

Synthesis of aromatic polyetherketones in trifluoromethanesulphonic acid

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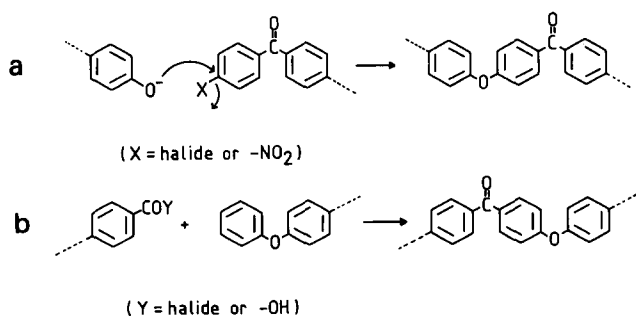
The superacid solvent trifluoromethanesulphonic acid ($H_0 = -14.6$) promotes rapid polycondensation of certain aromatic dicarboxylic acids with aromatic diethers at ambient temperature, to give linear polyketones of high molecular weight. Reactivity studies on a range of monomers and on model compounds indicate that the polymerization is inhibited by electron-withdrawing substituents on the same aromatic ring as the carboxylic acid function, and, in the ether component, by the transmission of electron-withdrawing effects between aromatic rings via the ether bridge. Monoacylation of diphenyl ether thus leads to very significant deactivation of the second, unsubstituted ring, so that this ether is not a satisfactory monomer for the present polyketone synthesis, whereas 1,4-diphenoxybenzene and 4,4'-diphenoxybiphenyl both undergo rapid diacylation, and hence polycondensation, at the terminal aromatic rings. Polymerizable one-component systems, designed for maximum self-reactivity, include (4-phenoxy)phenoxybenzoic acid and the previously unrecorded monomer 4-(4'-phenoxyphenyl)benzoic acid. Polymer characterization by ^{13}C nuclear magnetic resonance and differential scanning calorimetry indicates that condensations proceed with very high *para*-selectivity, giving crystalline polyketones with melting points in the range 320–470°C.

(Keywords: synthesis; polyetherketones; trifluoromethanesulphonic acid)

INTRODUCTION

Semi-crystalline, aromatic polyetherketones show very considerable promise as high-performance engineering materials because of their unique combination of toughness, stiffness, thermo-oxidative stability, resistance to hostile environments, and retention of physical properties at high temperatures¹. There are, in principle, two routes to polymers of this type, one involving base-promoted nucleophilic displacement by a phenol on a halogeno- or nitro-benzophenone^{2,3} (the polyether synthesis, *Scheme 1a*), and the other involving acid-promoted electrophilic condensation of an aromatic carboxylic acid or acid chloride with an aromatic ether⁴ (the polyketone synthesis, *Scheme 1b*).

Scheme 1



Scheme 1 Routes to aromatic polyetherketones

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Early investigations of the electrophilic route, however, failed to yield high polymers, because of premature crystallization from the solvents (e.g. dichloromethane) then employed⁵, and it was not until condensations were carried out using boron trifluoride as catalyst in anhydrous HF as solvent^{6,7} that high molecular weight was achieved in an electrophilic synthesis of a crystalline polyetherketone. Nucleophilic syntheses were similarly unsuccessful² until a solvent (diphenylsulphone) was discovered⁸ which enabled very high condensation temperatures (300–340°C) to be used, so allowing the polymer to remain in solution until high molecular weight was achieved. Most recently, the polyether synthesis has been approached by using a reversibly modified monomer to generate a more soluble, amorphous, polymer which only crystallizes on subsequent hydrolytic removal of the modifying (ketal) function⁹.

Strongly acidic solvents such as hydrogen fluoride solvate polyketones by protonation of the carbonyl groups, thereby retaining the polymer in solution even at low temperatures, and allowing electrophilic polycondensations to proceed to high molecular weight. Unfortunately, the volatility, corrosive nature, and toxicological properties of anhydrous HF militate against its routine use as a solvent for laboratory work, and some less hazardous alternatives, including polyphosphoric acid/aluminium chloride¹⁰ and phosphorus(V) oxide in methanesulphonic acid¹¹ have recently been investigated. Only moderate molecular weights (i.v. <0.65) were achieved in these systems, however, even under relatively forcing conditions.

It was discovered some years ago by Rose and Cinderey¹² (and independently by Roberts and Sadri¹³) that the superacid solvent trifluoromethanesulphonic acid, $\text{CF}_3\text{SO}_3\text{H}$ ($H_0 = -14.6$), promotes the condensation of carboxylic acids with activated aromatics to give *para*-substituted ketones in high yield. Since $\text{CF}_3\text{SO}_3\text{H}$ is relatively involatile (b.p. 162°C), non-corrosive to glassware, non-oxidizing, non-sulphonating, and once neutralized, virtually non-toxic, we have investigated the potential of $\text{CF}_3\text{SO}_3\text{H}$ as a catalyst and solvent for exploratory syntheses of polyketones. We now report that, within certain constraints imposed by monomer structure, this superacid provides a medium in which aromatic carboxylic acids polycondense rapidly with aromatic ethers at ambient temperature, to give polyetherketones whose molecular weight is limited only by the stoichiometry (or purity) of the monomers employed. The relationships between monomer structure and reactivity established in this work have been briefly discussed by one of us in a preliminary communication¹⁴.

RESULTS AND DISCUSSION

Monomer design

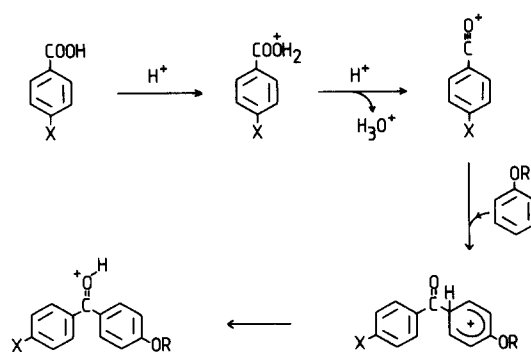
A striking feature of the kinetic data presented by Roberts and Sadri¹³ for condensation of toluene with aromatic carboxylic acids in trifluoromethanesulphonic acid is that the reaction rate slows dramatically when strongly electron-withdrawing ring-substituents ($-\text{NO}_2$, $-\text{NH}_3^+$) are introduced into the carboxylic acid. We find similar effects in the reactions of aromatic ethers with carboxylic acids, as shown in *Tables 1* and *2*, where half-lives are given for reactions of anisole with several potential diacid monomers and with a series of *p*-substituted benzoic acids in $\text{CF}_3\text{SO}_3\text{H}$ solution (0.5 M in anisole; 0.5 M in monocarboxylic acid or 0.25 M in dicarboxylic acid) at 30°C . Since trifluoromethanesulphonic acid has no ^1H resonances in the range $0 \leq \delta \leq 10$ ppm (the $-\text{OH}$ proton appears at ≈ 10.4 ppm relative to external TMS), it is a very convenient nuclear magnetic resonance (n.m.r.) solvent, and these results were obtained by monitoring the progressive disappearance of the methyl resonance of anisole and the appearance of a corresponding signal for the product 4-methoxybenzophenone some 0.4 ppm to higher field.

Although not to be considered as fully quantitative kinetic data, the structure-reactivity relationships revealed in *Tables 1* and *2* confirm the trend for electron-withdrawing ring-substituents in the carboxylic acid to inhibit the rate of ketone formation, and indicate that, reflecting this trend, some potentially useful monomers such as terephthalic acid and 4,4'-sulphonyldibenzoic acid are unlikely to give high molecular weight polymers on a reasonable timescale. However, the two diacids containing non-electron-withdrawing *para*-substituents (biphenyl-4,4'-dicarboxylic acid (A) and 4,4'-(1,4-phenylenedioxy)dibenzoic acid (B)) were both found to react rapidly with anisole (the three-ring diacid especially so; see *Table 1*) and were therefore chosen as monomers for polymerization studies.

In mechanistic terms, it seems unreasonable that electron-withdrawing substituents should reduce the absolute reactivity of an electrophile (rather, the reverse would be expected¹⁵), so that, when such substituents are present, the rate-determining step in the reaction must be

formation of a positively charged, reactive intermediate such as the acylium ion $[\text{ArCO}]^+$ (Reference 16) (or possibly the protonated mixed anhydride $[\text{ArCO}(\text{H})\text{OSO}_2\text{CF}_3]^+$, Reference 13), the formation of which will clearly be inhibited by electron-withdrawing substituents. When strongly electron-donating groups are present, however, a point is obviously reached at which formation of the intermediate electrophile is no longer rate-determining, since 4-hydroxybenzoic acid displays much the same reactivity towards anisole as benzoic acid itself, and is indeed slightly less reactive than 4-methylbenzoic acid (*Table 2*) despite the known stabilizing effect of a 4-OH substituent on the benzeneacylium ion¹⁷. We conclude that, when the carboxylic acid bears electron-donor substituents, the rate-determining step probably involves attack by the stabilized intermediate electrophile on the aromatic ether. A possible mechanism for ketone formation is shown in *Scheme 2*.

Scheme 2



Scheme 2 Proposed mechanism for ketone formation in trifluoromethanesulphonic acid

Table 1 Reaction half-lives for acylation of anisole by potential dicarboxylic acid monomers in trifluoromethanesulphonic acid

Diacid	$t_{1/2}$ (min)
4,4'-($\text{HOOC}-\text{C}_6\text{H}_4$) ₂ SO_2	810
1,3- $\text{C}_6\text{H}_4(\text{COOH})_2$	420
1,4- $\text{C}_6\text{H}_4(\text{COOH})_2$	360
4,4'-($\text{HOOC}-\text{C}_6\text{H}_4$) ₂	6.5
1,4-(4- $\text{HOOC}-\text{C}_6\text{H}_4\text{O}$) ₂ C_6H_4	2.0

Table 2 Correlation of Hammett substitution constant (σ) with reaction half-life for acylation of anisole by a series of 4-substituted benzoic acids in trifluoromethanesulphonic acid

X in 1,4- $\text{XC}_6\text{H}_4\text{COOH}$	σ	$t_{1/2}$ (min)
OH	-0.37	1.75
CH_3	-0.17	1.50
H	0	2.25
Ph	-0.01	3.00
F	+0.06	5.00
Cl	+0.23	6.25
CF_3	+0.54	40.0
NH_3^+	+0.82	∞

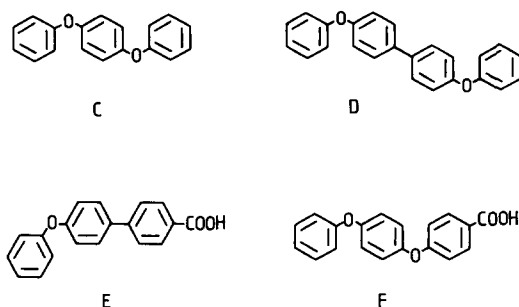
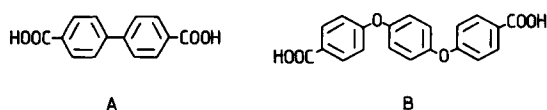
Since the aromatic ether can apparently be involved in the rate-determining step, it follows that the reactivity of the latter must also be taken into account when designing monomers for polyketone synthesis. We find, for example, that the acylation of one ring of diphenyl ether results in so dramatic a deactivation of the other ring towards electrophilic substitution, that, in the present context, diphenyl ether can be considered essentially a monofunctional reactant. We first studied the reaction between equimolar quantities of diphenyl ether and 4-methylbenzoic acid in $\text{CF}_3\text{SO}_3\text{H}$ (0.5 M in each reactant, 30°C), by monitoring the changes in intensity of ^1H n.m.r. methyl resonances of the starting material and product. The half-life for mono-acylation was identical to that for reaction with anisole (≈ 90 s), although this result actually implies a somewhat lower reactivity for diphenyl ether, since statistically it has twice the number of reactive sites as does anisole. When the reaction (monoacylation) was essentially complete, a second equivalent of carboxylic acid was added and the rate of formation of the diacylated product was monitored. No reaction was apparent at first, but after an hour a weak resonance corresponding to the expected diketone was evident, and the half-life for second-ring acylation was eventually estimated at ≈ 13 h. Acylation of one ring of diphenyl ether thus deactivates the second ring by a factor of > 500 , an effect presumably arising from transmission of the mesomeric electron-withdrawing power of a (protonated) *para*-carbonyl group to the bridging ether oxygen atom (Scheme 3).

Scheme 3



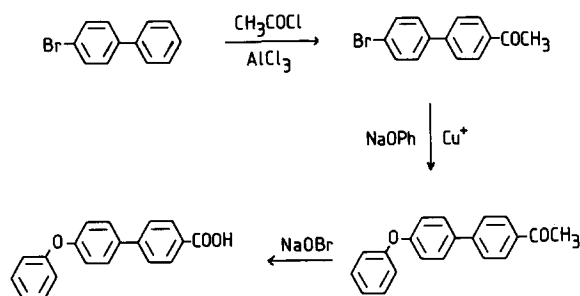
Scheme 3 'Through-bridge' deactivation of acylated diphenyl ether in strong acid solution

The enhanced positive charge on the bridging oxygen clearly results in drastic deactivation of the second ring towards electrophilic attack, so that diphenyl ether, and other potential monomers which are susceptible to this type of 'through-bridge' deactivation, such as 4,4'-diphenoxybenzophenone and 4,4'-diphenoxydiphenyl sulphone, are likely to be relatively unreactive substrates for polyetherketone synthesis. Conversely, ethers such as 1,4-diphenoxybenzene (C) and 4,4'-diphenoxybiphenyl (D) have phenoxy groups which are not intrinsically deactivated by through-bridge effects, and which moreover are far enough apart for acylation on one such group not to affect the reactivity of the other. Indeed we found that these two compounds underwent rapid diacylation by 4-methyl benzoic acid (complete reaction in < 2 min using a two-fold excess of the carboxylic acid) and were hence the ethers chosen for polymerization studies.



On the basis of these structure-reactivity studies we also designed two single-monomer systems for polyetherketone synthesis in $\text{CF}_3\text{SO}_3\text{H}$. The simplest such potential monomer is of course 4-phenoxybenzoic acid, but our results suggested that the 'through-bridge' deactivating effect of the carboxyl group would seriously inhibit self-condensation, and indeed only low molecular weight material (i.v. < 0.25) could be obtained from this compound (see Figure 2). In contrast, the three-ring monomers 4-(4'-phenoxyphenyl)benzoic acid (F) and 4-(4'-phenoxyphenyl)benzoic acid (E) have structures with no obviously inhibiting features, and these two materials were prepared as promising candidates for self-polycondensation. The synthesis of 4-(4'-phenoxyphenyl)benzoic acid (a previously unrecorded compound) involved acetylation of 4-bromobiphenyl, Ullmann condensation of the product with sodium phenoxide, and finally hypobromite oxidation of the resulting 4-phenoxy-4'-acetyl biphenyl (Scheme 4).

Scheme 4



Scheme 4 Synthesis of 4-(4'-phenoxyphenyl)benzoic acid

Since trifluoromethanesulphonic acid is not only a solvent and catalyst but also a reactant in the ketone synthesis (two moles of $\text{CF}_3\text{SO}_3\text{H}$ are consumed per mole of ketone produced; see Scheme 2), the effect on reaction half-life of varying the molar ratio of $\text{CF}_3\text{SO}_3\text{H}$ to monomers was also investigated. Results are shown in Figure 1 for the reaction between equimolar quantities of anisole and 4-chlorobenzoic acid in the presence of increasing amounts of the superacid solvent. Above a mole ratio of $\approx 20:1$ ($\text{CF}_3\text{SO}_3\text{H}$:anisole) the rate increases only slowly, but as this ratio is reduced below 10:1 the reaction half-life increases dramatically. For polymerization studies we chose to work at a solvent/monomer mole ratio of 35:1, which gave near-maximum reactivity at a convenient monomer concentration ($\approx 10\%$ w/v).

Polymerization studies

As noted above, compounds A-F (two diacids, two diethers and two ether-acids) were identified as

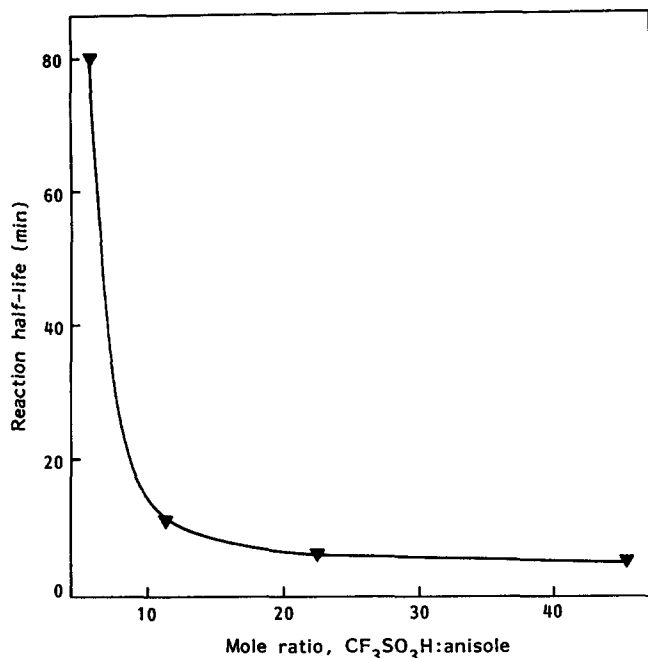


Figure 1 Effect of $\text{CF}_3\text{SO}_3\text{H}$ concentration on the rate of acylation of anisole by 4-chlorobenzoic acid (1:1 mole ratio)

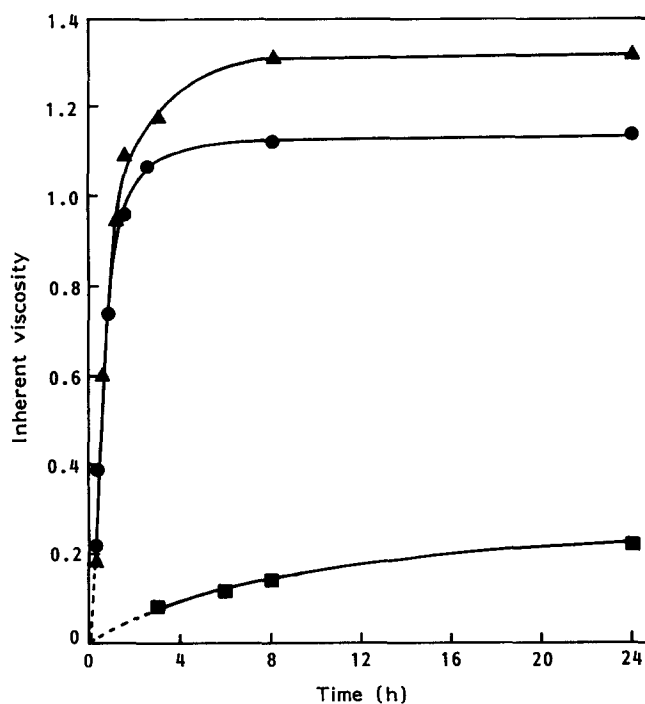


Figure 2 Inherent viscosity versus time for self-polycondensation of 4-phenoxybenzoic acid (■), 4-(4-phenoxyphenoxy)benzoic acid (●), and 4-(4'-phenoxyphenyl)benzoic acid (▲), all containing 2 mol% of 1,4-diphenoxybenzene to control molecular weight

potentially reactive monomers for polyetherketone synthesis in trifluoromethanesulphonic acid. Polycondensations were carried out simply by dissolving the monomer(s) (≈ 5 g total weight) in $\text{CF}_3\text{SO}_3\text{H}$ (50 cm^3), in the presence of a small quantity (1–5 mol%) of 1,4-diphenoxybenzene or 4,4'-diphenoxybiphenyl to 'end-cap' the polymer and thereby provide molecular weight control. After 24 h at room temperature the viscous red solution was added dropwise to a large excess of water,

and the resulting tough beads of polymer were dried, milled to powder, extracted with boiling dimethylacetamide and then acetone (the polymers were insoluble in non-protonating solvents) and finally dried under vacuum at 120°C . The effectiveness of 1,4-diphenoxybenzene (C) in providing molecular weight control was established by polymerizing monomer E in the presence of 1, 2 and 5 mol% of the diether, reactions which yielded polymers of inherent viscosity 2.06, 1.03 and 0.43 respectively. Only in reactions involving 4,4'-diphenoxybiphenyl (D) was good molecular weight control not achieved, as a result of the relative insolubility of this monomer in trifluoromethanesulphonic acid. Indeed, this diether seems to dissolve only by reaction with the carboxylic acid, so that, for example, polycondensations of 4,4'-diphenoxybiphenyl with the three-ring diacid (B) in the presence of 2% and 4% molar excess (on total monomers) of this diether yielded, after 24 h, polymers of almost identical inherent viscosity (1.04).

The progress of a polycondensation could be followed by periodically quenching 5 cm^3 aliquots of the reaction solution into water, isolating the precipitated polymer, and monitoring inherent viscosity as a function of time. Results for three single-monomer polymerizations are shown in Figure 2, which confirms not only the design of reactive monomers E and F but also the predicted failure of 4-phenoxybenzoic acid as a starting material for this type of polyketone synthesis.

Details for a series of 24 h polymerizations using several combinations of monomers A–F are given in Table 3. These data demonstrate the ability of trifluoromethanesulphonic acid to promote the formation of a wide range of high molecular weight, all-aromatic polyetherketones, some of which, because of their very high melting points ($>450^\circ\text{C}$, see below) and associated insolubility in non-acid solvents, may not be accessible by the nucleophilic polyether synthesis.

Polymer characterization

Thermal transitions in the range 100 – 500°C were measured by differential scanning calorimetry (d.s.c.) and are given in Table 4. All the polymers save one proved semi-crystalline, and, not unexpectedly, melting points and glass transition temperatures tended to increase with the ratio of direct bonds between the aromatic rings to other types of linking group ($-\text{O}-$ and $-\text{CO}-$). A sample of the polymer derived from monomer E extracted only with

Table 3 Viscosity data for polyetherketones synthesized in trifluoromethanesulphonic acid

Monomers	End-capper, mol% on total monomers	Inherent viscosity ^a
A + C	C, 2%	0.85
A + D	D, 2%	1.43
B + C	C, 1%	1.53
B + D	D, 2%	0.84
B + D	D, 4%	0.84
E	C, 1%	2.06
E	C, 2%	1.03
E	C, 5%	0.43
F	C, 2%	1.03
F	C, 4%	0.63
E + F	C, 2%	1.58
A + D + 2E	C, 2.5%	1.33

^a Measured at 30°C on 0.1% solutions in 95% sulphuric acid

Table 4 D.s.c. data for polyetherketones

Polymer ^a	Monomers	I.v.	T _g (°C) ^b	T _m (°C) ^c	ΔH _{fus} (J g ⁻¹) ^c
[φOφOφCO] _n	nucleophilic	1.05	146	343/336	70/41
[φOφOφCO] _n	F	1.03	147	334/328	51/31
[φOφOφCO] _n	B+C	1.53	150	327/323	36/31
[φOφφCO] _n	E	1.03	207	458/-	72/-
[φOφφCO] _n	E	0.43	-	462/452	102/68
[φOφOφCOφφCO] _n	A+C	0.85	183	431/421	72/48
[φOφφOφCOφφCO] _n	A+D	1.43	209	462/424	64/38
[φOφφOφCOφOφOφCO] _n	B+D	0.84	159	361, 383/367	43/46
1:1 copolymer	E+F	1.58	169	-	-
1:1:2 copolymer	A+D+2E	1.33	206	457/-	74/-

^a φ = 1,4-phenylene

^b T_g onset, second run

^c first/second run

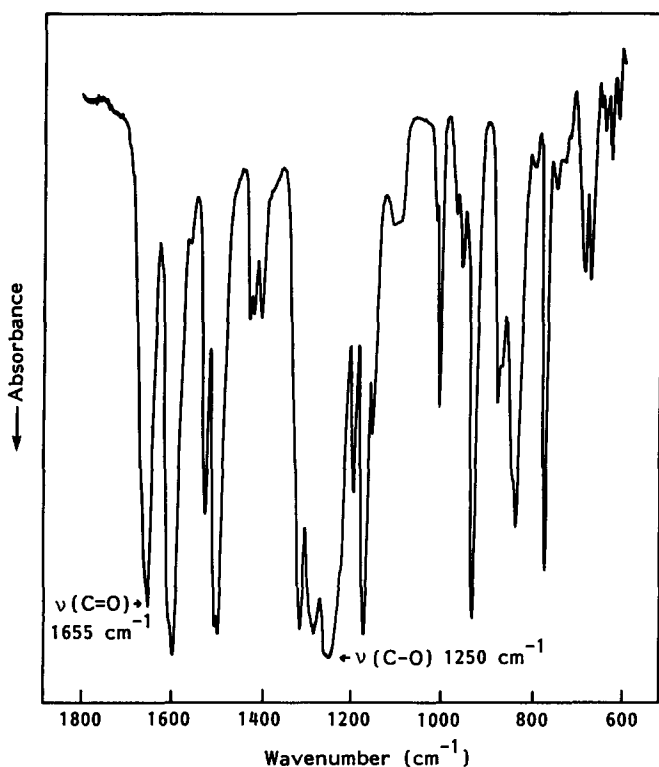


Figure 3 Infrared spectrum of $[-C_6H_4-C_6H_4-CO-C_6H_4-O-]_n$ as cast film

water and acetone at room temperature, showed a significant crystallization exotherm during the first d.s.c. scan, but this feature was not observed for most samples, which were treated successively with refluxing acetone and dimethylacetamide as part of the normal isolation procedure. It therefore seems likely that the polymers, as initially precipitated, are in fact of quite low crystallinity and only develop the high levels observed by d.s.c. on contact with organic solvents at high temperature, or subsequently on cooling from the melt.

The polyketones derived (a) from monomer F and (b) from monomers B+C should be identical both with each other and with the commercial polymer PEEK obtained via the nucleophilic route. However, the lower melting points and heats of fusion observed for the two polyketones produced via the present electrophilic synthesis (Table 4) suggest either that the latter have less 'perfect' structures (perhaps due to a small degree of *ortho* substitution) or that trace amounts of residual

trifluoromethanesulphonic acid are promoting polymer degradation near the melting point.

The polymer derived from monomers B+D showed a unique double melting peak (360/380°C) on the first d.s.c. scan, though the higher-temperature peak was only evident as a rather weak shoulder on a strong endotherm at 360°C during the second run. Crystallization from the melt was observed for all homopolymer structures, although polymers with melt temperatures in excess of 450°C (and therefore scanned to $\approx 500^\circ\text{C}$) underwent significant degradation above the melting point. This was reflected in much reduced values for T_m, and for the heats of fusion ΔH_f, on repeated d.s.c. scans. Although clearly not processable in the molten state, such very high melting polymers can be fabricated to a limited extent by wet-spinning fibres or casting films from solution in trifluoromethanesulphonic acid, in both cases using water as the precipitating solvent. The infrared (i.r.) spectrum of crystalline $[-C_6H_4-C_6H_4-CO-C_6H_4-O-]_n$ (ν(C=O) = 1655 cm⁻¹), obtained from such a solution-cast film, is shown in Figure 3.

The random 1:1 copolymer derived from E+F is essentially amorphous, even in the 'as made' state, so that the two structural units (one containing a biphenyl group) are clearly unable to fit into the same crystal lattice. Conversely, the random 1:1:2 copolymer from A+D+E is very appreciably crystalline, having a melting point and heat of fusion very close to values for the corresponding homopolymers (Table 4). This result is consistent with the view¹⁸ that ether and ketone groups in aromatic polyetherketones are crystallographically interchangeable, since the copolymer can be written in the form $[-C_6H_4-X-C_6H_4-X-C_6H_4-]_n$, where X is randomly -O- or -CO- in an overall 1:1 ratio. Crystallographic studies of this particular polymer structure are currently in progress, and will be reported in a future publication.

As pointed out elsewhere⁹, the insolubility of crystalline aromatic polyketones in nearly all organic solvents is a serious obstacle to their detailed spectroscopic characterization. However, we find that ¹H n.m.r. spectra can be readily obtained using trifluoromethanesulphonic acid as solvent (external TMS reference), and, as an example, the 200 MHz ¹H n.m.r. spectrum of $[-C_6H_4-C_6H_4-CO-C_6H_4-O-]_n$, is shown in Figure 4. Such spectra, although broad, are generally consistent with the polymers having all-*para* structures, but in view of the d.s.c. results (Table 4), which raise the possibility of less than 100% *para* substitution, a more clear-cut result would be desirable. Such a result is

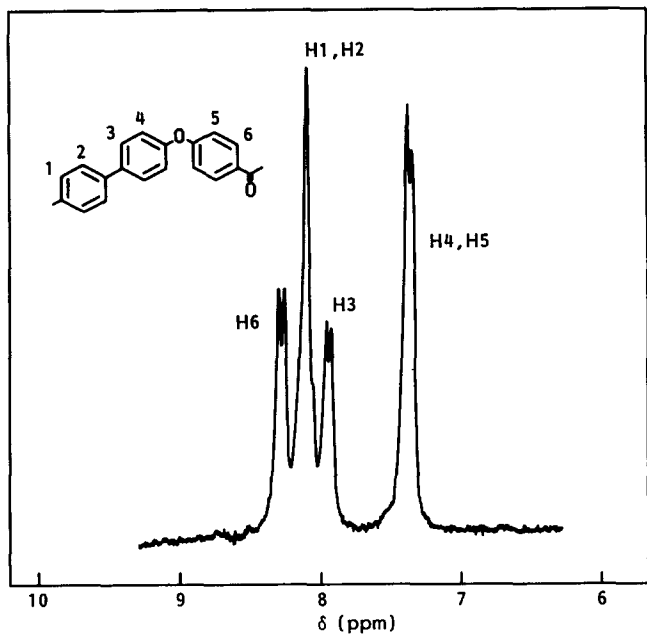


Figure 4 ^1H n.m.r. spectrum (200 MHz) of $[-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CO}-\text{C}_6\text{H}_4-\text{O}-]_n$ in trifluoromethanesulphonic acid

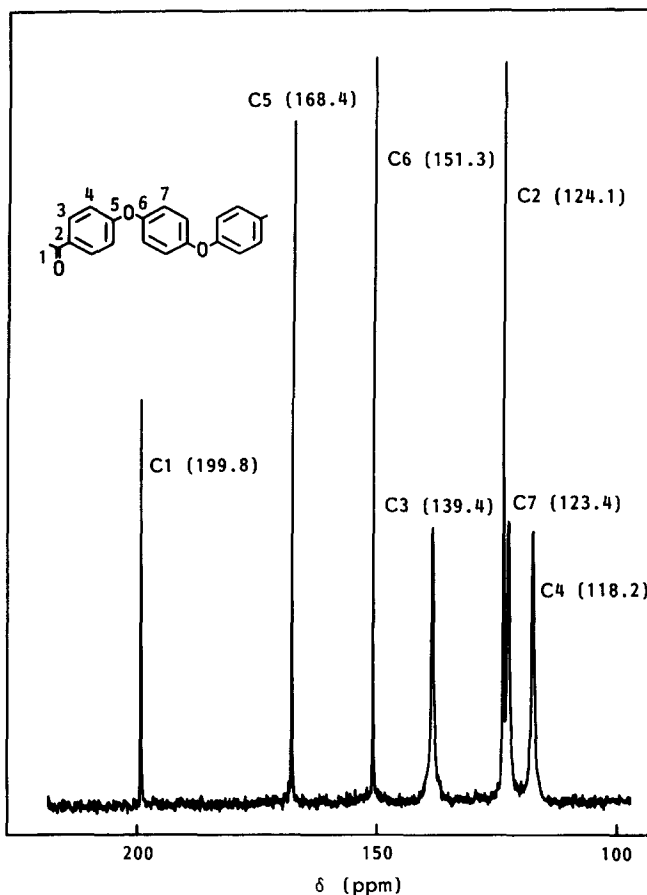


Figure 5 ^{13}C n.m.r. spectrum of $[-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{CO}-\text{C}_6\text{H}_4-\text{O}-]_n$ in methanesulphonic acid/dichloromethane- d_2 (4:1)

potentially available in the form of ^{13}C n.m.r. data, but unfortunately the strong quartet resonance of the solvent $^{13}\text{CF}_3$ group lies in the aromatic region and is therefore superimposed on the spectrum of the polymer, possibly obscuring weaker resonances. We have found a more satisfactory solvent for one such polymer however, and

the ^{13}C n.m.r. spectrum of $[-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{CO}-\text{C}_6\text{H}_4-\text{O}-]_n$ (i.v. = 1.03), derived from monomer F, in $\text{CH}_3\text{SO}_3\text{H}/\text{CD}_2\text{Cl}_2$ (4:1, v/v) solution is shown in Figure 5. (A much higher concentration (> 20% w/v) of polymer can be obtained in this mixed-solvent system than in methanesulphonic acid itself, and the deuterated solvent provides a lock signal for the spectrometer.) At the observed *s/n* ratio of > 50:1, the absence of a second carbonyl resonance corresponding to the *ortho*- $[-\text{OC}_6\text{H}_4\text{CO}-]$ unit indicates a reaction selectivity for *para* substitution of > 98% and, indeed, this spectrum is indistinguishable from that of the same polymer prepared via the nucleophilic route, which clearly must have a pre-determined, all-*para*, substitution pattern. Unfortunately, the other homopolymers prepared in this work proved insufficiently soluble in $\text{CH}_3\text{SO}_3\text{H}/\text{CD}_2\text{Cl}_2$ for comparable ^{13}C n.m.r. data to be obtained.

EXPERIMENTAL

Instrumentation and analysis

Proton and ^{13}C n.m.r. spectra were obtained using JEOL FX 200 and FX 100 spectrometers respectively, and i.r. spectra were run on a Perkin-Elmer PE197 spectrophotometer. Thermal transitions were measured using a Mettler DSC 20 instrument ($20^\circ\text{C min}^{-1}$ scanning rate). Elemental analyses were provided by the Characterization and Measurement Group of the Research and Technology Department at ICI, Runcorn.

Materials

Starting compounds and solvents were commercially available materials and were used as received. Trifluoromethanesulphonic acid was obtained from Fluorochem Ltd and, because of its extremely hygroscopic nature, operations involving this material were carried out, as far as was practicable, under dry nitrogen.

Monomers

4-Phenoxybenzoic acid, diphenyl ether, isophthalic acid, and terephthalic acid, were purchased from Aldrich. Biphenyl-4,4'-dicarboxylic acid (m.p. $> 350^\circ\text{C}$) was obtained from K and K and was purified by recrystallization of its acid chloride from toluene, followed by hydrolysis in boiling water. 1,4-Diphenoxybenzene, m.p. 76°C (literature: $76\text{--}77^\circ\text{C}^{19}$); 4,4'-diphenoxy-biphenyl, m.p. 156°C (literature: 155°C^{20}); 4-(4-phenoxy)phenoxybenzoic acid, m.p. 187°C (literature: 183°C^{21}); and 1,4-diphenoxybenzene-4',4''-dicarboxylic acid, m.p. 333°C (literature: $331\text{--}333^\circ\text{C}^{22}$), were prepared by known or slightly modified methods from the literature, and were recrystallized to constant melting point before use.

4-(4'-Phenoxyphenyl)benzoic acid. To a stirred solution containing 4-bromobiphenyl (109.6 g) and aluminium chloride (83.3 g) in nitrobenzene (500 cm^3) under nitrogen, was added acetyl chloride (45 cm^3) over ≈ 15 min. After stirring for 18 h at room temperature, the solution was quenched into a mixture of ice-water (1000 cm^3) and concentrated hydrochloric acid (300 cm^3), and the resulting yellow solid was filtered off, washed acid-free, and dried. The nitrobenzene phase was washed with water until neutral, and evaporated to give a

dark yellow solid, which was washed with hexane and dried. The two solids were combined and recrystallized from acetone to give 97.4 g of 4-acetyl-4'-bromobiphenyl, m.p. 130°C. This material was added, under dry nitrogen, to a solution of sodium phenoxide (prepared *in situ* by reaction of phenol, 44 g, with sodium methoxide, 24.8 g, in 700 cm³ of pyridine, and distilling out 200 cm³ of pyridine/methanol azeotrope). Copper(I) chloride (10 g) was added, and the mixture stirred at reflux for 26 h. After cooling, the dark solution was poured into 5 M hydrochloric acid (2500 cm³) and the resulting pale brown suspension was stirred for 2 h before filtering off the solid, which was then washed acid-free, dried and recrystallized successively from ligroin (b.p. 100–120°C) and ethanol to give 66.3 g of pale yellow, crystalline, 4-acetyl-4'-phenoxybiphenyl (m.p. 131°C). This compound (50 g in 500 cm³ of dioxan) was treated with a solution of bromine (130 g) and sodium hydroxide (117 g) in 585 cm³ of water, with the temperature maintained between 35 and 40°C, and the mixture was stirred at 40°C for 22 h before acidifying with concentrated hydrochloric acid (700 cm³) and filtering off the pale cream precipitate. After washing with water, drying, and recrystallizing from propan-2-ol/2-ethoxyethanol, 34.5 g of white, crystalline, 4-(4'-phenoxyphenyl)benzoic acid was obtained: m.p. 241°C; i.r. $\nu(\text{C}=\text{O})$ 1680 cm⁻¹; found, C, 78.4, H, 4.8%; calculated, C, 78.6, H, 4.8%.

Reactivity studies

Trifluoromethanesulphonic acid solutions (10 cm³ each) containing the carboxylic acid (10 mmol for monoacids; 5 mmol for diacids) and the aromatic ether (10 mmol) were prepared separately and then mixed rapidly at room temperature. A small aliquot was quickly transferred to an n.m.r. tube and the methyl resonance region appropriate to either *p*-toluic acid or anisole and the corresponding ketone product was scanned, initially at 15 s intervals, and then at intervals depending on the observed reaction rate.

Polymerization studies

Polycondensations were carried out by dissolving the monomer(s) (\approx 5 g) and end-capping agent (1,4-diphenoxybenzene or 4,4'-diphenoxybiphenyl) in CF₃SO₃H (50 cm³), and allowing the deep orange-red solution to stand at room temperature for 24 h. The now-viscous solution was run dropwise into water (500 cm³) with vigorous stirring, and the resulting beads of polymer were stirred in boiling water for 1 h, filtered off, washed with acetone, and dried. The beads were then powdered

using an ultracentrifuge mill (0.5 mm screen), and the milled polymer was treated successively with refluxing dimethylacetamide, water, and acetone, and was finally dried under vacuum at 120°C to give a white or pale cream powder. Inherent viscosities were measured at 30°C on 0.1% solutions of polymer in 95% sulphuric acid.

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