Polyterephthaloylenes: the Electrochemical Polymerisation of Terephthaloyl Halides

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By analogy with the cathodic cleavage, elimination and polymerisation of 1,4-bis(halomethyl)benzenes, benzene-1,4-diacylchlorides are shown similarly to undergo cathodic polymerisation to the linear polyterephthaloylenes.

The cathodic cleavage of 1,4- and 1,2-bis(halomethyl)benzenes[1] is a route to quinodimethane intermediates 1, which in many cases polymerise. The 1,4-derivatives may be electrochemically converted, in good yields, into poly-p-xylylenes (2, Parylene); similar methods, involving other than halide leaving groups, have received commercial attention.[2] The probable mechanistic route is given in Scheme 1 and is supported by experiments,[3] which trap the proposed quinodimethanes and in which paracyclophanes are formed. Terephthaloyl halides should similarly cleave reductively to give intermediates which may be represented as 3 or 4 and which should polymerise to linear polymers of the type 5.

The recent work of Peters et al.[4] and of Barba et al.[5] has shown that acid halides do indeed cleave cathodically; aliphatic acyl chlorides reduce to the corresponding aldehydes whereas the major products from aromatic acyl chlorides are esters of stilbene diol. Their results are summarised in Scheme 2, which also indicates likely mechanisms. The reversible reduction potentials for acyl radicals have recently been estimated by Lund et al.[6] and the aromatic cases are found to be reduced more easily than the aliphatic ones, i.e. further electron transfer may be fast for the aromatic acyl radicals. In
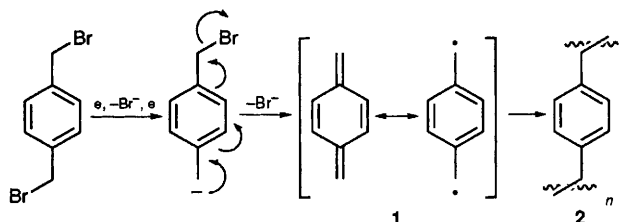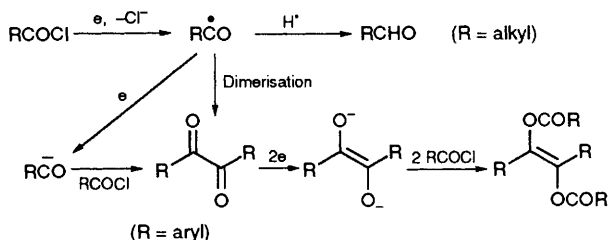
these cases, therefore, dimerisation via reaction between acyl anion and acid chloride is the more likely pathway.

Reduction of the diacyl chlorides, e.g. terephthaloyl chloride, was accomplished by Nallaiah[7] using sodium naphthalene radical anion in tetrahydrofuran solution. In that case a yellow–brown polymer was obtained in ca. 70% yield. The IR spectrum and the ^{1}H NMR spectrum indicated hydroxy and carbonyl groups and a ratio of aromatic proton signals to others which together were best rationalised in terms of a random copolymer of the type 6. Oxidation of these polymers gave 'polybenzils' of the type 5.

Polymers such as 5 and 6 are themselves easily reducible and in contrast to reduction by radical anions electrochemical reduction of terephthaloyl chloride is likely to proceed further. The earlier experiments (Scheme 2) show clearly that coupling is followed by further reduction and trapping of the enolic dianions by the acyl chloride starting materials. By analogy with our work[3] on the cathodic formation of polymers via quinodimethanes we have explored the electrochemical behaviour of terephthaloyl chloride, and of related compounds, and are prompted to report the results of experiments which produce novel polymers almost certainly through electrogeneration of the intermediates 3 or 4, a diketene. The polymerisation of ketenes is well known[8] but the reactions envisaged here may equally be expected to proceed via acyl diradicals.

Cyclic voltammetry of terephthaloyl chloride, attempted using a Hg bead cathode and MeCN–Et$_4$NBr (0.1 mol dm^{-3}) electrolyte, gave unsatisfactory results owing to fouling of the Hg cathode. An indication of the appropriate reduction potential was obtained by plotting a steady state voltammetric curve at a stirred Hg pool cathode. An approximate $E_{\frac{1}{2}}$ value of -1.8 V (Ag/Ag$^+$) was thus estimated. Controlled potential coulometry by exhaustive electrolysis at -1.8 V (Ag/Ag$^+$), in the same electrolyte, suggested 4 F mol^{-1} reduction. This is consistent with the contention that there is further reduction following radical coupling—the value determined[3] for 1,4-

Scheme 1

Scheme 2
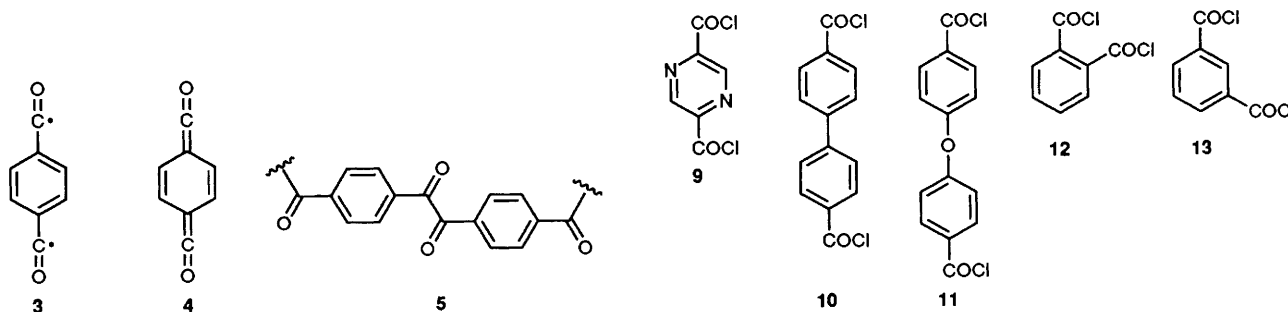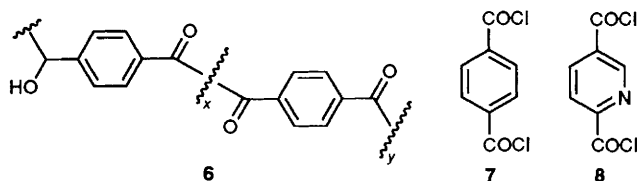
bis(bromomethyl)benzenes in the cathodic formation of polymers of the type 2 is 2 F mol^{-1}

Preparative scale controlled potential electrolyses of the 1,4-diacyl chlorides 7–13 were performed on 1–2 g scales at −1.0 to −1.8 V (Ag/Ag$^+$), in a divided cell and at a stirred mercury pool cathode using about 100 cm^3 of MeCN–Et$_4$NBr (0.1 mol dm^{-3}) as electrolyte. Good yields of polymers were obtained in most cases and they were insoluble in all common organic solvents. The exception was for compound 13 in which the acyl groups are *meta* to each other. The results of preparative-scale electrolyses are summarised in Table 1 together with relevant physical properties. The melting/softening points could be measured reproducibly but, at lower temperatures, changes in the DSC behaviour varied with sample history.

An attempt was made to elucidate as fully as possible the key structural features of the polymer obtained in highest yield, that from terephthaloyl chloride 7. The pale-yellow insoluble material gave in the solid state ^{13}C NMR spectrum signals at δ 200, 173, 167, 139, 132 and 130. Assignments were helped by the use of both CPMAS and NQS (non-quaternary suppression) experiments. The FTIR spectrum (KBr disc) contained absorptions at ν = 3436(str), 2925(m), 1793(m), 1735(str), 1718(str), 1701(str), 1687(str), 1654(m), 1637(m), 1607(m), 1507(2), 1407(m), 1234(str), 1099(str), 1099(m), 1005(m) and 729(m) cm^{-1}. The carbonyl absorption signals in the region 1793–1687 cm^{-1} are especially significant and may be assigned to the functionality: –C(O)C(O)– (1793), ArCO$_2$R (1735 or 1718), ArCO$_2$H (1701 or 1687 and the 2925 band), and ArCOR (1687). Signals at 2544 and 2660 cm^{-1} may be ascribed to hydrogen bonded and dimeric carboxylic acid functions. The band at 1234 cm^{-1} is characteristic of the C–O–C link of an ester group. The very strong absorbtion at 3436 cm^{-1} is indicative not only of OH groups but also of a significant amount of included water, even in the dried sample.

Further evidence of structure comes from direct pyrolysis/mass spectrometric measurements. A plot of ion current *vs.* probe temperature gives maxima corresponding to significant thermal fragmentations of the polymer. Mass spectra were measured at the appropriate temperatures. At 350 °C fragmentation gave rise to prominent species at m/z = 135.0447 (base peak) and at 271.0914. We rationalise these in terms of, respectively, formula 14 [C$_8$H$_7$O$_2$$^+$ requires m/z 135.0446] and 15 [C$_{16}$H$_{15}$O$_4$$^+$ requries m/z 271.0970]. At a lower temperature, 164 °C, the main pyrolysis fragments are at m/z = 166.0281 [terephthalic acid, C$_8$H$_5$O$_4$, M$^+$· requires

166.0269] and at 121.0240 [M$^+$·–CO$_2$H, C$_7$H$_5$O$_2$, requires 121.0293].

Thermogravimetric analysis (TGA) of the material has been carried out and two successive losses of mass are observed in the ranges 150–230 and 230–280 °C, respectively; each corresponds to ca. 25% loss of the total mass. The insolubility of the polymer precludes measurement of its molecular mass.

The analytical data taken together is compelling evidence for a polymer structure including as a key feature a unit such as 16. The proposed assignment of the ^{13}C NMR data is indicated on the structure 16 and plausible fragmentations consistent with the results of the pyrolysis–MS experiments are also indicated by dashed lines. Given that 16 has a molecular mass of 564 and that –OC(Ph)CO$_2$H is 149, loss of that fragment in the TGA experiment would account for a 149/564 (26%) mass loss—as observed.
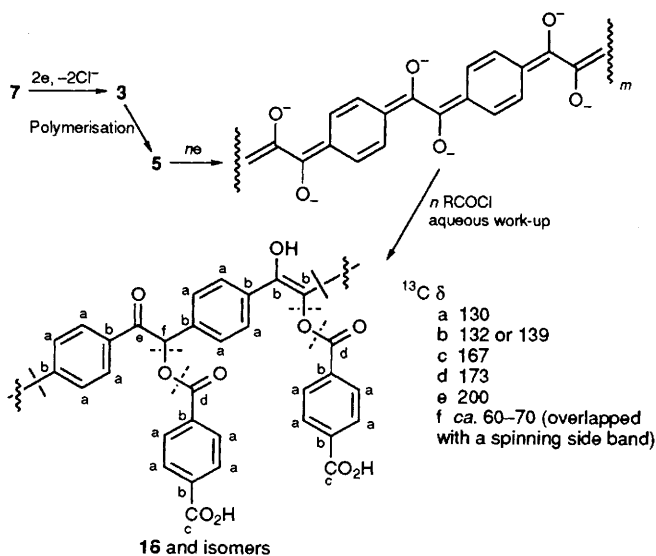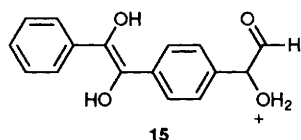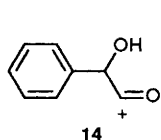
Although the above is powerful evidence for structure 16 being a prominent part of the polymer the results of repeated elemental analyses do not fit in. For 16, C$_{32}$H$_{20}$O$_{10}$, the results were: required(found); C(%) 68.08(51.39), H(%) 3.62(2.74). We have so far been unable to reconcile this discrepancy beyond suggesting that a significant amount of water remains strongly bound within the material—the IR spectrum gives some support for this hypothesis. One of the 25% mass losses at >200 °C may also be rationalised in terms of dehydration. From this a molecular mass of (564 + 18n) gives the observed increment of 25% at n = 10.4; thus an empirical formula of C$_{32}$H$_{40.8}$O$_{20.4}$ is indicated and the calculated carbon figure (51.1%) at least is close to that found.

A polymer structure including 16 is entirely consistent with the results of reduction[7] by naphthalene radical-anion and the predicted further reduction likely in the electrochemical route. An overall mechanism is indicated in Scheme 3; although the analogy with quinonedimethane production (Scheme 1) would suggest a diketene intermediate there is no evidence for this and it is simpler to envisage coupling of diacyl radicals of the type 3. The fact that the 1,3-diacyl chloride 13 does not polymerise is consistent with the formation of diradicals such as 3, or even diketenes such as 4 requiring a stepwise pathway similar to that shown for quinodimethanes (Scheme 1). This is precluded for 13. At first sight a similar distinction should hold for 10 *vis à vis* 11; both give polymers on reduction. In this case however the oxygen-atom in 11 may not entirely insulate the two benzene rings from conjugative interaction because the oxygen lone pairs can participate in a π-molecular orbital of a diacyl diradical.

Table 1 Cathodic polymerisation of diacylchlorides

Starting material	$-E_{red}$^{a}/V	Q/F mol^{-1}	Polymer yield (%)	M.p./softening pt./°C
7	1.8	4.5	95	ca. 310
8	1.5	3.8	82	142^b
9	1.5	3.2	64	140^b
10	1.5	2.5	57	ca. 300^c
11	1.5	2.8	79	ca. 270^c
12	1.0	2.0	26	ca. 240^c
13	1.5	—	0^d	—

^{a} Voltage *vs.* Ag/Ag$^+$; Hg pool cathode; MeCN–Et$_4$NBr (0.1 mol dm^{-3}). ^{b} M.p. by differential scanning calorimetry. ^{c} With decomposition. ^{d} No polymer formed.

14

15

^{13}C δ
a 130
b 132 or 139
c 167
d 173
e 200
f ca. 60–70 (overlapped with a spinning side band)

16 and isomers

Scheme 3

It is not possible at this stage to be sure about the exact level of reduction of the complete polymer or to what extent cross-linking has occurred. The further chemistry and properties of these novel materials are under active examination.

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