxy)benzene **6**.

In contrast to bis(*para*-aminophenoxy)benzenes, which form high-molecular-weight polyimides with a variety of dianhydrides including **7**, 1,2-bis(2′-aminophenoxy)benzene only forms low-molecular-weight polyimide with **7**.

It was concluded that polymer **9** contains a high proportion of macrocyclic oligomers. It is further concluded that the high content of cyclic oligomers arises from a strong predisposition of the series of *ortho*-catenated phenylenes in the diamine to enhance the probability of ring closure in competition with propagation during poly(amic acid) formation. The existence of macrocycles is sustained on imidization to yield macrocyclic polyimides. It is not yet certain if this predisposition is a feature of the *ortho*-aminophenoxy unit itself or is a consequence of a series of *ortho*-catenated units; this will be clarified in subsequent studies.

It is also concluded that the populations of macrocycles do not conform with previous theoretical treatments which suggested that the populations of such species should follow the statistics of random coil conformations for long chains.

Acknowledgements

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