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Differential reactivity of aromatic diamines during polyimide formation in water

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ABSTRACT

A series of mono and di-imide compounds were synthesized by the reaction of common aromatic diamines with 4,5-dichlorophthalic acid in aqueous solution (at temperature between 160 °C and 200 °C) as a precursor to determining the chemical reactivity changes in these diamines during copolyimide synthesis under the same conditions. The reactivities of the second amino group were shown to reduce dramatically, in number of examples, after substitution had occurred on the first amino group. The effect of these reactivity changes on polymer and copolymer properties was examined by the synthesis of a series of polymers containing two of the diamines with very different reactivity behaviours.

The model compounds and polymers were characterized by FTIR, ^{1}H NMR and where possible by mass spectroscopy. The polymers were also characterized by GPC, Tg and some mechanical properties.

1. Introduction

Over many years polyimides have been shown to be very useful, thermally stable polymers for a large range of high technology applications, especially in aerospace [1] and electronics applications [2]. In much of this early work thermal stability has been the major goal, so that highly aromatic structures, with the minimum of aliphatic or other chemically active side groups, have been included as part of the structure [3,4] and reactivity changes during polymerization have not been considered a major factor. In relatively recent times more functional variations of the polyimide structure have been produced in attempts to use the products as membranes for applications in water purification, gas separation, electrolysis and related technologies [5]. In order to accomplish this, monomers with extra (or latent) functional groups have been used in the polyimide synthesis process. While these active side chain groups have been designed to help in subsequent molecular modification, cross-linking or ionic bonding, by and large little attention is paid to their influence on the details of the actual polymerization reaction.

The common synthesis method used for producing polyimides employs the reaction of a tetra-carboxylic acid dianhydride with a diamine monomer in dry, dipolar, aprotic solvents such as N,N′-dimethylformamide (DMF) or N-methyl-2-pyrrolidinone (NMP). In this technique a polyamic acid is formed quickly even at low temperatures because the anhydrides are normally very reactive. From this polyamic acid intermediate the final polyimide is produced by either thermal cyclisation at high temperatures or chemical cyclodehydration. While it is well known that variations in diamine or dianhydride reactivity (as the reaction progresses) can make a significant difference in the kinetics of the polymerization reaction [1,6,7], the effects have generally not been given a great deal of attention as a synthetic problem. This has even been the case with copolymers, where changes in reactivity can make a large difference to co-monomer ratios in a polymer and hence have a dramatic effect on copolymer properties. There have been a few extreme situations reported, especially with hetero-aromatic monomers, where the diamine

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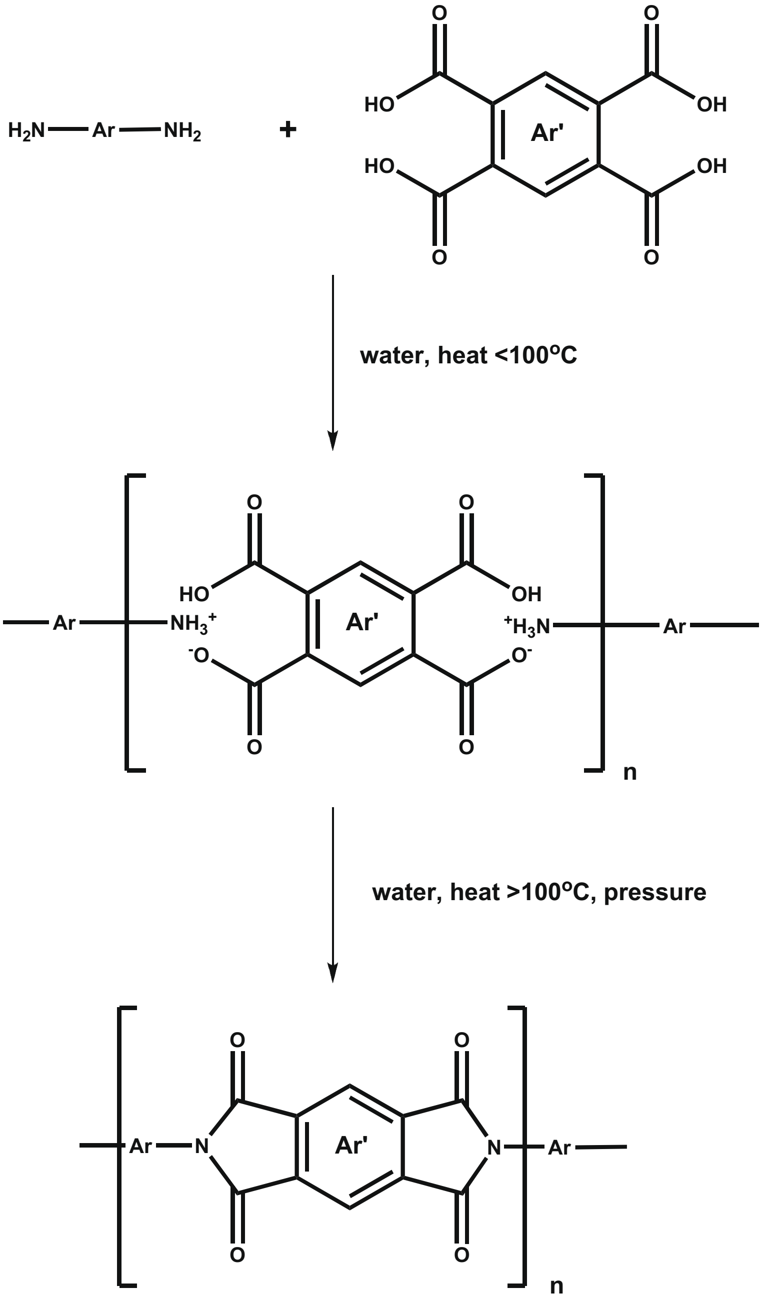
reactivity has been modified to such an extent that polymerization reactions are prevented after the reaction of the first amino group of the diamine monomer [8].

Over the last few years our group has developed a different polyimide synthetic technique using water, at high temperatures as the reaction solvent [9–13]. This method has some advantages over the standard polymerization methods due to the reduced solvent costs, minimised environmental problems and more completely cyclised structures produced. While the detailed mechanism of this aqueous polymerization is still unknown it is believed to go via a salt intermediate of the type shown in Scheme 1 and there is very little evidence of any polyamic acid intermediate in the final cyclisation reaction [14].

This polymerization reaction is a step growth polymerization so, if further polymerization steps are to occur at either the salt or the imide stage of the reaction, the electronegativity of the unreacted amine or acid group on a conjugated aromatic ring will often be changed substantially from that on the original monomer. For example the pK_a values (protonation) of the first and second amine groups on *p*-phenylenediamine are very different, with the second amine



Scheme 1. General reaction for aqueous imidisation process.

requiring a very strong acid for protonation ($\log k_{h1} = 6.38$ and $\log k_{h2} = 3.66$ at 20 °C) [15]. Thus further polymerization at the first salt formation stage appears unlikely for this monomer. Similarly the formation of an electron withdrawing imide group on the first amino group of such a diamine will lower the remaining amine pK_a and its reactivity. The effect will be less than the protonation effect above and may allow polymerization under some conditions.

The electronegativity effects in the polymerization reaction associated with the tetra-functional carboxylic acid part of the structure will be much more complex and difficult to predict. Such effects should also be considerably greater in the aqueous synthesis than those seen with the standard two-step mechanism of polyimide formation. This enhancement will also apply to the effects of other functional groups present in the various monomers. However it is probable that results from studies carried out under the aqueous polymerization techniques may point to effects generally un-noticed in the standard synthesis technique.

The reactivity changes mentioned above have become important in much of our work with polyimide synthesis for membrane applications as they are evident in large variations in yield, molecular weight and properties of copolymer materials with different types of monomers and monomer substitution patterns. Therefore we have now undertaken a more systematic model compound and polymer study with a range of monomer types using our microwave-assisted, high throughput synthesis technique [12]. In the current study the results have been concentrated on the reactivity changes in the diamine units of the polyimide materials but, as we have also found that the tetra-acid reactivity changes are important, further work is planned.

2. Experimental procedure

2.1. Materials

Bisphenol A diphthalic anhydride (BPADA) was obtained from General Electric Company, Inc. and purified by refluxing (with stirring) in acetic anhydride containing a catalytic amount of *p*-toluene sulphonic acid to convert dicarboxylic acid groups to anhydride. The diphthalic anhydride was then collected by filtration (after cooling) and washed with diethyl ether before drying overnight, under vacuum in the presence of P_2O_5. 1,3-Bis(4-aminophenoxy)benzene (TPE-R) and 4,4′-diaminobenzophenone (4,4′-DABP) were obtained from CHRISKEV Company, Inc., KS, USA and used without further purification. 1,4-Phenylenediamine (*p*-PDA); 3,3′-diaminodiphenyl sulphone (3,3′-DDS); 4,4′-diaminodiphenyl sulphone (4,4′-DDS); 4,4′-oxydianiline (4,4′-ODA); 3,5-diaminobenzoic acid (3,5-DAB) and 4,5-dichlorophthalic acid (4,5-DCP) were obtained from ALDRICH and used without further purification.

2.2. Measurements

Products soluble in suitable solvents were characterized by Nuclear Magnetic Resonance spectroscopy (NMR), Fourier Transform Infrared spectroscopy (FTIR), Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC). ^1H and ^{13}C NMR spectra were recorded in deuterated dimethyl sulphoxide (DMSO)-d_6 or deuterated chloroform ($CDCl_3$) on a Bruker DRX 500 or a Bruker Av 400 spectrometer. FTIR spectra were obtained either as a film or as a KBr disc using a Perkin-Elmer Spectrum 2000 FTIR instrument. GPC was performed using tetrahydrofuran (THF) or N,N-dimethylformamide (DMF) as eluent with polystyrene standards. A Mettler-Toledo DSC821e thermal analysis instrument was used for DSC on samples of approximately 10 mg under nitrogen at a scan rate of 10 °C/min. Positive ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using ionization energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000–10,000 using PFK as the reference compound. The imide synthesis reactions were performed in a Biotage Initiator 60 microwave reactor.

2.3. Model compound synthesis

Typical reaction procedure. Equivalent stoichiometric amounts of aromatic tetra-carboxylic acid and aromatic diamine in degassed water are added to a 20 mL microwave reactor vial to form a poly(amine-carboxylic acid) salt. This aqueous salt suspension is sealed with butyl rubber plug and aluminium collar crimped in place. The microwave reactor is programmed as per the desired reaction temperature (150–200 °C) and time. Upon completion and cooling, the polyimide precipitates as a solid product and is collected by filtration. For soluble mixtures the product ratio (mono to di-substituted) was determined by ^{13}C or ^1H NMR, however, the solubilities of the mono- and di-substituted products were often very different so that physical separation and purification was also used to confirm the results.

2.3.1. Imide formation with 4,5-dichlorophthalic acid (4,5-DCP) and 3,5-diaminobenzoic acid (3,5-DAB)

Four lots of 4,5-DCP (0.94 g, 4 mmol); 3,5-DAB (0.304 g, 2 mmol) and degassed water (15 mL) were placed in four separate 20 mL microwave reactor vials. Each vial was sealed and separately programmed as follows: Vial one was heated to 160 °C, vial two 180 °C, vial three to 190 °C and vial four 200 °C. The reaction time was 1 h for each vial. Upon completion the polyimide precipitated as a solid product. The products were separately removed from each reactor vial by filtration, washed with hot water (20 mL) and methanol (20 mL). The product was dried in a vacuum oven at room temperature overnight. The yields and characterization details are recorded in Tables 1 and 2. All of the other model compound reactions were carried out under identical conditions.

2.4. Polymer synthesis

2.4.1. Polyimide formation with monomers Bisphenol A diphthalic acid (BPADA) and 1,3-Bis(4-aminophenoxy)benzene (TPE-R)

BPADA (0.796 g, 1.43 mmol), TPE-R (0.38 g, 1.3 mmol) and degassed water (15 mL) were placed in a 20 mL

Table 1
Properties of polyimide model compound from reaction with 2 equivalents of 4,5-dichlorophthalic acid at 190 °C for 1 h.

Diamine	Mono- (M) or di-substituted (D)	Soluble in DMSO	FTIR (cm^{-1})	T_m by DSC (°C)	Mass spectrometry (*m*/*z*)	NMR in DMSO-d_6 (ppm vs TMS)
p-Phenylene diamine (**1**)	M[a]	–	–	–	–	–
	D	No	1778, 1721, 1372, 761	>450	503.9222	–
3,5-Diaminobenzoic acid (**2**)	M	Yes	3497, 3404, 1780, 1721, 1698, 1626, 1387, 766	350	349.9842	12.9(b, CO_2H), 8.25(s), 7.2(s), 7.1(s), 6.8(s), 5.7(b, NH_2)
	D	Yes	1783, 1732, 1689,1356, 762	398	547.9144	13.2(b, CO_2H), 8.3(s), 8.15(s), 7.8(s)
3,3′-Diaminodiphenyl sulphone (**3**)	M	Yes	3383, 1781, 1725, 1620, 1364, 766	261	445.9889	7.9(s), 7.2(m), 7.1(s), 7.0(d), 6.8(d), 5.7(b, NH_2)
	D	Yes	1781, 1727, 1378, 766	296	643.9172	8.3(s), 8.1(s), 8.0(m), 7.8(2d)
4,4′-Diaminodiphenyl sulphone (**4**)	M	Yes	3385, 3223, 1786, 1726, 1626, 1373, 769	344	445.9884	8.3(s), 8.0(d), 7.6(dd), 6.6(d), 6.2(s,NH_2)
	D	–	–	–	–	–
4,4′-Diaminobenzophenone (**5**)	M	Yes	3347, 3223, 1780, 1720 , 1618, 1377,760	293	410.0214	8.3(s), 7.75(2d), 7.55(2d), 6.6(d), 6.2(b, NH_2)
	D	–	–	–	–	–
1,3-Bis(4-aminophenoxy) benzene (**6**)	M[a]	–	–	–	–	–
	D	No	1778, 1715, 1396, 769	366	687.9739	–
4,4′-Oxydianiline (**7**)	M[b]	Yes	3319, 1781, 1715, 1667, 1384, 770	242	612.9528[c]	10.5(s), 8.25(d), 8.0(s), 7.9(s), 7.7(d), 7.4(d), 7.3(d), 7.1(m), 6.95(d), 6.8(d), 6.6(d)
	D	No	1781, 1716, 1667, 1383, 767	334	595.9495	–

[a] The mono-substituted species is able to be formed, however, in this experiment two molar equivalents of the dicarboxylic acid were used and only the di-substituted materials isolated.
[b] The mono-imide species in this example has an amic acid moiety on the second amine and thus is di-substituted but not a di-imide.
[c] $[M-H]^-$ determined by electrospray negative ion mass spectrometry.

Table 2
Reaction of 4,5-dichlorophthalic acid with aromatic diamines percentage yield: mono-imide (M) and di-imide (D).

Aromatic diamine	160 °C/1 h	180 °C/1 h	190 °C/1 h	200 °C/1 h
(**1**) 1,4-Phenylenediamine	70M[a]/20D	76D	63D	63D
(**2**) 3,5-Diaminobenzoic acid	91M	60M/20D	39M/32D	13M/52D
(**3**) 3,3′-Diaminodiphenyl sulphone	20M/40D	15M/45D	54D	54D
(**4**) 4,4′-Diaminodiphenyl sulphone	72M	82M	74M	72M
(**5**) 4,4′-Diamino-benzophenone	86M	86M	83M	79M
(**6**) 1,3-Bis(4-aminophenoxy) benzene	82D	80D	85D	83D
(**7**) 4,4′-Oxydianiline	72M[a]/8D	66M[a]/16D	57M[a]/25D	5M[a]/78D

[a] The mono-imide species in this example has an amic acid moiety on the second amine and thus is di-substituted but not a di-imide.

microwave reactor vial. The reactor vial was sealed with butyl rubber plug and aluminium collar crimped in place. The reaction temperature and time was programmed as follows. The reaction vial was heated to 90 °C for 10 min; the temperature was then ramped to 190 °C and held for a further 1 h. On cooling the polyimide precipitated out as a solid product and was collected by filtration before being washed with hot water (20 mL) and methanol (20 mL). It was then dissolved in dichloromethane (20 mL) and re-precipitated by adding the solution drop-wise to a stirred methanol solution (100 mL) at room temperature. The final polyimide material was filtered, dried in a vacuum oven at room temperature overnight and collected as coarse off-white fibres (0.95 g, 91%). The polyimide product proved soluble in a number of different solvents, including $CDCl_3$, DMSO-d_6/$CDCl_3$ (1:1), DMF and THF. δ_H($CDCl_3$, 400 MHz) 7.85 (d, aromatic 2H), 7.40–7.25 (m, aromatic 12H), 7.15 (d, aromatic 4H), 7.05 (d, aromatic 4H), 6.8 (d, aromatic 2H), 1.75 (s, aliphatic 6H). FTIR (cm^{-1}): 2972 (methyl C—H), 1775 (imide C=O sym), 1719 (imide C=O assym), 1379 (imide C—N). GPC(THF) Mw: 232700, Mn: 134800, Polydispersity: 1.73.

2.4.2. Polyimide formation with monomers Bisphenol A diphthalic acid (BPADA), 1,3-Bis(4-aminophenoxy)benzene (TPE-R) and 10% 3,5-diaminobenzoic acid (3,5-DAB)

BPADA (0.857 g, 1.54 mmol), TPE-R (0.3683 g, 1.26 mmol), 3,5-DAB (0.0213 g, 0.14 mmol) and degassed water (15 mL) were placed in a 20 mL microwave reactor vial. The reaction was programmed as per the procedure in Section

2.4.1 and the product collected as off-white fibres (0.94 g, 85%). The polyimide product was soluble in $CDCl_3$, DMSO-d$_6$/$CDCl_3$ (1:1), DMF and THF. δ_H($CDCl_3$, 400 MHz) 8.15 (s, aromatic-H on 3,5-DAB), 7.85 (d, aromatic 2H), 7.4–7.25 (m, aromatic 12H), 7.1 (d, aromatic 4H), 7.0 (d, aromatic 4H), 6.8 (d, aromatic 2H), 1.75 (s, aliphatic 6H). FTIR (cm^{-1}): 2970 (methyl C—H), 1776 (imide C=O sym), 1721 (imide C=O assym), 1378 (imide C—N), 1698 (shoulder peak, acid COOH). GPC (THF) Mw: 49200, Mn: 22900, Polydispersity: 2.15.

2.4.3. Polyimide formation with monomers Bisphenol A diphthalic acid (BPADA), 1,3-Bis(4-aminophenoxy)benzene (TPE-R) and 20% 3,5-diaminobenzoic acid (3,5-DAB)

BPADA (0.796 g, 1.43 mmol), TPE-R (0.304 g, 1.04 mmol), 3,5-DAB (0.04 g, 0.26 mmol) and degassed water (15 mL) were placed in a 20 mL microwave reactor vial. The reaction was programmed as per the procedure in Section 2.4.1 and the product collected as off-white fibres (0.8 g, 79%). The polyimide product was soluble in $CDCl_3$, DMSO-d$_6$/$CDCl_3$ (1:1), DMF and THF. δ_H($CDCl_3$, 400 MHz) 8.15 (s, aromatic-H on 3,5-DAB), 7.85 (d, aromatic 2H), 7.4–7.25 (m, aromatic 12H), 7.1 (d, aromatic 4H), 7.0 (d, aromatic 4H), 6.8 (d, aromatic 2H), 1.75 (s, aliphatic 6H). FTIR (cm^{-1}): 2969 (methyl C—H), 1777 (imide C=O sym), 1722 (imide C=O assym), 1375 (imide C—N), 1695 (shoulder peak, acid COOH). GPC (THF) Mw: 26600, Mn: 12800, Polydispersity: 2.07.

3. Results and discussion

In contrast to the conventional two-step synthesis of polyimides, our previous research on the aqueous polyimide synthesis technology has shown that the optimum reaction conditions can vary greatly, depending on the individual monomers used [9,10,12]. In order to obtain the best conditions for a particular set of monomers (to obtain the highest yield and/or molecular weight), preliminary studies using our high throughput microwave-assisted method [12] were carried out. Important reaction parameters include time, temperature, concentration and stirring but the most important variable in this step-growth polymerization is generally stoichiometry so monomer purity is of critical importance. The structures of the aromatic diamines used in these experiments are detailed in Fig. 1.

While the diamines are relatively easy to purify and are generally stable, the anhydrides and especially their acids are not. The anhydrides hydrolyse significantly or retain purification solvents and the acids either dehydrate or adsorb variable amounts of water. While these effects do not interfere with the actual polymerization reaction the stoichiometric balance can be critically disturbed, particularly in small-scale reactions. By thermogravimetric analysis (TGA) it is possible to determine the amount of stoichiometric and non-stoichiometric moisture in the tetra-carboxylic acid. Non-stoichiometric moisture (or adsorbed moisture) is lost on heating from 80 °C to 120 °C and stoichiometric moisture (or that lost due to anhydride formation from 1,2-dicarboxylic acids) is lost in a single step from around 170 °C to 250 °C depending on the particular tetra-carboxylic acid. It was also possible to determine the mass required for exact stoichiometry using non-pristine tetra-carboxylic acids by our automated high-throughput optimization method using the robotic Biotage microwave reactor platform [12]. Using this technique a series of mass ratios of tetra-carboxylic acid to diamine are reacted and the product molecular weight determined by GPC to give the optimal ratio for formation of high polymer.

3.1. Model compound synthesis

Once the reaction conditions had been optimized for stoichiometry the next step in this particular study was to determine the effect of changes in reactivity of the amine monomers using a model aromatic 1,2-dicarboxylic acid. The most convenient 1,2-dicarboxylic acid from both a reactivity point of view and ease of product analysis (by ^{1}H, ^{13}C, NMR and FTIR) was found to be 4,5-dichlorophthalic acid. The reactions were carried out over a range of temperatures and at a 2:1 stoichiometric ratio of dicarboxylic acid to diamine with otherwise identical conditions (for example, reaction time, stirring rate, etc.). However, previous model compound work [14] has indicated that some model imide structures can be significantly hydrolysed back to amic acid structures and even to the starting monomers in the course of the reaction so yields are not always optimized. This hydrolysis reaction appears to depend on the solubility of the various products in water at the reaction temperatures and is not seen in the polymeric products unless they contain ionisable side groups. The reaction results are shown in Table 1 but only the yields of mono- and di-imide compounds are recorded, not those of any intermediates or starting materials. Table 1 records the properties of the resulting imide model compounds.

The results shown in Tables 1 and 2 cover a wide range of common diamines used in polyimide synthesis from a poorly conjugated and deactivated (by the electron withdrawing sulphone group) diamine such as 3,3′-di-amino-diphenylsulphone (3,3′-DDS) to a highly conjugated and ‘initially’ activated diamine such as *para*-phenylenediamine (*p*-PDA). The most striking example of changes in amine reactivity after the first amine group had reacted is shown with amines **3** and **4** (the two isomeric di-amino-diphenylsulphones). The 4,4′-substituted diamine produced no di-substituted imide model compound even at the highest reaction temperatures, which indicated that the second amino group had been highly deactivated by the first reaction. In contrast the 3,3′-substituted diamine produced di-substituted product at all temperatures and only some mono-substituted imide at the lowest reaction temperature, showing that the deactivation of the second amino group was comparatively minor. For other extremes in reactivity it can be seen that where the amine groups are well separated and activated, amine **6** (TPE-R), there is no noticeable change in amine reactivity after the first reaction so only the di-substituted imide compound was produced at all reaction temperatures. In contrast for the diamino benzophenone structure (amine **5**) the change in reactivity was so great after the first substitution that no di-substituted product could be obtained.

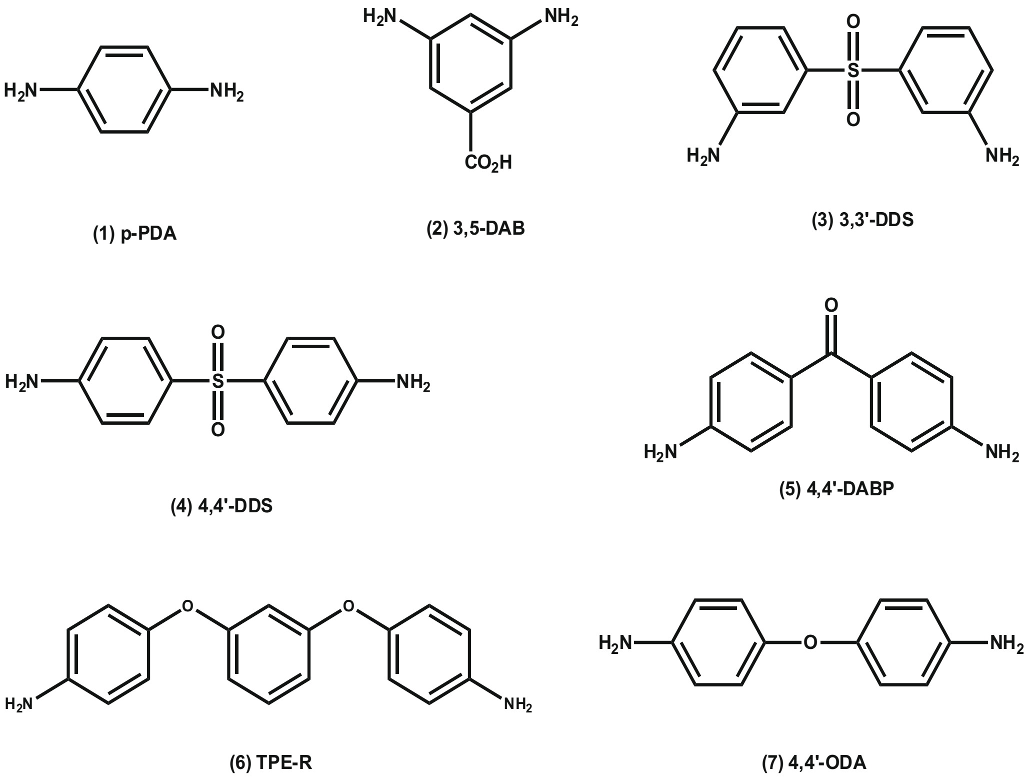

(1) p-PDA
(2) 3,5-DAB
(3) 3,3'-DDS
(4) 4,4'-DDS
(5) 4,4'-DABP
(6) TPE-R
(7) 4,4'-ODA

Fig. 1. Chemical structures of diamine monomers used in this study.

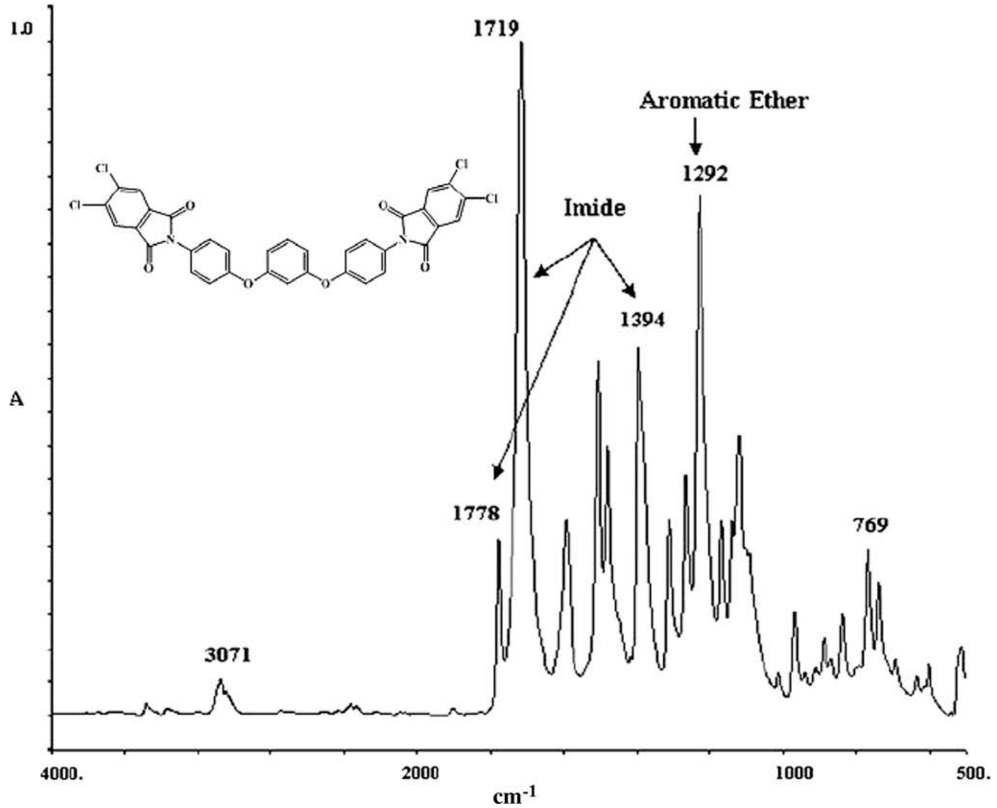


Fig. 2. FTIR spectrum of di-imide from 4,5-dichlorophthalic acid and 1,3-bis(4-aminophenoxy)benzene.

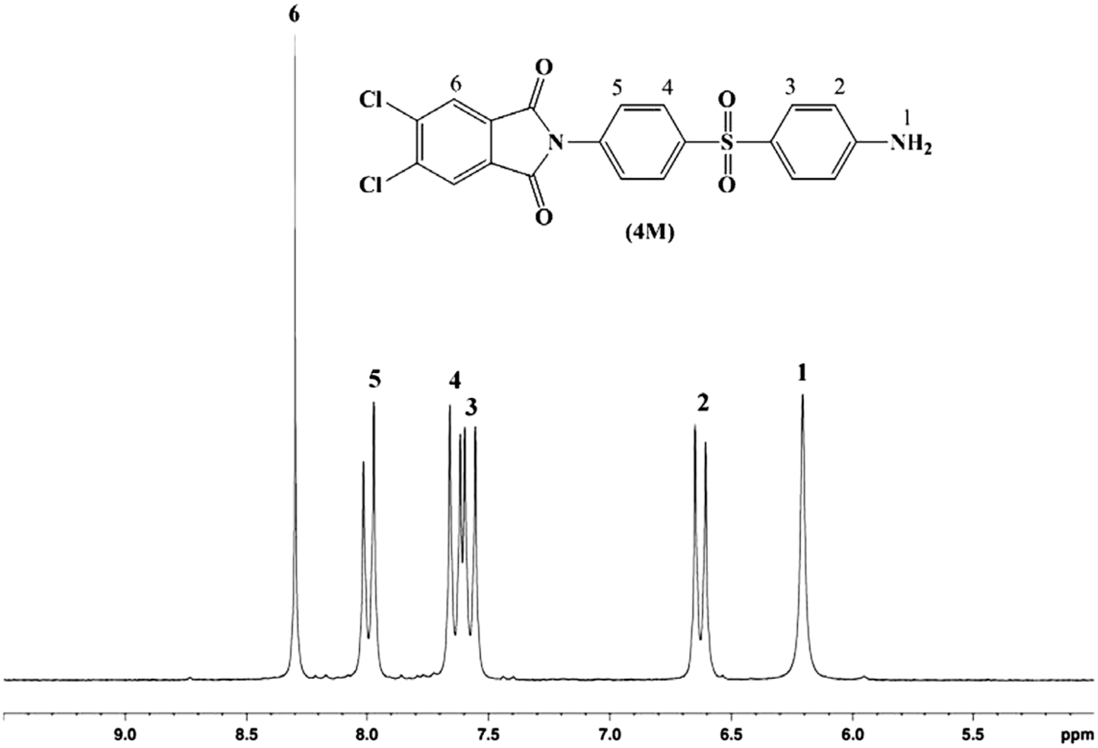


Fig. 3. ^{1}H NMR of mono-imide from 4,5-dichlorophthalic acid and 4,4′-diamino diphenyl sulphone.

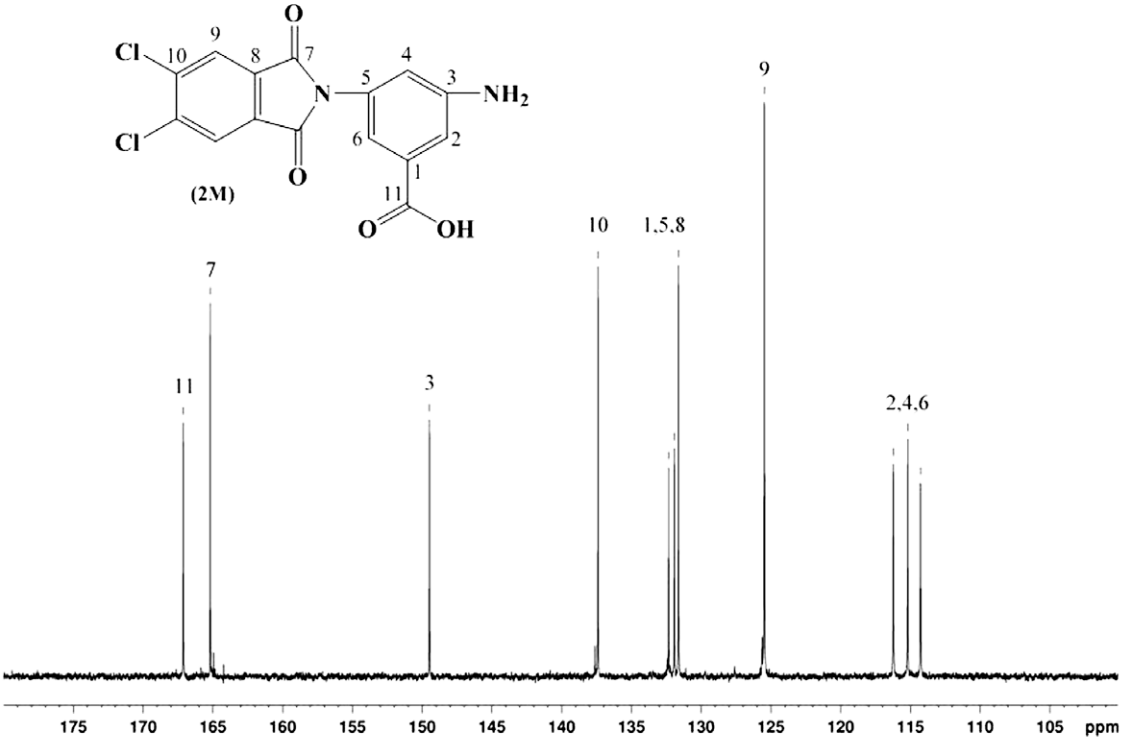


Fig. 4. ^{13}C NMR of mono-imide from 4,5-dichlorophthalic acid and 3,5-diamino benzoic acid.

Table 3
Copolymerization of TPE-R and 3,5-DAB with BPADA.

Diamines	Tetra-acid	Mwt.	Tg (DSC) (°C)
100% TPE-R/0% 3,5-DAB	BPADA	240K	199
90% TPE-R/10% 3,5-DAB	BPADA	49K	186
80% TPE-R/20% 3,5-DAB	BPADA	26K	190
0% TPE-R/100% 3,5-DAB	BPADA	6K	217

Diamines with other functional groups in the molecule are often used in polyimide synthesis to provide grafting points on the final polymer or achieve polyimides with unusual properties. Examples include amines such as **2**, with a carboxylic group or amines with sulphonic acid groups, both of which are used in membrane structures [5]. While the sulphonic acid substituted diamine could not be converted into an imide derivative by the aqueous synthesis method because the products hydrolysed under the reaction conditions, the carboxylic acid structure did not have similar problems. However, under all conditions it produced mixtures of mono- and di-imides with the latter predominating at high temperatures.

The reaction mechanisms which produce polyimides from the starting diamines and tetra-carboxylic acids in water are complex and much less well understood than those found in the standard synthesis methods in polar organic solvents. In Table 2, we have only reported the yields of mono- and di-imide model compounds, the bulk of the other products were starting monomers, however, with diamine **1** (*para*-phenylenediamine) and **7** (oxydianiline) significant quantities of intermediate compounds were also found. In the case of diamine **1** the intermediate isolated was the monoimide–monoamine structure and for diamine **7** the intermediate was the monoimide–monoamic acid. In both these cases these intermediates must have been unusually insoluble or stable in water at the reaction temperatures.

The FTIR spectrum of model compound (**6D**) in Fig. 2 is typical of a fully imidised aromatic structure, with strong imide peaks at 1778, 1719, 1394 and 769 cm^{-1}. What is particularly important, however, is that there are almost no peaks above 2000 cm^{-1}; only a small aromatic C—H peak at 3071 cm^{-1} and an imide overtone peak at 3476 cm^{-1}. The spectrum of the mono-substituted imide model compounds, in contrast, show either two or three quite strong and sharp N—H peaks in the same spectral region. Any uncyclised structures present in imide polymers or model compounds contain very broad peaks in these positions. This method of synthesis using water as solvent minimises such defects of structure in the polymer chain as they are normally readily hydrolysed at high temperatures, except for structures **1** and **7**.

The ^{1}H NMR spectrum of the mono-imidised aromatic amine shown in Fig. 3 indicates two very different A_2B_2 couplings from the originally symmetrical diamine. This highlights the substantial change in polarity caused by a single imide substitution on an aromatic diamine. In the *para* substituted DDS (**4**) this, combined with the electron withdrawing nature of the bridging sulphone group, greatly reduces the reactivity of the remaining amine. For the *meta* substituted structure the deactivating effect is minor and almost all of the NMR peaks are at significantly lower chemical shifts.

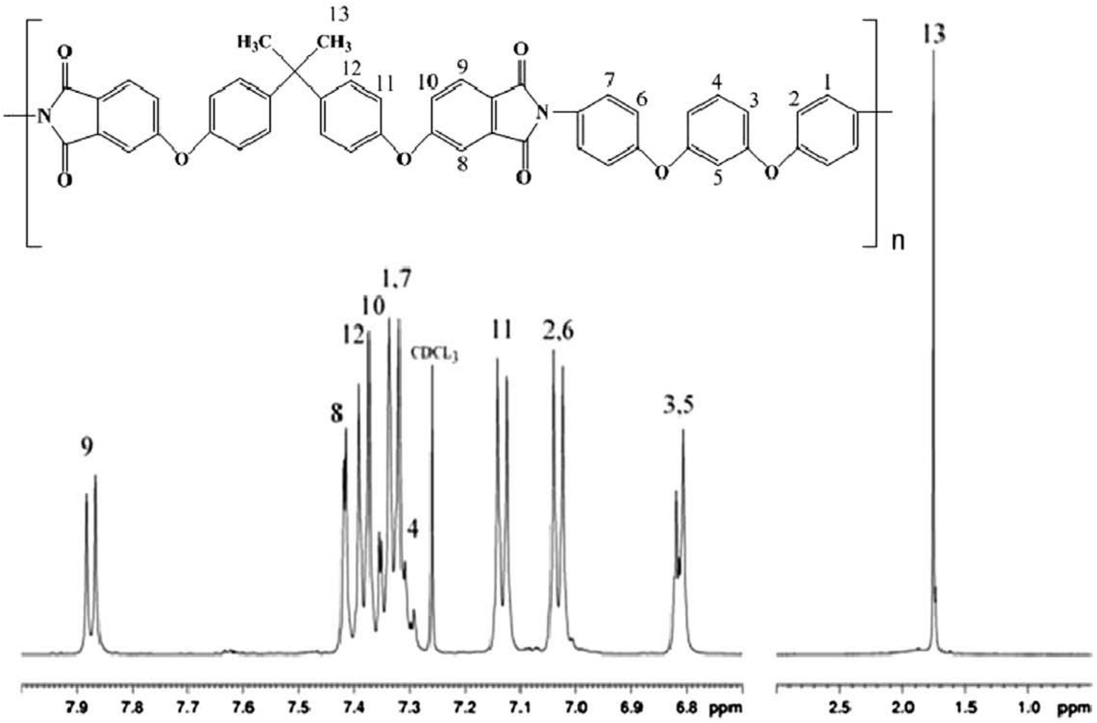


Fig. 5. ^{1}H NMR of polyimide from Bisphenol A diphthalic acid (BPADA) and 1,3-Bis(4-aminophenoxy)benzene (TPE-R).

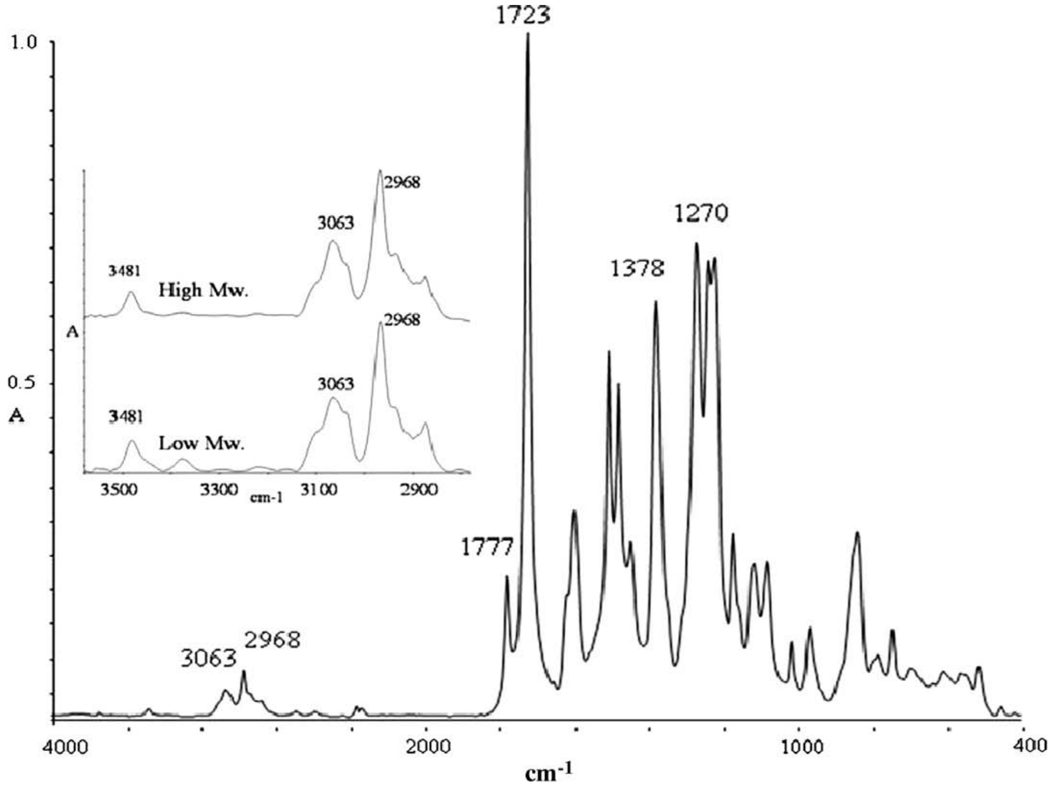


Fig. 6. FTIR spectrum of polyimide from Bisphenol A diphthalic acid (BPADA) and 1,3-Bis(4-aminophenoxy)benzene (TPE-R).

The spectrum illustrated in Fig. 4 is a ^{13}C NMR spectrum of the mono-imide (**2M**) formed from 3,5-diaminobenzoic acid (**2**). The relaxation time used for this spectrum was 10 s for each pulse and so is a reasonable approximation of a quantitative spectrum. The structure confirmed by the chemical shifts in this spectrum illustrates the point that the *meta* substituted carboxylic acid has an electron withdrawing effect that reduces the nucleophilicity of the amines. When this effect is coupled with an imide substitution on the first aromatic amine it further reduces the nucleophilicity of the remaining amine such that it is not possible to form an imide under the conditions employed in this study.

Further model compound work is planned with a range of tetra-carboxylic acids and a selected aromatic diamine to determine if any changes in reactivity can be quantified from electronic effects in the tetra-carboxylic acid monomer.

3.2. Polymer synthesis

When it comes to the synthesis of polymers, in contrast to model compounds or even oligomers, it is more difficult to determine the influence of reactivity changes on the product properties. However, some of the most important effects should include decreases in polymer molecular weight and the corresponding increases in end group structures as well as defect groups along the chain. In the latter two cases the groups are primary amines or carboxylic acids with broad FTIR peaks around 3380 cm^{-1} and are easy to detect, especially when the aqueous synthesis technique is used. This is because the final imidisation step is more complete and defect groups (such as cross-links) are generally less prevalent [10]; which is thought to be as a result of the imidisation occurring in a very simple solvent at a lower temperature than in the conventional method. Our previous studies have certainly indicated that the more reactive and well spaced diamines, generally, produce much higher molecular weight products.

In order to quantitate the effect of amine deactivation during polymerization, one of the least effected amines was used in a series of copolymerization reactions carried out under identical conditions with different percentages of a deactivating diamine (as determined by the previous model compound results). In this work the active diamine (TPE-R) and BPADA were copolymerized with different amounts of 3,5-diamino-benzoic acid as shown in Table 3. Molecular weights were determined by GPC in DMF and the end group levels were indicated by NMR and FTIR (e.g. Figs. 5 and 6).

The results showed that, with the TPE-R homopolymer, molecular weights of up to 240 K were possible with the best monomer stoichiometry and amine end groups (at ~3375 cm^{-1}, Fig. 6) were not detectable. However, even with small quantities of the deactivated amine, molecular weights were drastically reduced and the level of amine end groups greatly increased. The physical property changes included significant changes in Tg (table 3) and the ability to cast into strong, clear membranes from a range of solvents: from CH_2Cl_2 to NMP. The TPE-R/BPADA homo-polymer membrane, in particular, was clear and colourless and had a high tensile strength. This membrane on high temperature (∼190 °C) stretching showed elongations of up to 800% with strong molecular alignment and a great increase in tensile strength. In contrast the copolymer membranes were brittle especially at higher 3,5-DAB levels.

4. Conclusions

The results of this study have confirmed, by model compound reactions, that the reaction of the first amino group in an aromatic diamine can greatly influence the reactivity (deactivate) the second group, when using the aqueous imidisation technique. This influence is greatest where the diamine has other electron withdrawing groups in the molecule and where direct conjugation between the two amine groups is strong. In the case of polyimide formation in aqueous solution it has also been shown that the above deactivation of amino groups can greatly influence the molecular weight and end group levels of homo- and copolymers containing different aromatic diamines. The physical properties of the resulting polymers and copolymers are also influenced by these changes.

Based on the total yields and ratios of mono-imide to di-imide products, the order of reactivity of the second amine after initial imidisation of the aromatic diamines used in this study can be listed as follows:

TPE-R (**6**) > *p*-PDA (**1**) > 3,3′-DDS (**3**) > 4,4′-ODA (**7**) > 3,5-DAB (**2**) > 4,4′-DABP (**5**) > 4,4′-DDS (**4**)

It appears possible that similar changes in reactivity could be found to influence copolymerizations in reactions carried out under standard conditions (with aprotic polar solvents). This was certainly the case with the heterocyclic di-amines previously studied [7,8] but whether the effect is noticeable with the less deactivated di-amines studied here is not so certain.

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