Polyesters with controlled thermal decomposition

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Two main-chain rigid-rod-like polyesters containing pendent t-butyl ester groups were synthesized. Simultaneous thermogravimetric analysis and Fourier-transform infra-red spectroscopy were applied to monitor the formation of isobutylene as well as other gaseous products that evolved at elevated temperatures. The polymers were also characterized by microscopy, differential scanning calorimetry and infra-red spectroscopy before and after thermal treatment.

(Keywords: thermal degradation; polyester; controlled release)

INTRODUCTION

Simultaneous thermogravimetric analysis and Fourier-transform infra-red spectroscopy (t.g.a./*FT*i.r.) for monitoring chemical reactions is a recent advance that offers detailed, quantitative measurements of the thermal behaviour of synthetic polymers[1–7]. Most studies thus far have focused on identifying degradation products[1–8] or compositional analysis[2,6,7]. Other polymer-oriented applications such as monitoring curing reactions have also been reported[2]. For example, t.g.a./*FT*i.r. has been employed to follow the formation of poly(phenylene-vinylene) from its soluble precursor[8].

It is well known that small structural modifications of liquid-crystalline polymers (LCPs) change the physical properties of these materials. For example, the incorporation of flexible chains as pendent groups on liquid-crystalline polyesters[9] and polythiophene[10] significantly improves solubility. In this paper, we report on the properties of two rod-like polyesters with repeat units comprising an aromatic ring substituted with pendent t-butyl esters. Using the t.g.a./*FT*i.r. to examine such a polyester affords one the opportunity to follow the thermal conversion of the t-butyl esters to carboxylic acid groups concurrent with the release of isobutylene. This process may also be viewed as a model for the delivery of small molecules from functionalized polymers. An application that may be envisioned would utilize these polymers coated as a film: a switch may be triggered thermally through employing a gas detector connected to a transducer. Moreover, the resulting pendent carboxylic acid groups after deprotection should subsequently modify the polymer's properties. We have also applied d.s.c. and i.r. to probe these aspects of the system.

EXPERIMENTAL

Materials

All reagents were supplied by Aldrich Chemical Co., unless stated otherwise. t-Butylhydroquinone was recrystallized using chloroform with activated charcoal and vacuum dried prior to use. 2-Bromoterephthalic acid was refluxed with freshly distilled thionyl chloride and fractionally distilled to prepare 2-bromoterephthaloyl chloride. Tetrachloroethane was purified by standard techniques[11].

Synthesis of monomers

2,5-Bisbenzyloxybenzoic acid (**1**). This was prepared from gentisic acid by alkylating with benzyl chloride according to the procedure of Hill[12]. The procedure of Field and Engelhardt was used to prepare the 2-hydroxyterephthalic acid[13].

2,5-Bisbenzyloxybenzoyl chloride (**2**). This was prepared by reacting 2,5-bisbenzyloxybenzoic acid (**1**) with an excess of oxalyl chloride in methylene chloride. The solution was stirred in an inert atmosphere while venting the gaseous by-products. When the reaction was complete, the volatiles were removed by vacuum distillation, yielding a white crystalline solid. The solid was recrystallized from hexanes and was recovered in 88% yield after filtration as water-white needle-like crystals with m.p. 89.5–90.5°C. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 5.1 (s, 2H, O–$C\underline{H}_2$–Ph); 5.2 (s, 2H, O–$C\underline{H}_2$–Ph); 6.9 (d, 1H, Ar-H *p* to COCl); 7.18 (m, 1H, Ar–$\underline{H}$ *m* to COCl); 7.3–7.5 (m, 10H, benzyl Ar–H); 7.7 (d, 1H *o*-COCl). I.r. (KBr): u 3060, 3030 (w, Ar–H); 1780 (s, acid chloride C=O); 1620 cm^{-1} (w, aromatic C=C). Fast atom bombardment mass spectroscopy gave $m/e = 352$ (M^+) with a fragment at 317 due to the loss of Cl.

t-Butyl-2,5-bisbenzyloxybenzoate (**3**). This was prepared by esterification of acid chloride **2** with t-butanol. A dry, argon-flushed reaction vessel equipped with a magnetic stirrer and an addition funnel was charged with 10.0 g of t-butanol, 50 ml of methylene chloride, 10 g of pyridine and 1.0 g of 4-dimethylaminopyridine. The reaction vessel was then cooled to ~0°C. The acid chloride **2** (0.6 mol)

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was dissolved in 100 ml of methylene chloride and then added dropwise, via the addition funnel, to the stirred t-butanol solution. After addition was completed, the reaction vessel was allowed to warm to room temperature. Reaction progress was monitored by t.l.c. (acetone/hexanes 2/3) and was determined to be complete when **2** had been completely consumed. The organic layer was then extracted with water, HCl (dil.), $NaHCO_3$ (sat.) and water, 3 × 30 ml each, and dried with magnesium sulfate. The drying agent was removed, followed by evaporation to remove the solvent. This process yielded the t-butyl 2,5-bisbenzyloxybenzoate as a single-component homogeneous material by t.l.c. (acetone/hexanes 2/3) in >90% yield, m.p. 83–85°C. ^1H n.m.r. ($CDCl_3$) δ (ppm): 1.5 (s, 9H, $C(C\underline{H}_3)_3$); 5.0 (s, 2H, $O{-}C\underline{H}_2{-}Ph$); 5.1 (s, 2H, $O{-}C\underline{H}_2{-}Ph$); 6.8 (d, 1H, Ar-H *p* to COCl); 6.95 (m, 1H, Ar–H *m* to COCl); 7.3–7.5 (m, 11H, Ar–H). I.r. (KBr): u 3040 (w, Ar–H); 2990 (m, aliphatic CH), 1740 (vs, ester C═O); 1660 cm^{-1} (m, aromatic C═C). Fast atom bombardment mass spectroscopy gave $m/e = 390$.

t-Butyl 2,5-dihydroxybenzoate (**4**). This was prepared by deblocking the bisbenzyl ether protecting groups in **3** using ammonium formate with Pd/C catalyst in a 1/1 tetrahydrofuran (THF)/methanol solution at room temperature[14]. When the reaction was complete, as indicated by t.l.c. (acetone/hexanes 2/3), the solution was filtered through a pad of celite to remove the catalyst. The volatiles were removed and the remaining residue was dissolved in diethyl ether. The organic layer was extracted with dilute HCl followed by water. The organic layer was dried using magnesium sulfate, filtered to remove the drying agent and evaporated to remove the volatiles. The resulting white solid was obtained in >95% yield and had a m.p. of 83.5–84.5°C. The following spectroscopic data were recorded for the product. ^1H n.m.r. ($CDCl_3$) δ (ppm): 1.58 (s, 9H, $C(C\underline{H}_3)_3$); 5.8 (s(b), 2H, Ar–O$\underline{H}$); 6.85 (d, 1H, Ar–H *m* to –COO-t-Bu); 7.0 (d, d, 1H, Ar–H *p* to –COO-t-Bu); 7.3 (d, 1H, Ar–H *o* to COO-t-Bu). I.r. (KBr): u 3400–3200 (s, Ar–O–H); 3040, 3020 (m, Ar–H); 2990, 2840 (s, aliphatic CH); 1685 (s, ester C═O); 1620 cm^{-1} (s, Ar C═C). T.l.c. (acetone/hexanes 2/3, R_f 0.46) proved that the product consisted of a single homogeneous component and therefore was used without further purification.

2-Hexyloxyterephthaloyl chloride (**6**). This was prepared from dimethyl-2-hydroxyterephthalate (**5**) by first alkylating the phenol with 1-bromohexane using the following procedure. A magnetically stirred two-necked reaction vessel equipped with a reflux condenser and an addition funnel was charged with dry acetonitrile, 3 mol of pulverized K_2CO_3 (anh.) and 2 mol of 1-bromohexane. The addition funnel was charged with 1 mol of dimethyl-2-hydroxyterephthalate in acetonitrile. The reaction vessel was heated to reflux and the terephthalate solution was added dropwise to the reaction pot. After complete consumption of the hydroxyterephthalate, as indicated by t.l.c. (hexanes/acetone 9/1), the reaction solution was cooled to room temperature and filtered to remove potassium salts. The filtrate was washed with acetone, and the volatiles were removed from the mother liquor. The resulting residue was then hydrolysed to the corresponding diacid by treatment with alcoholic KOH. After acidification with 6 N HCl the solid was collected by vacuum filtration. The diacid was recrystallized from acetone, yielding a pale white solid, m.p. 216–220°C, and was recovered in high yield, >85%, from the starting hydroxyterephthalate. Conversion to the diacid chloride was accomplished by refluxing a mixture of the 2-hexyloxyterephthalic acid with thionyl chloride in toluene with a trace of dimethyl formamide (DMF). After the conversion was complete, toluene and excess thionyl chloride were removed by vacuum distillation. The resulting oil was fractionally distilled (138–143°C, 1 mmHg) and 2-hexyloxyterephthaloyl chloride was obtained as a clear colourless viscous oil in 78% yield. ^1H n.m.r. ($CDCl_3$) δ (ppm): 1.0 (t, 3H, $(CH_2)_5\underline{C}H_3$); 1.4–1.9 (m, 8H, $({-}OCH_2{-}(\underline{C}H_2)_4{-}CH_3)$); 4.18 (t, 2H, $({-}O\underline{C}H_2{-}(CH_2)_4{-}CH_3)$); 7.63 (d, 1H $J = 1$ Hz, Ar–H *o* to –OR); 7.75 (d of d, 1H $J = 6$ Hz, 1 Hz, Ar–H *m* to –OR); 8.05 (d, 1H $J = 6$ Hz, Ar–H *p* to –OR). I.r. (neat): u 3140, 3100, 3040 (w, Ar–H); 2980, 2960, 2840 (vs, aliphatic CH); 1790, 1770 (vs, formoyl chloride and Fermi resonance band); 1610 cm^{-1} (s, aromatic C═C). Fast atom bombardment mass spectroscopy gave $m/e = 302$ with fragments at 267 and 232 due to the loss of two Cl atoms.

Polymer synthesis

Both polymers were prepared using standard conditions[15]. In the preparation of polymer **I**, t-butyl-2,5 dihydroxybenzoate (**4**), 3.1662 g (15.06 mmol), was condensed with 2-hexyloxyterephthaloyl chloride (**6**), 5.0635 g (15.06 mmol), in 80 ml of freshly distilled tetrachloroethane (TCE) with 5.0 ml of pyridine. The polymerization was run at room temperature for 24 h. After the polymerization was complete, the polymer solution was precipitated into methanol, redissolved in chloroform and reprecipitated into methanol. The solid polymer was collected by vacuum filtration and vacuum dried to yield a white solid in 80% yield. ^1H n.m.r. ($CDCl_3$) δ (ppm): 1.0 (m(b), 3H, $(CH_2)_5C\underline{H}_3$); 1.38–1.9 (m(b), 17H, $({-}OCH_2{-}(C\underline{H}_2)_4{-}CH_3)$ and 9H, $C(C\underline{H}_3)_3$); 4.2 (m(b), 2H, $({-}OC\underline{H}_2{-}(CH_2)_4{-}CH_3{-})$); 7.2–8.3 (m(b), 6H, Ar–H). I.r. (KBr): u 3040 (w, Ar–H); 2960, 2940, 2860 (s, aliphatic CH); 1745, 1720 (vs, t-butyl ester and backbone Ar ester C═O); 1610 cm^{-1} (m, Ar C═C). Polymer **I** gave $\eta_{inh} = 0.52\ dl\ g^{-1}$ using chloroform as a solvent at a concentration of 0.5 g dl^{-1} at 30°C.

In the preparation of polymer **II** 2-t-butylhydroquinone, 2.7568 g (16.5 mmol), and t-butyl-2,5-dihydroxybenzoate (**4**), 3.3036 g (15.7 mmol), were condensed with 2-bromoterephthaloyl chloride, 9.097 g (32.2 mmol), in 120 ml of freshly distilled TCE with 10 ml of pyridine. The reaction was run at room temperature for 3.0 h. The reaction vessel was heated to 70°C and stirred for an additional 2 h. The viscous polymer solution was then cooled to room temperature and diluted with 150 ml of chloroform. When the material completely dissolved it was precipitated into methanol, washed with methanol, filtered and dried. The polymer was redissolved in chloroform, reprecipitated into methanol, collected by filtration and vacuum dried. The polymer was recovered in >92% yield. ^1H n.m.r. ($CDCl_3$) δ (ppm): 1.38–1.7 (m, 18H, $-COOC(C\underline{H}_3)_3$ and $Ar{-}C(\underline{C}H_3)_3$); 7.2–8.6 (m, 13H, Ar–H). I.r. (KBr): u 3040 (w, Ar–H); 2960, 2940, 2860 (m, aliphatic CH); 1745, 1720 (vs, t-butyl ester and Ar ester C═O); 1610 (w, Ar C═C). Polymer **II** gave $\eta_{inh} = 1.59\ dl\ g^{-1}$ using chloroform as a solvent at a concentration of 0.5 g dl^{-1} at 30°C.

Microscopy

A Zeiss Universal Polarizing Microscope equipped with cross polarizers and a Leitz Wetzlar model 350 hot stage were used for microscopic characterization of polymer samples sandwiched between plain glass slides.

Thermogravimetric analysis/Fourier-transform infra-red spectroscopy

Experiments were performed using a Biorad FTS-45 t.g.a./*FT*i.r. system consisting of a Digilab FTS-45 Fourier Transform Infrared Spectrophotometer with a liquid-nitrogen-cooled, broad-band, mercury cadmium telluride (MCT) detector (at 4 cm^{-1} resolution) coupled to a Polymer Labs PL Omnitherm TGA 1000. Specific details of this integrated system have been discussed elsewhere[1,2]. T.g.a. sample sizes for these studies ranged from 5 to 10 mg. With the system under a nitrogen purge, a heating rate of 10°C min^{-1} was used to scan the samples from 25°C to as high as 825°C. The i.r. cell and the heated line that transfers evolved gases from the t.g.a. to the *FT*i.r. were both maintained at 200°C. Spectral searches were done with Search 32 (Version 5.00) system software containing Sadtler and EPA libraries.

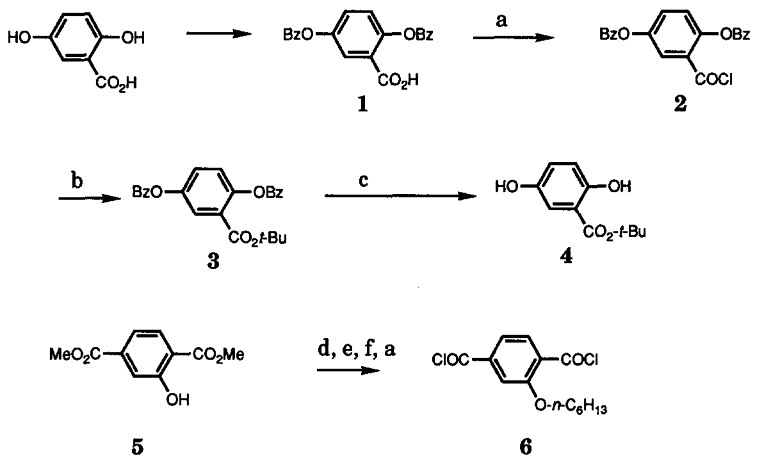
Differential scanning calorimetry and infra-red spectroscopy

A Perkin–Elmer DSC-7 interfaced with PE 7500 computer was used for differential scanning calorimetry. All samples were run at 20°C min^{-1}. Infra-red spectra (KBr pellet) on the samples removed from the d.s.c. pans after each of the scans were recorded on a Nicolet 20 DXC *FT*i.r. spectrophotometer.

RESULTS AND DISCUSSION

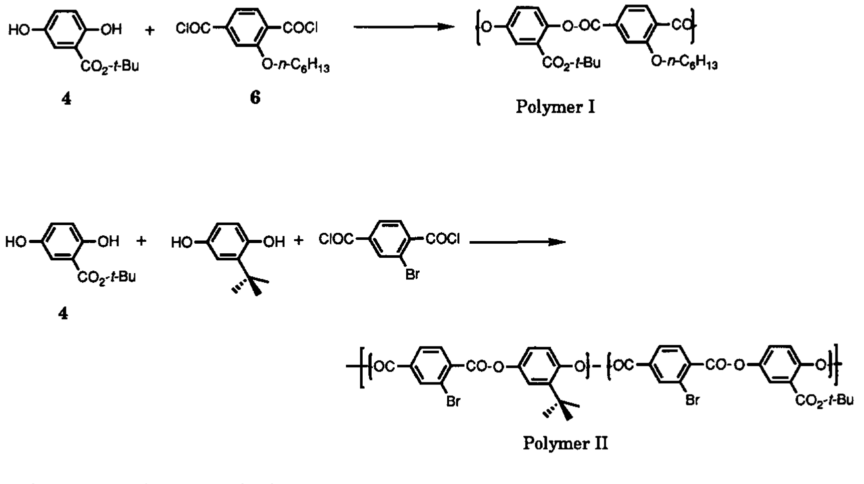
Synthesis and general characterization

Following the procedure outlined in *Scheme 1* using commercially available starting materials, the substituted monomers were prepared and isolated in high yield. The rod-like polyesters were subsequently synthesized through a condensation polymerization using tetrachloroethane as the solvent, and pyridine as the catalyst and acid acceptor[13]; *Scheme 2* gives the reaction sequence for polymers **I** and **II**. In both cases, the resulting viscous polymer solution was precipitated into a large volume of methanol. After redissolving the polymer in chloroform, it was reprecipitated, filtered and vacuum



a ClCOCOCl CH_2Cl_2 DMF(2 drops); b t-Butanol, 10% 4-DMAP in Pyridine;
c 5% Pd/C , $NH_4^+HCO_2^-$, THF/MeOH; d 1-Br -n-C_6H_{13}, K_2CO_3; e KOH/ EtOH/H_2O;
f HCl(dil)

Scheme 1 Monomer synthesis



Scheme 2 Polymer synthesis

dried. Polymer **I** was obtained as a white solid in 80% yield, while polymer **II** was recovered in >90% yield as milky white solid. N.m.r. and i.r. spectroscopy on each sample support the proposed polymer structures.

Films cast from chloroform solution of polymer **I** were brittle and could not be creased without cracking. For polymer **II**, a tough flexible film was obtained, which had a somewhat greater resistance to cracking upon creasing. The latter's improved mechanical properties are probably a consequence of the significant difference in molecular weight of the two polymers: the inherent viscosities of polymers **I** and **II** were 0.52 and 1.59 dl g^{-1}, respectively. Both polymers formed white, translucent films, and both were soluble in a variety of chlorinated solvents such as chloroform, methylene chloride and tetrachloroethane. Polymer **I** also dissolves in THF.

The materials were also examined using polarized-light optical microscopy. Polymer **I** softens at 135°C and converts to a birefringent fluid at 175°C, exhibiting a grainy texture that appears to be a nematic liquid-crystal phase. Further heating results in decomposition at 190°C as evidenced by the formation of bubbles in the molten sample. Above 190°C, the texture of the birefringent melt becomes less well defined until the sample becomes uniformly isotropic at ~240°C. Upon cooling from the isotropic state, the sample forms a weakly birefringent glassy solid at ~200°C, the texture of which is not the same as that obtained during the first heating cycle.

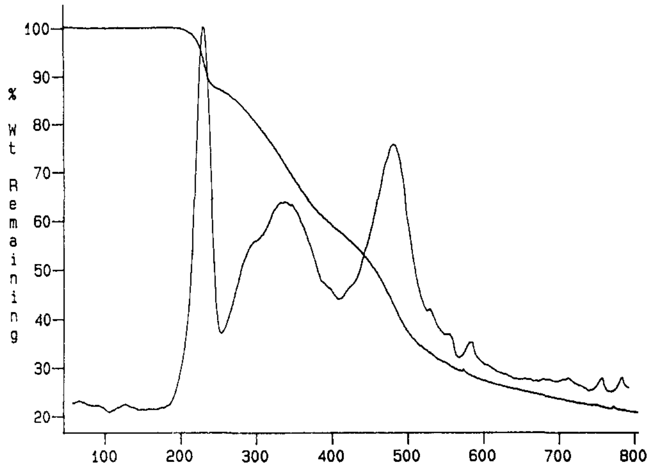


Figure 1 Thermogravimetric analysis (heating rate = 10°C min^{-1}) displaying weight-loss and first-derivative curves for polymer I

Polymer **II** gives a birefringent melt at ~207°C. Further heating of the sample results in decomposition at 214°C as indicated by the evolved gas. The gas evolution continues up to ~245°C where the sample appears to resolidify, forming a weakly birefringent glassy solid. Subsequent heating of this glassy solid up to ~325°C (the maximum temperature of the hot stage) does not yield a melting transition.

Thus microscopy is able to ascertain that gases are evolved and that the fluidity of the material has been influenced by heating. However, both the d.s.c. and t.g.a./*FT*i.r. experiments described below supply much greater detail than microscopy as to the nature of the changes in the materials that are involved.

Thermogravimetric analysis/Fourier-transform infra-red spectroscopy

Polymer I. The t.g.a. scan indicates (*Figure 1*) that the polymer undergoes three major weight-loss processes between room temperature and 800°C in a nitrogen atmosphere. The onset of weight loss occurs at 197°C. The three maxima of the derivative curves occur at 231, 337 and 481°C, indicative of a multi-step degradation.

The shape of the evolved gas profile (EGP) (not shown) corresponds to the t.g.a. derivative curve. Spectra were recorded at each of the peak maxima and at higher temperatures to determine the nature of the volatile degradation product(s). As indicated in *Figure 2d*, the first gaseous product to evolve from the degrading polymer ($T_{max} = 231°C$) appears to be an unsaturated hydrocarbon. The spectrum of this evolved gas excellently matches that of the library spectrum for isobutylene except for a minor component of carbon dioxide: the hit index parameter obtained for this search was 0.19, a relatively low value (0.00 is a theoretically perfect match), and no other library spectra were even close to such a superb fit. Moreover, the weight loss for this first transition is ca. 13%, which is the theoretical value expected for the cleavage of the isobutyl group from all of the repeat units. The spectrum from the second degradation region ($T_{max} = 337°C$) corresponds to carbon dioxide (*Figure 2c*). During the third degradation step ($T_{max} = 481°C$, *Figure 2b*), another unsaturated hydrocarbon evolves along with carbon dioxide. After

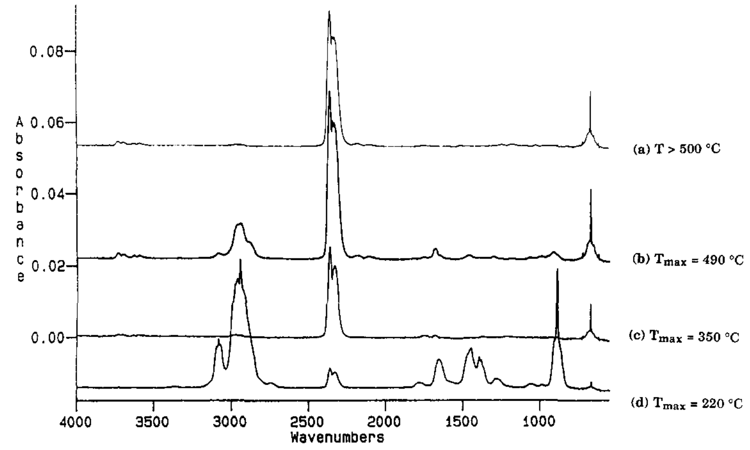


Figure 2 Infra-red spectra of the thermal degradation products from polymer I at various temperatures: (a) 680°C, (b) 495°C, (c) 310°C, (d) 246°C (heating rate = 10°C min^{-1}). Spectra are essentially identical to those observed at the T_{max} quoted in the text and displayed on the diagram

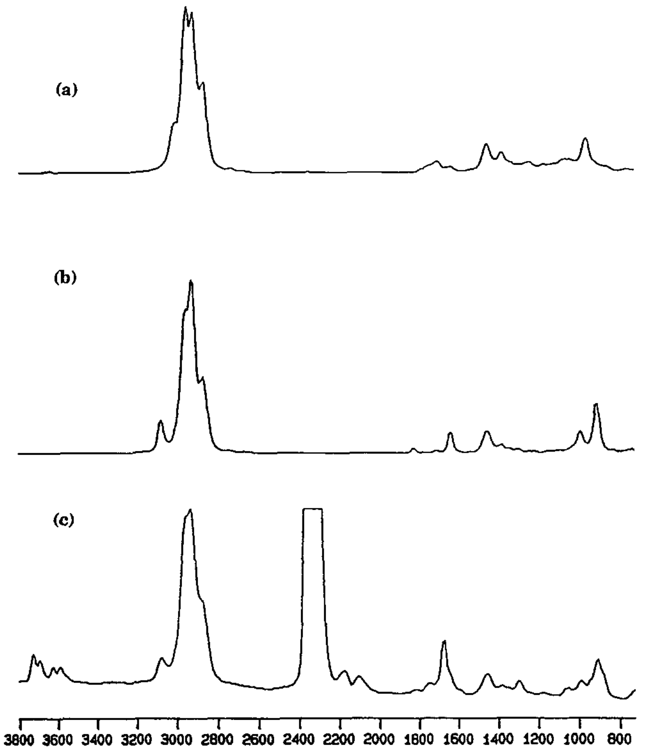


Figure 3 I.r. spectra of (a) 2-hexene, (b) 1-hexene and (c) the degradation product from polymer I at 495°C

subtracting the latter from the spectrum, the degradation product was identified as probably 1- or possibly 2-hexene or a mixture of the two isomers (*Figure 3*). At higher temperatures ($T \geqslant 500$°C), carbon dioxide is still the predominant product along with minor hydrocarbon components (*Figure 2a*). A search was unable to best-fit a single product.

T.g.a./*FT*i.r. results suggest the following degradation mechanism in a nitrogen atmosphere. Initially, the first bond to break, as expected, is the t-butyl group of the ester, as indicated by the appearance of isobutylene. This degradation is cleanly isolated from all other thermal reactions occurring at higher temperature. This indicates that a necessary requirement for controlled-release application has been fulfilled. It appears that the subsequent generation of carbon dioxide is a result of elimination of the resulting acid side group, but it may also include the beginning of backbone degradation of the polyester, which leads to a more continuous weight loss *versus* temperature profile. The third peak is associated with the much sharper loss of the hexyl ether side chain from the aromatic ring. As expected, this bond has lower stability than those in the aromatic rings yet higher than that of the ester linkages in the backbone. At the end of the run (825°C), ca. 21% weight retention, a carbonaceous char remains. The polymer comprises 34% aromatic rings by weight, and at higher temperature, as the polymer chars, some of these are also volatilized as evidenced by the myriad of minor high-temperature products. Since the experiment was done under nitrogen, total combustion does not occur.

Polymer II. The second polymer also appears to have three derivative weight-loss peaks, the same basic shape for the t.g.a. curve as that of polymer **I**. The spectrum recorded from the EGP at the first decomposition reveals that the volatile product is almost pure isobutylene with no carbon dioxide. This transition temperature (228°C) is very close to that of polymer **I**; the weight loss is ~10% of the total weight, which is close to the theoretical value (7%) for complete cleavage of the ester protecting group to an acid.

The second transition is broad (ca. 285°C), and the apparent cumulative weight loss is close to the theoretical value (13%) for the further and exclusive elimination of the pendent carboxylic acid group. The *FT*i.r. spectra recorded in this region contain only carbon dioxide. Centered at 530°C, slightly higher than for the other polymer, is the third and major weight loss, which *FT*i.r. shows to be overwhelmingly carbon dioxide, presumably originating from the backbone ester groups. Other very minor components also exist including an ester/acid mixture (absorbances at 1767, 1675 cm^{-1}). Indeed, the final weight (30.5%) is lower than what one would expect if only the aromatic rings remained. Evolution of isobutylene due to the degradation of the attached t-butyl group directly on the phenyl ring could not be independently distinguished. This is an expected result in light of the greater stability of an alkyl–phenyl bond relative to the alkoxy–phenyl in polymer **I**.

Differential scanning calorimetry

Polymer I. The heats of the thermal degradation were measured by differential scanning calorimetry (*Figure 4a*); the samples were later analysed by i.r. to confirm structural modifications (*Figure 5*). In both polymers **I** and **II**, liquid-crystalline transitions are not clearly visible; therefore, we cannot state unequivocally that the

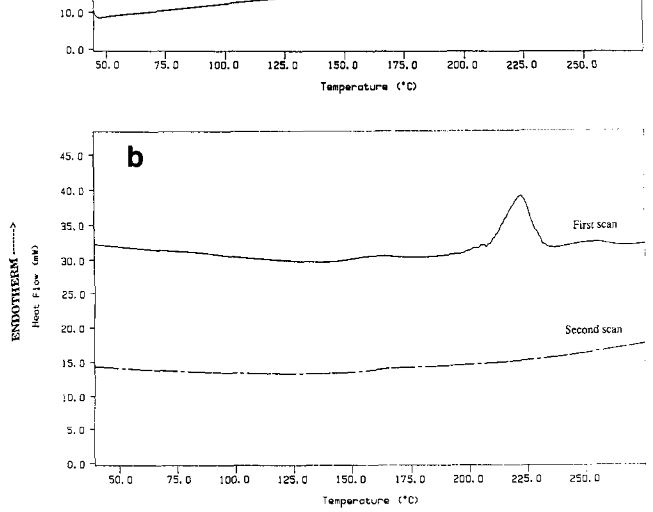


Figure 4 D.s.c. scans of (a) polymer **I** (three cycles, heating rate = 20°C min^{-1}), and (b) polymer **II** (two cycles, heating rate = 20°C min^{-1})

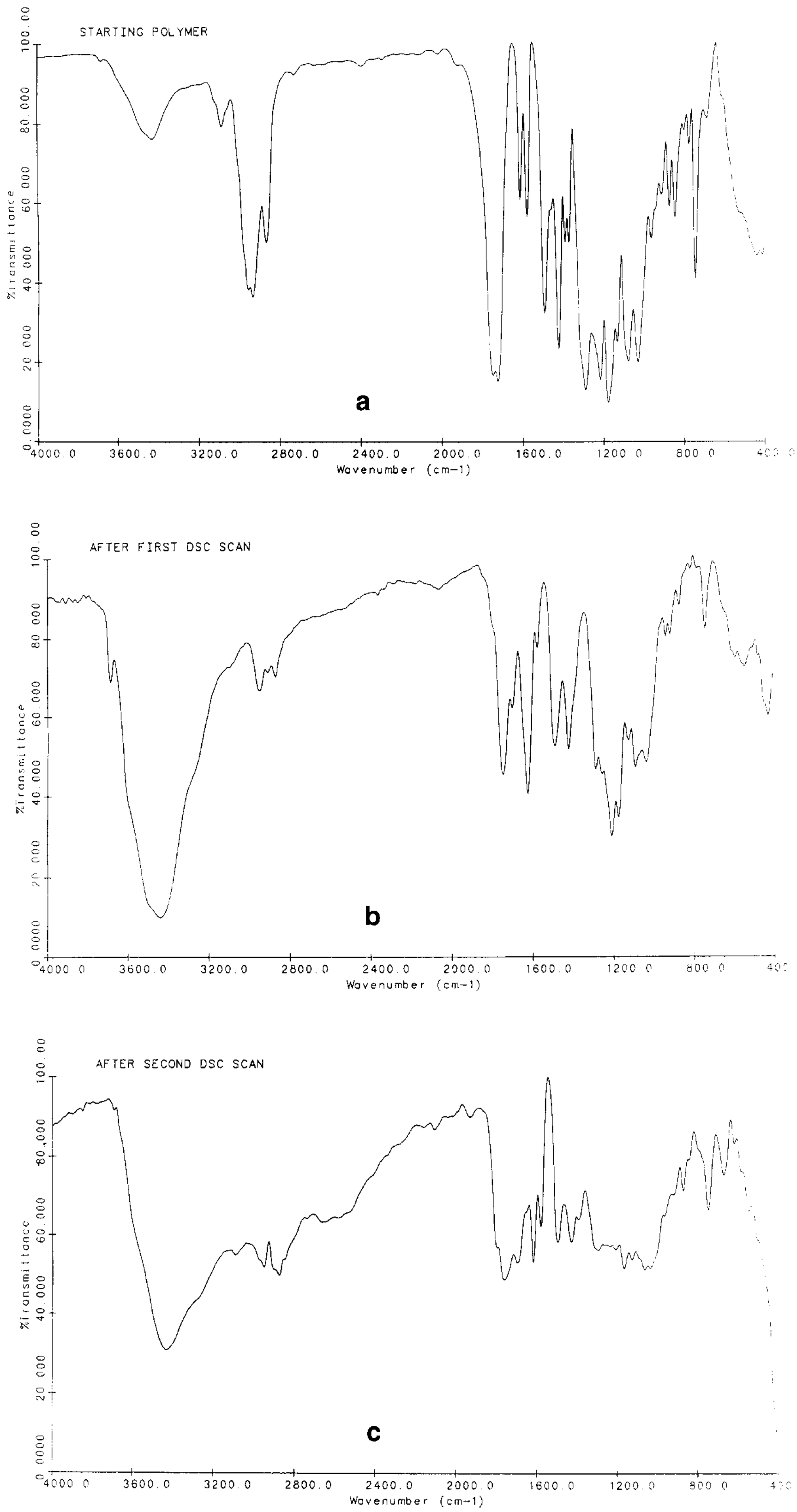


Figure 5 Infra-red spectra of polymer **I** (a) before thermal treatment (KBr pellet), (b) after heating to 275°C (KBr pellet), and (c) after heating to 275°C, cooling to room temperature followed by reheating to 275°C (KBr pellet)

polymers are liquid-crystalline. In addition, we are focusing herein on the chemical reactions, the subject of our study, which have a much higher heat of transition. The first heating scan exhibits an endothermic peak having an onset at 225°C, which corresponds to the removal of the t-butyl group of the t-butoxy ester. This temperature corresponds to that of the first degradation reaction detected by t.g.a./*FT*i.r.. The temperature during this d.s.c. scan was not allowed to exceed 275°C.

Comparing the i.r. spectrum of the sample after this first d.s.c. scan (*Figure 5b*) with that for the virgin polymer (*Figure 5a*) reveals distinct changes in the carbonyl stretching region. The virgin polymer (*Figure 5a*) possesses two ester carbonyl stretching peaks due to main-chain ester linkage (1743 cm^{-1}) and the pendent t-butyl ester linkage (1720 cm^{-1}). After the first heating (*Figure 5b*), the peak at 1720 cm^{-1} is no longer present, but a new peak appears at 1695 cm^{-1} assignable to the carbonyl stretching vibration of the carboxylic acid group. The appearance of a strong, broad absorption centred at ca. 3430 cm^{-1} characteristic of carboxylic acids supports this contention. Thus the combination of t.g.a./*FT*i.r., d.s.c. and standard i.r. spectroscopy of the d.s.c. samples allows the unambiguous determination of the first thermal degradation reaction.

A second sample was heated to 275°C, cooled to room temperature and reheated in order to examine the structure of the residual polymer prior to further degradation. Interestingly, the second thermal scan of this sample (*Figure 4a*) yields an exothermic peak having an onset at 190°C. This exothermic transition is probably a consequence of reactions of the liberated carboxylic acid groups and might correspond to a condensation reaction. The infra-red spectrum of the d.s.c. sample obtained after the second scan is shown in *Figure 5c*. A residual peak due to carbonyl stretch of carboxylic acid and a broad peak at 1752 cm^{-1} having a shoulder at 1790 cm^{-1} are evident. Such a spectrum strongly suggests the possibility of interchain anhydride formation, i.e. crosslinking. A final, third d.s.c. scan of the sample after it was again heated to 275°C is featureless. Thus, partial crosslinking seems to have made the polymeric network too immobile for any significant physical or chemical changes to occur below this temperature. These results are in accord with the fact that the microscopy revealed a different behaviour in fluidity after the first heating scan.

*Polymer **II**.* The first d.s.c. scan of polymer **II** (*Figure 4b*) showed an endothermic peak having an onset at about 210°C. This peak can be assigned to deblocking of the t-butyl ester by removal of the t-butoxy group. However, on rescanning the sample, no transition was detected unlike the case of polymer **I**. In polymer **II**, the concentration of t-butyl ester groups is much lower than that present in polymer **I**. Therefore, in the initial heating of polymer **II**, the concentration of carboxylic acid groups produced may be too low to effect significant anhydride formation upon subsequent heating that can be detected by d.s.c. The infra-red spectrum of polymer **II** before heating showed two carbonyl peaks at 1765 and 1740 cm^{-1}. The spectrum of the sample obtained after the first heating showed that the 1740 cm^{-1} peak had almost disappeared and had been replaced by a new peak at 1705 cm^{-1} assigned to the carbonyl stretching vibration of the carboxylic acid group. Thus, in analogy to polymer **I**, the infra-red data confirm deblocking of the t-butyl ester groups in polymer **II**.

CONCLUSIONS

We synthesized two main-chain, wholly aromatic, polyesters containing thermally labile pendent groups. By combining t.g.a./*FT*i.r., microscopy and d.s.c. analyses with infra-red spectroscopy of the d.s.c. samples, we were able to determine the relative thermal stability of these pendants. By careful control of the temperature to which the materials were subjected, we also demonstrated the feasibility of controlled release of pendent groups without destroying the backbone of the polymer.

REFERENCES

1 Compton, D. A. C., Johnson, D. J. and Mittleman, M. L. *Res. Dev.* 1989, **31** (2), 142

2 Compton, D. A. C., Johnson, D. J. and Mittleman, M. L. *Res. Dev.* 1989, **31** (4), 68

3 Mittleman, M. L., Thomsen, J. R. and Wilkie, C. A. *Polym. Mater. Sci. Eng.* 1990, **63**, 957

4 Maurin, M. B., Dittert, L. W. and Hussain, A. A. *Thermochim. Acta* 1991, **186**, 97

5 Mittleman, M. L. and Wilkie, C. A. *Polym. Mater. Sci. Eng.* 1991, **64**, 90

6 McEwen, D. J., Lee, W. R. and Swarin, S. J. *Thermochim. Acta* 1985, **86**, 251

7 Smith, D. E. *Thermochim. Acta* 1976, **14**, 370

8 Schlenoff, J. B. and Wang, L.-J. *Macromolecules* 1991, **24**, 6653

9 Lenz, R. W. *Polym. J.* 1985, **17**, 105

10 Patil, A. O., Ikenoue, Y., Wudl, F. and Heeger, A. J. *J. Am. Chem. Soc.* 1987, **109**, 1858

11 Perrin, D. D. and Armarego, W. L. F. 'Purification of Laboratory Chemicals', 3rd Edn., Pergamon Press, Oxford, 1988

12 Hill, R. A., Carter, R. H. and Staunton, J. *J. Chem. Soc., Perkin Trans.* 1981, **1**, 2570

13 Field, L. and Engelhardt, P. R. *J. Org. Chem.* 1970, **35**, 3647

14 Kelly, R. C., Gebhard, I. and Wienienski, N. *J. Org. Chem.* 1986, **51**, 4590

15 Jin, J.-I., Antoun, S., Ober, C. and Lenz, R. W. *Br. Polym. J.* 1980, **12**, 132