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A new synthetic route for the preparation of alkenyl functionalized aryl cyanate ester monomers

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Abstract

A new, simplified synthetic route is reported for a novel family of functionalized cyanate monomers. Importantly, the synthetic route has fewer purification requirements, making it a potentially cheaper and more efficient route than previously reported syntheses. The products have been characterized extensively using nuclear magnetic resonance spectroscopy, infrared spectroscopy, and elemental analysis. Bearing alkenyl groups, these materials have the ability to form copolymeric networks with a wide variety of monomers, to yield high performance composite matrices. Crown copyright © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Cyanate esters; Alkenyl groups; Synthesis

1. Introduction

During the last decade, aromatic cyanate esters (CEs) have emerged as a new class of thermosetting resins for use as prepreg matrices in both the aerospace and electronics industries [1]. Being derived from the cyanation of hydroxyl containing species, a variety of backbone structures have been studied which, in turn, impart varying chemical, mechanical and electrical properties, and glass transition temperatures (T_g) ranging from 160°C to 355°C. CEs cure via addition polymerization of three cyanate monomers [2] to produce a heterocyclic ring referred to as a *sym* triazine or cyanurate. Reaction of difunctional monomers in this way leads to network formation. Since the early 1980s, considerable effort has been expended in the toughening of resin systems [3], and the blending of CEs with epoxies, bismaleimides (BMIs), elastomers and thermoplastics has been examined in a number of studies [4–7]. While it is not believed that BMIs and CEs coreact directly [8,9] (instead forming interpenetrating networks), the development of special 'modifier' resins, which have the ability to react with e.g. both CE and BMI homopolymer networks, offers interesting possibilities. The development of linked interpenetrating networks (LIPNs) enables the inherent brittleness and relatively poor processability of the BMI to be offset by incorporation of the inherently tough CE: the resulting polymers can display superior properties [10] to the respective homopolymers.

The modifiers which we have reported previously have possessed symmetrical structures, being typically dicyanates bearing either two allyl [8,11–14] or propenyl [10] groups positioned *ortho* to the cyanate group; the structures resulting directly from the synthetic procedure employed. These methods [8,10–14] comprise a number of (albeit high yielding) time-consuming steps which, in turn, involve many processing steps resulting in the inefficient production of side products. The somewhat simpler route reported in this paper largely overcomes these shortcomings. When used as envisaged, as modifiers for polymeric materials, the symmetrical nature of the former compounds and the difunctional nature of each end group means that crosslink densities in the modified polymeric materials are high. Lower crosslink densities are preferred as they result in a tougher composite material when the modified polymeric material is used as a matrix for a composite.

In this paper we report a new synthetic route (and extensive characterization) of a novel family of functionalized cyanate monomers. These materials also have the ability to form tough, copolymeric networks with a wide variety of high performance materials (e.g. epoxy and BMI resins). However, importantly the synthetic route is greatly simplified and has fewer purification requirements, making it a potentially cheaper and more efficient route. In a subsequent paper [15], we will report the thermal and mechanical properties exhibited by this exciting new family of materials.

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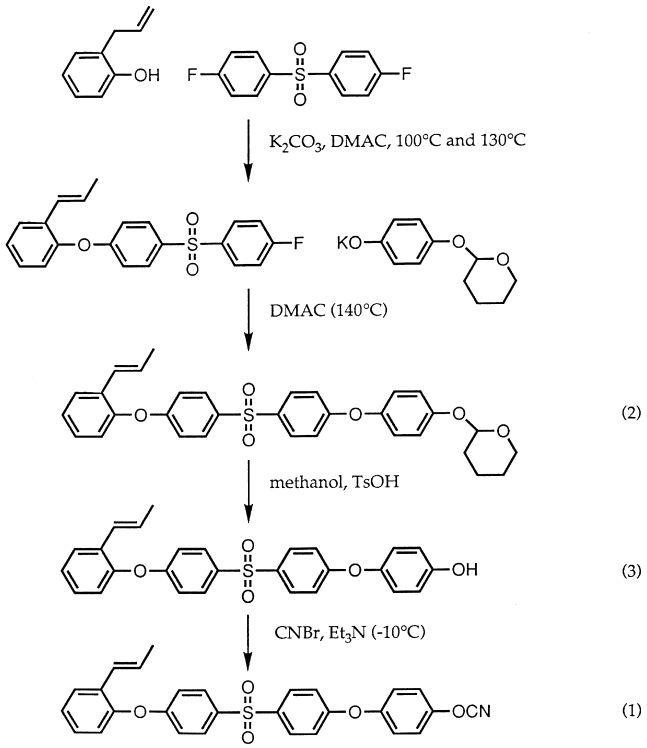


Scheme 1. Reaction scheme for modifier 4rPOCN.

2. Experimental

2.1. Equipment

Infrared spectra (of Nujol mull samples on NaCl plates) were recorded on a Perkin Elmer System 2000 spectrometer. Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C) were recorded on a Brüker AC300 spectrometer operating at approximately 300 and 75 MHz, respectively. Chemical shifts are quoted from a tetramethylsilane (TMS) internal standard. HPLC analysis was performed using a Waters system using UV detection (270 nm). Elemental analyses were carried out on a Leeman Laboratories 440 elemental analyser.

2.2. Materials

All reagents were purchased from Aldrich Chemical Co. and were used as received unless otherwise stated.

2.3. Synthesis of four-ring propenyl cyanate, 4rPOCN (*1*)

2.3.1. Tetrahydropyranyl (THP)/propenyl phenoxy-terminated oligomer (*2*)

A three-necked 250 cm^3 round bottomed flask, equipped with a magnetic stirrer bar, dropping funnel and a Dean–Stark trap, was charged with *bis*(4-fluorophenyl)sulphone (25.4 g, 100 mmol), 2-allylphenol (13.4 g, 100 mmol) and potassium carbonate (15 g, 110 mmol). N,N′-Dimethylacetamide (DMAC) (100 cm^3) was added and the mixture heated at 100°C overnight (approximately 16 h), then at 130°C for 2 h. After the reaction mixture had cooled to approximately 90°C, hydroquinone mono-THP ether potassium salt (30 g, 130 mmol) and toluene (30 cm^3) were added. The mixture was heated under reflux to remove water (3 cm^3 was collected in the Dean–Stark trap), then at 140°C overnight (16 h). After the reaction mixture had cooled to room temperature, water (100 cm^3) was added and the product extracted into diethyl ether (2 × 150 cm^3). The ethereal fractions were washed with sodium hydroxide solution (2 M, 2 × 100 cm^3) and water (2 × 100 cm^3), then dried over magnesium sulphate and combined. The solvent was removed by rotary evaporation to leave a light brown glassy solid (yield 53.4 g, 98.5 mmol, 98.5%). It was noted from the ^{1}H NMR spectrum that the allyl side chains from allylphenol had isomerized to the corresponding *trans*-propenyl group (see Scheme 1). This compound was not isolated and characterized as its THP derivative **2**, but rather as its deprotected analogue **3**.

2.3.2. Hydroxy/propenyl phenoxy-terminated oligomer (*3*)

Compound **2** (51.4 g, 94.8 mmol) was dissolved in methanol (200 cm^3) in a 500 cm^3 round bottomed flask fitted with a reflux condenser. 4-Toluenesulphonic acid (1 g, catalytic) was added and the mixture heated under reflux for 2 h, then allowed to cool to room temperature. Water (200 cm^3) was added and the product extracted into diethyl ether (2 × 150 cm^3) and washed with further water (2 × 100 cm^3). The ethereal fractions were dried over magnesium sulphate, combined and the solvent removed by rotary evaporation to give a light brown solid (yield 35.2 g, 76.9 mmol, 81.1%). As expected, a distribution of products was present, complicating the analysis. A small amount of the unsymmetrical compound **3** was isolated by chromatography for full characterization (silica column, ether:hexane 1:2 eluent).

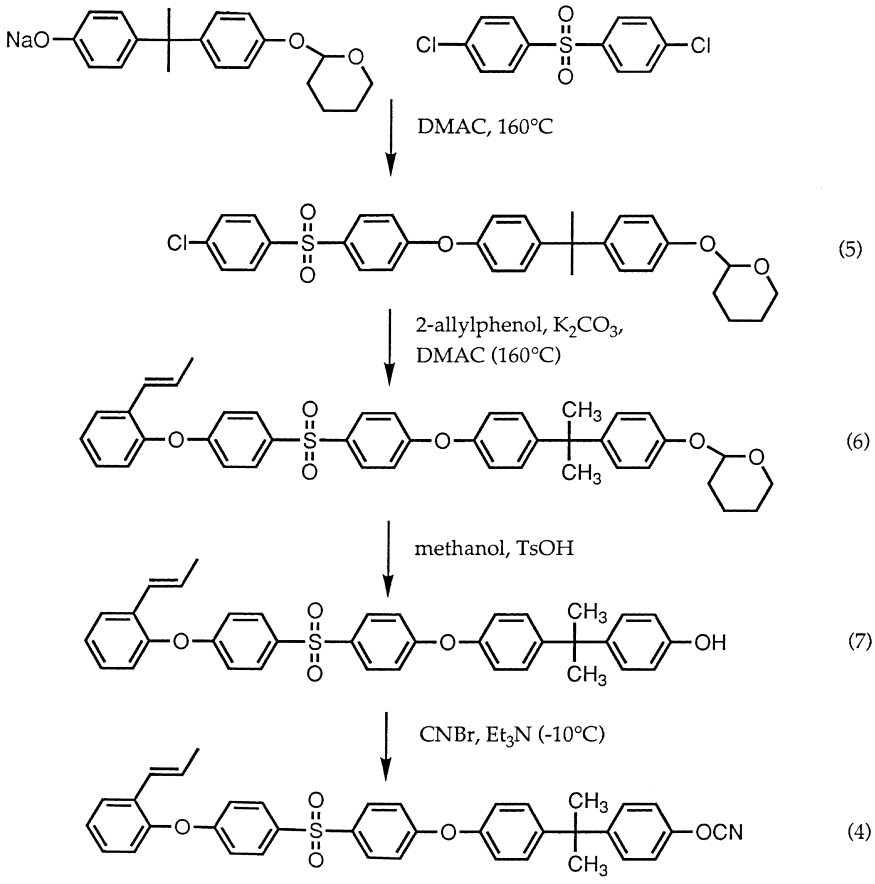
^{1}H NMR ([CD$_3$]$_2$CO), δ: 1.80–1.85 (d, J = 7 Hz, 3H), 6.25–6.40 (m, 1H), 6.49–6.50 (d, J = 15 Hz, 1H), 6.90–7.05 (m, 9H), 7.20–7.35 (quintet, J = 7 Hz, 2H), 7.65–7.70 (d, J = 7 Hz, 1H), 7.90–8.00 (m, 4H), 8.40–8.60 (s, 1H).

^{13}C NMR and DEPT ([CD$_3$]$_2$CO), δ: 18.86 (–CH$_3$), 117.35 (–CH–), 117.54 (–CH–), 117.69 (–CH–), 122.43 (–CH–), 122.77 (–CH–), 124.98 (–CH–), 126.67 (–CH–), 127.77 (–CH–), 129.06 (–CH–), 129.35 (–CH–), 130.64 (–CH–), 130.70 (–CH–), 131.52 (–C–), 136.25 (–C–), 136.80 (–C–), 147.93 (–C–), 151.85 (–C–), 155.76 (–C–), 163.09 (–C–), 163.97 (–C–).

Microanalysis. % Found: C (70.4), H (4.9), N (0). % Expected for $C_{39}H_{22}O_5S$: C (70.7), H (4.8), N (0).

2.3.3. 4-Ring propenyl cyanate, 4rPOCN (*1*)

A 250 cm^3 round bottomed flask was charged with compound **3** (34.1 g, 74.5 mmol) and cyanogen bromide (8.00 g, 75.5 mmol) in a solution of acetone (100 cm^3) (see Scheme 2). The solution was cooled to −10°C and triethylamine (freshly distilled) (7.60 g, 75.5 mmol) was added dropwise, at such a rate that the temperature of the



Scheme 2. Reaction scheme for modifier 5rPOCN.

reaction mixture was maintained at a temperature between −5°C and −10°C. After the addition of the triethylamine, the reaction mixture was allowed to warm to room temperature and the product extracted into dichloromethane (2 × 100 cm^3) and washed with water (2 × 100 cm^3). The extracts were dried over magnesium sulphate, combined and the solvent removed by rotary evaporation to give a light brown glassy solid, m.p. 50–52°C (yield 34.3 g, 71.0 mmol, 95.3%). The infrared spectrum gave characteristic peaks at 2236 and 2270 cm^{-1} (C≡N stretch). HPLC analysis revealed the presence of a number of species arising from this synthetic route. Although the associated analyses supported the supposition that the target compound **1** was present as the major constituent (62%), model compound studies would be required to determine the nature of the remaining byproducts (Fig. 1 and Table 1). A sample

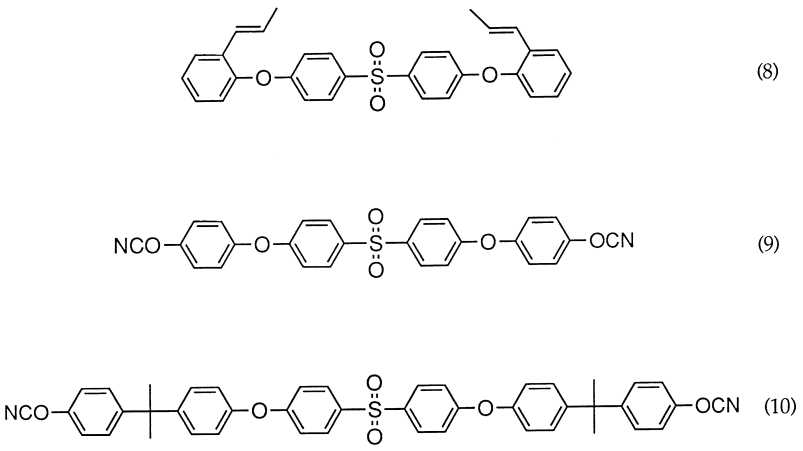


Fig. 1. Side products from modifier preparations.

Table 1
Variation in reaction mixture composition from model reactions

Reaction temperature (°C)	Yield (g) (**8**, **11** and **12**)	Yield (%)	% **8**	% **11**	% **12**
100	3.91	83	23	59	18
110	4.03	86	16	68	16
120	4.10	87	19	64	17
130	4.30	91	12	66	22
140	2.26	48	10	65	25
150	3.53	75	9	63	28
160	3.24	69	7	50	43

of the major constituent was isolated by chromatography (silica column, ether:dichloromethane:hexane 1:9:20 eluent) for analysis and subsequently identified as compound **1**.

^{1}H NMR ($CDCl_3$), δ: 1.75–1.85 (d, $J = 7$ Hz, 3H), 6.20–6.35 (doublet of quartets, $J = 15$ Hz and 7 Hz, 1H), 6.40–6.50 (d, $J = 15$ Hz, 1H), 6.40–7.35 (m, 11H), 7.55–7.60 (m, 1H), 7.80–8.00 (m, 4H).

^{13}C NMR and DEPT ($CDCl_3$), δ: 14.06 (–CH_3), 18.81 (–CH_3), 108.58 (–C–), 116.89 (–CH–), 117.11 (–CH–), 117.95 (–CH–), 121.33 (–CH–), 121.85 (–CH–), 124.03 (–CH–), 125.71 (–CH–), 126.89 (–CH–), 128.19 (–CH–), 128.49 (–CH–), 129.77 (–CH–), 129.86 (–CH–), 130.74 (–C–), 134.62 (–C–), 136.54 (–C–), 149.18 (–C–), 150.76 (–C–), 153.45 (–C–), 161.00 (–C–), 162.36 (–C–).

Microanalysis. % Found: C (69.5), H (4.3), N (2.8). % Expected for $C_{28}H_{21}NO_5S$: C (69.6), H (4.4), N (2.9).

2.4. Synthesis of 5-ring propenyl cyanate, 5rPOCN (*4*)

2.4.1. THP/chloro-terminated oligomer (*5*) and THP/propenyl phenoxy-terminated oligomer (*6*)

A three-necked 1 l round bottomed flask, equipped with a Dean–Stark trap, was charged with bisphenol-A mono-THP ether/sodium salt (66.8 g, 200 mmol), *bis*(4-chlorophenyl)-sulphone (57.4 g, 200 mmol) and potassium carbonate (3 g, 22 mmol). DMAC (600 cm^3) and toluene (200 cm^3) were added and the mixture heated under reflux with stirring until no more water was being removed (approximately 6 cm^3 was collected). Toluene was removed by distillation until the temperature of the reaction mixture reached 160°C — the reactants were stirred at this temperature for a further 2 h. After the reaction mixture had cooled to about 90°C, potassium carbonate (28 g, 200 mmol), 2-allylphenol (27.0 g, 200 mmol) and toluene (200 cm^3) were added. The mixture was heated under reflux until no further water was given off (approximately 3 cm^3 was collected after 1 h). The toluene was removed by distillation and the reaction mixture heated to 160°C for a further 2 h, then allowed to cool to room temperature. The resulting mixture was poured into water (500 cm^3) and the product extracted into diethyl ether (600 cm^3 + 300 cm^3) and washed with sodium hydroxide solution (2 M, 300 cm^3), water (300 cm^3) and brine (300 cm^3). The ethereal solutions were dried over magnesium sulphate and combined and the solvent removed by rotary evaporation to leave a light brown glassy solid (yield 127.4 g, 198 mmol, 98.9%). It was noted from the ^{1}H NMR spectrum that the allyl side chains from allylphenol had isomerized to the corresponding *trans*-propenyl group (see Scheme 2). This compound was not isolated and characterized as its THP derivative **6**, but as its deprotected analogue **7**.

2.4.2. Hydroxy/propenyl phenoxy-terminated oligomer (*7*)

Compound **6** (127.4 g, 193 mmol) was dissolved in methanol (500 cm^3) in a 1 l round bottomed flask. 4-Toluenesulphonic acid (2 g, catalytic) was added and the solution heated under reflux for 2 h, then allowed to cool to room temperature. The product was extracted into diethyl ether (600 cm^3 + 300 cm^3) and washed with water (2 × 300 cm^3). The ethereal fractions were dried over magnesium sulphate, combined and the solvent removed by rotary evaporation to give a light brown solid, m.p. 76–78°C (yield 114.0 g, 192 mmol, 99.5%). HPLC analysis showed a distribution of products was present. A small amount of the unsymmetrical compound **7** was isolated by chromatography for full characterization (silica column, ether:dichloromethane:hexane 1:3:4 eluent).

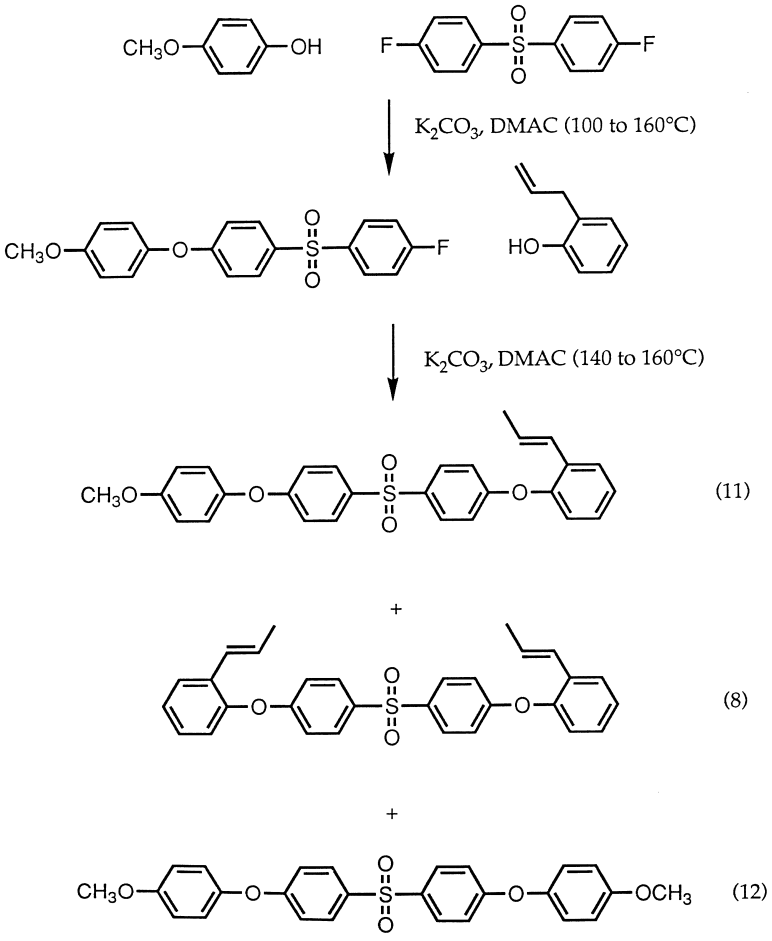
^{1}H NMR ($CDCl_3$), δ: 1.65 (s, 6H), 1.80–1.85 (d, $J = 7$ Hz, 3H), 6.15–6.35 (m, 1H), 6.40–6.50 (d, $J = 15$ Hz, 1H), 6.75–6.80 (d, $J = 8$ Hz, 2H), 6.90–7.25 (m, 13H), 7.35–7.60 (m, 1H), 7.80–7.90 (m, 4H).

^{13}C NMR and DEPT ($CDCl_3$), δ: 16.78 (–CH_3), 30.99 (–CH_3), 42.04 (–C–), 114.69 (–CH–), 116.97 (–CH–), 117.62 (–CH–), 119.68 (–CH–), 121.35 (–CH–), 124.24 (–CH–), 125.66 (–CH–), 126.99 (–CH–), 127.86 (–CH–), 128.21 (–CH–), 128.43 (–CH–), 128.50 (–CH–), 129.67 (–CH–), 129.71 (–CH–), 129.90 (–CH–), 130.85 (–C–), 135.06 (–C–), 135.30 (–C–), 142.47 (–C–), 147.92 (–C–), 151.00 (–C–), 152.64 (–C–), 153.65 (–C–), 162.12 (–C–), 162.29 (–C–).

Microanalysis. % Found: C (74.0), H (5.5), N (0). % Expected for $C_{36}H_{32}O_5S$: C (74.9), H (5.6), N (0).

2.4.3. 5-ring propenyl cyanate, 5rPOCN (*4*)

A 250 cm^3 round bottomed flask was charged with compound **7** (26.24 g, 44.4 mmol) and cyanogen bromide (4.71 g, 44.4 mmol) dissolved in acetone (100 cm^3) (see



Scheme 3. Model compound reaction scheme.

Scheme 2). The solution was cooled to −10°C and triethylamine (freshly distilled) (4.50 g, 44.4 mmol) was added dropwise, at such a rate that the temperature of the reaction mixture was maintained at a temperature between −5°C and −10°C (this took approximately 30 min). After the addition of the triethylamine, the reaction mixture was allowed to warm to room temperature and the product extracted into dichloromethane (2×100 cm^3) and washed with water (2×100 cm^3). The extracts were dried over magnesium sulphate, combined and the solvent removed by rotary evaporation to give a light brown glassy solid, m.p. 54–56°C (yield 25.5 g, 44.3 mmol, 99.7%). The infrared spectrum gave characteristic peaks at 2237 and 2270 cm^{-1} (C≡N stretch). A sample of the major product **4** was isolated by chromatography (silica column, ether:dichloromethane: hexane 1:9:20 eluent) for analysis.

^{1}H NMR ($CDCl_3$), δ: 1.70 (s, 6H), 1.80–1.85 (d, J = 7 Hz, 3H), 6.40–6.50 (d, J = 15 Hz, 1H), 6.70–6.85 (m, 1H), 6.90–7.10 (m, 8H), 7.40–7.60 (m, 1H), 7.85–7.95 (m, 4H).

^{13}C NMR and DEPT ($CDCl_3$), δ: 16.84 (–CH_3), 30.83 (–CH_3), 42.50 (–C–), 108.87 (–C–), 114.90 (–CH–), 117.04 (–CH–), 117.68 (–CH–), 119.95 (–CH–), 121.36 (–CH–), 124.10 (–CH–), 125.69 (–CH–), 126.91 (–CH–), 128.21 (–CH–), 128.36 (–CH–), 128.74 (–CH–), 129.25 (–CH–), 129.57 (–CH–), 129.70 (–CH–), 130.80 (–C–), 134.95 (–C–), 135.55 (–C–), 146.49 (–C–), 149.38 (–C–), 150.87 (–C–), 153.03 (–C–), 161.81 (–C–), 162.28 (–C–).

Microanalysis. % Found: C (73.2), H (5.2), N (2.3). % expected for $C_{37}H_{31}NO_5S$: C (73.8), H (5.2), N (2.3).

2.5. Synthesis of the model compounds

A three-necked, round bottomed flask, equipped with a magnetic stirrer bar, dropping funnel, condenser and a Beckman thermometer was charged with *bis*(4-fluorophenyl)sulphone (2.54 g, 10 mmol), potassium carbonate (13.8 g, 1 mmol) and DMAC (40 cm^3). The reaction mixture was heated to the required temperature and allowed to equilibrate. 4-Methoxyphenol (1.24 g, 10 mol), dissolved in DMAC (10 cm^3), was added dropwise over a period of 30 min (see Scheme 3). The reaction mixture was heated for a further 3.5 h and allowed to cool to a temperature (120°C or lower) suitable for the addition of the next reactants. Potassium carbonate (13.8 g, 10 mmol) and 2-allylphenol (1.34 g, 10 mmol) were added and the reaction mixture was heated at 160°C for a further 2 h. It was then allowed to cool to room temperature and the product extracted into

diethyl ether (2×50 cm^3), washed with sodium hydroxide solution (2 M, 50 cm^3) and water (2×50 cm^3), and dried over magnesium sulphate. The extracts were combined and the solvent removed by rotary evaporation to give a light brown glassy solid. Yields and purities for the various reaction temperatures are given in Table 1.

3. Results and discussion

3.1. General preparative method

A preparative route for 4rPOCN is shown in Scheme 1. One equivalent of both 2-allylphenol and *bis*(4-fluorophenyl)sulphone were dissolved in DMAC, in the presence of potassium carbonate. The mixture was heated at 110°C for 18 h, then at 120°C for 4 h. After cooling, hydroquinone mono-THP ether potassium salt was added (together with extra potassium carbonate), excess water removed by azeotrope (toluene) and the mixture heated at 140°C for 6 h before work-up. At this stage there were no unprotected phenolic –OH groups to react with the base, so the residual potassium carbonate was sufficient to catalyze the isomerization of the allyl side chains (from 2-allylphenol) to propenyl moieties. After hydrolysis of the THP groups, the resulting hydroxy-terminated product **3** was cyanated to yield the required product **1**.

The bisphenol-A based compound, 5rPOCN (**4**), was made using a similar method (Scheme 2), with a few minor differences: *bis*(4-chlorophenyl)sulphone was used rather than *bis*(4-fluorophenyl)sulphone, because it is much cheaper. However, the reduced reactivity of the chloro derivative required a reaction temperature of 160°C. At this temperature the propenyl side chains on the product also underwent slow hydrolysis, making it necessary to minimize the amount of time that the reaction mixture spent at this temperature, after addition of the 2-allylphenol. Consequently, the 2-allylphenol was the last reagent to be added (the addition of the bisphenol-A THP derivative being the first step).

3.2. Identification of contaminants

During the synthesis of both 4rPOCN (**1**) and 5rPOCN (**4**), side reactions did occur leading to a mixture of products (although in both cases the target compound, the unsymmetrical cyanate, predominated). HPLC (UV detection at 270 nm) was used to determine approximate compositions of the reaction mixtures; the raw integrals for each peak were subsequently corrected for relative UV absorbance (after the compound had been isolated). Initially, the identities of the byproducts were not known, but in all cases a small sample of each of the compounds present was isolated (either by separation from a mixture by column chromatography or synthesized directly), the contaminants were identified using a variety of both existing (authentic) and newly prepared model compounds. This allowed positive identification and the measurement of the UV spectrum, and hence determination of the relative absorbance. For example, compound **8** is available commercially as Compimide 122 [16] and full characterization data are available, while compound **9** has been prepared and characterized previously [17]. Compound **10** was prepared on a small scale during this work using the cyanation route outlined earlier from the corresponding hydroxy-terminated oligomer.

As a result, it was established that the synthesis of 4rPOCN yielded the target compound **1** in a yield of 62% and byproducts in the form of **8** (21% of the total product) and **9** (17% of the total). Similarly, the synthesis of 5rPOCN yielded the target compound **4** in a yield of 63%, but also yielded compounds **8** (27% of the total product) and **10** (10% of the total). The structures of the side products (**8**, **9**, and **10**) of the two reaction sequences are shown in Fig. 1.

3.3. General preparative method for the model compounds

In order to identify the nature of reaction byproducts using HPLC as described above, it was first necessary to prepare a series of model compounds using one equivalent of 4-methoxyphenol and *bis*(4-fluorophenyl)sulphone, followed by one equivalent of 2-allylphenol (Scheme 3). This resulted in a mixture containing three compounds, but by varying the reaction temperature the composition of the mixture of products could be altered significantly. As the difference in reactivity between the two identical halogens in *bis*(4-halophenyl)sulphone derivatives is not very great, one would expect the use of a lower temperature to give better selectivity. However, it should be noted that for optimum yield of the oligomers, the *bis*-halophenyl compound should preferably comprise two different halo groups of markedly differing reactivity. A series of experiments was carried out on model systems based on the above to identify the optimum reaction temperature. Experiments were carried out in a three-necked, round bottomed flask, equipped with a magnetic stirrer bar, dropping funnel, condenser and a Beckman thermometer. The thermometer was connected to the hotplate stirrer used to heat the oil bath and allowed the reaction mixture to be maintained at a preselected temperature to within a single degree Celsius.

3.4. Use of model compound studies to determine optimum reaction conditions

From a cursory examination of the reaction of 2-allylphenol with *bis*(4-fluorophenyl)sulphone, it was apparent that close attention to both stoichiometry and reaction temperature would be important to avoid capping the dihalide with alkenyl-substituted phenyl rings (preventing the eventual production of the cyanate). Consequently, a series of reactions involving model compounds was used to determine the optimum reaction conditions for the first step of the preparation of 4rPOCN.

Initially, one equivalent of 4-methoxyphenol was added

to *bis*(4-fluorophenyl)sulphone in DMAC solution with potassium carbonate. After approximately 4 h, 2-allylphenol was added. A range of temperatures between 100°C and 160°C was used for the first part of the reaction (Scheme 3). For the second step, a temperature of at least 140°C was used (or the same temperature as the first step, whichever was the higher), to ensure complete isomerization of the allyl groups. This would reduce the number of different isomers present in the product **11**. HPLC was again used with reasonable success to measure the relative amounts of different species present after reaction at temperatures up to 140°C.

At higher temperatures the integrals obtained were increasingly inconsistent with those expected, based on the synthetic steps employed. The amounts of **8** and **12** should be approximately the same, and this turned out to be the case at lower temperatures. At higher temperatures a much higher proportion of **12** appeared to be present (from HPLC data) (Table 1). The maximum amount expected would be 25%, however ^{1}H NMR data suggested that a side reaction (possibly the substitution of fluorine for −OH) was occurring which could account for the inflated HPLC integrals. Furthermore, the isolated yield was reduced at higher temperatures (Table 1), meaning that the extracted product did not necessarily have the same composition as the product mixture (NMR data showed the ratio of propenyl groups to methyl groups to be about 4:5 in the 160°C experiment, compared with 1:1 for temperatures up to 130°C). Unfortunately, the exact nature of the side products defied further analysis.

From these experiments it was decided that 130°C was the optimum temperature for the reaction (and this was used in the subsequent synthesis of 4rPOCN). It should be noted that the synthesis of the cyanates was typically carried out on a much larger scale (ca. 50–250 g as opposed to < 5 g for the model compounds), thus allowing the efficient use of a Dean–Stark trap to remove water and help prevent side reactions.

4. Conclusions

A new, simplified synthetic route has been developed for the preparation of functionalized cyanate monomers. By having fewer purification requirements, the route is potentially cheaper and more efficient than previously reported syntheses. A series of experiments involving model compounds revealed that the synthesis was optimally undertaken at 130°C in order to reduce side reactions and increase the yield of the desired monomer. In a subsequent paper we will report the results of the addition of these modifiers to blends of commercial CEs and BMIs and the effect on the physicochemical properties of the resulting copolymers.

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