Thermotropic polyesters: controlled decomposition of poly(1,4-phenylene terephthalate-co-t-butyl-1,4-phenylene terephthalate)

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The elimination of t-butyl substituents from poly(1,4-phenylene terephthalate-*co*-t-butyl-1,4-phenylene terephthalate) and from a model compound, t-butylhydroquinone dibenzoate, was investigated. Thin-layer chromatography showed that the t-butyl groups could be thermally eliminated from the model compound at 320°C or at lower temperatures using Friedel–Crafts catalysts. The t-butyl substituents were not found to be removable from the polymer by thermal means, but the cleavage was achieved under the influence of trifluoromethanesulphonic acid, for which the best treatment temperature was below 25°C. Side reactions were also detected.

INTRODUCTION

Thermotropic liquid-crystalline polyesters are attractive for manufacture of high-strength high-modulus (HSHM) materials from their nematic states. However, rigid-rod homopolyesters such as poly(4-oxybenzoate)(POB) and poly(1,4-phenylene terephthalate) (PPT) are highly crystalline, insoluble in all solvents other than a few very strong acids that appear to cause dissociation, and unsuitable for melt processing because they do not melt below their decomposition temperatures. Although some techniques such as copolymerization and substitution may be used to modify the polymer structures so that they can be processed more easily, the potential application of those rigid-rod polymers as HSHM materials with high thermal resistance is limited. If the homopolymer structures could be re-formed after processing, the products should have superior chemical and thermal stability to the copolymers and their higher crystallinity should lead to superior mechanical properties.

A previous study[1] has shown that the high melting temperature of PPT (I) can be depressed to about 370°C by introducing t-butylhydroquinone comonomer units (II) into its backbone. This paper describes a study of the elimination of t-butyl substituents both from that copolymer (I-*co*-II) with [s] = 50 mol%, where [s] is the mole per cent of unit II in the copolymer, and from the model compound t-butylhydroquinone dibenzoate (III).
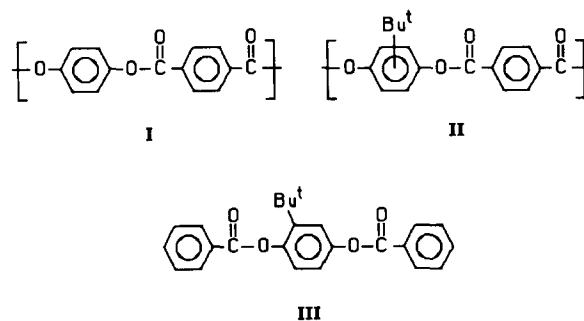
De-t-butylation has been studied widely since the t-butyl group can serve as a positional protective group for the preparation of aromatic compounds. McOmie and Saleh[2] examined the use of 70% trifluoroacetic acid (TFA) for the dealkylation of a series of t-butylated phenols. Their results showed that by refluxing with this reagent t-butyl groups can be removed from mono-, di- or tri-t-butylphenols. They also noticed that the de-t-butylation occurred much more easily with *ortho-* than with *para*-t-butylphenols, because dealkylation removes the steric compression, which is greater in the former than in the latter. Svanholm and Parker[3] published kinetic studies on de-t-butylation of phenols with 100% TFA at room temperature. They found that *ortho*-debutylation occurred very rapidly but that *para*-debutylation did not take place.

Tashiro and Fukata[4] systematically investigated the catalytic effect of $AlCl_3$–CH_3NO_2 for the trans-t-butylation of 4,4'-dihydroxydiphenylmethanes in toluene. They reported that not only t-butyl but also benzyl

groups were transferred to toluene used both as a solvent and as an acceptor of the alkyl group. Tashiro *et al.*[5] treated 2,2'-diamino-4,4'-di-t-butylbiphenyl with phosphoric acid at various temperatures. Their results indicated that the de-t-butylation reaction occurred at above 180°C, and the degree of debutylation increased with increase of reaction time and with elevation of reaction temperature.

More recently, Olah *et al.*[6] have reported the application of Nafion-H, referred to as a superacidic-perfluororesinsulphonic acid, as a convenient catalyst under whose influence t-butyl-substituted aromatic compounds were easily de-t-butylated very efficiently to the corresponding aromatic compounds in refluxing toluene solution.

Polymer transformations involving de-t-butylation have appeared recently. Risse and Sogah[7,8] reported an approach to the synthesis of high-molecular-weight poly(aryl ether ether ketone) (PEEK) that included synthesis of a soluble amorphous prepolymer by introduction of removable t-butyl substituents, followed by removal of the substituents to give the final crystalline polymer. Their work proved the effectiveness of Lewis acids and trifluoromethanesulphonic acid for elimination of t-butyl groups from substituted PEEK. No residual t-butyl groups could be detected after reaction at ambient temperature for 24 h when using trifluoromethane-sulphonic acid, which acted simultaneously as catalyst for de-t-butylation and as solvent for the resulting polymer.

McGrath *et al.*[9] had earlier reported a similar approach to PEEK synthesis. They disclosed the synthesis of a copolymer with t-butyl substituents and the subsequent reaction with $AlCl_3$. The cleavage of t-butyl substituents by the reaction with $AlCl_3$ amounted to only about 50% owing to the insolubility of the product in the solvent used.

EXPERIMENTAL

Materials

t-Butylhydroquinone (Aldrich) was employed after recrystallization. Benzoyl chloride was purified by distillation. Trifluoromethanesulphonic (triflic) acid (Aldrich), trifluoromethanesulphonic anhydride (Aldrich) and polyphosphoric acid (BDH) were used as received.

The model compound, t-butylhydroquinone dibenzoate (III), was synthesized from t-butylhydroquinone (120 mmol, 20 g) dissolved in 10% potassium hydroxide solution; benzoyl chloride (360 mmol) was added dropwise to the system with stirring. The white precipitate was filtered off and recrystallized from ethanol. Yield, 29%; m.p., 162°C. Elemental analysis (%): calculated, C 76.97, H 5.93; found, C 77.10, H 5.90. I.r. (KBr): 2957, 1737, 1600, 1493, 1365, 1171, 712 cm^{-1}.

Hydroquinone dibenzoate (HQDB) was prepared from hydroquinone (45.4 mmol, 5 g) and benzoyl chloride (113.5 mmol). Yield, 72%; m.p., 207°C (lit. 204°C[10], 207°C[11]). I.r. (KBr): 1735 cm^{-1}.

The synthesis and properties of the copolymer I-*co*-II ([s] = 50 mol%) have been reported previously[1].

Product characterization

Infra-red (i.r.) spectra were recorded on a single-beam Perkin–Elmer Fourier transform i.r. spectrometer (model 1725x) using a resolution of 4 cm^{-1} and a scan speed of 0.2 cm^{-1}/min. The final spectrum was an average of 10 scans of each sample. A potassium bromide (KBr) technique was employed owing to the low solubility of the polymers in common organic solvents. For quantitative analysis, the polymer sample was ground with KBr (BDH) for 40 min. After drying at 120°C under vacuum, a KBr pellet was pressed from the mixture.

Thin-layer chromatography (t.l.c.) was used to evaluate the products of elimination reactions of the model compound. The reaction mixture was dissolved in a mixture of ethyl acetate and petroleum ether (b.p. = 40–60°C) (1:4 by volume). Each chromatogram was developed on a silica-gel-coated plate (Aldrich, 10×10 cm^2). After developing, the plate was dried with hot air and the locations of spots were determined under ultra-violet radiation. Each component was identified by comparison with standard reference compounds, which were run on the same plate.

Optical observations, differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) were carried out using the procedures described previously[1].

Solid-state ^{13}C nuclear magnetic resonance (n.m.r.) experiments were performed at the Industrial Research Laboratories, University of Durham (UDIRL), on a Varian VXR 300 MHz spectrometer with ^{13}C resonance frequency of 75.4 MHz. Samples were spun at the magic angle at a speed of 5 kHz with a cross-polarization (c.p.) contact time of 3 ms at room temperature.

Elimination reactions

Thermal treatment of the copolymer was conducted in a tube immersed in a vapour bath at 330°C under nitrogen for 4 h.

Treatments of the model compound (III) with polyphosphoric acid (PPA) were carried out in nitrogen at elevated temperatures. At lower temperatures ($\leqslant 180$°C), nitrogen was passed through the reaction mixture. When temperatures higher than 180°C were required, the reaction was performed in a sealed glass tube (9 mm in diameter, 80 mm in length). After sample charging, the tube was gradually exposed to vacuum and nitrogen successively. The tube filled with nitrogen was sealed before heating. After a fixed period of time, the tube was removed and cut open. Most of the sample residues at this stage were grey or dark brown in colour.
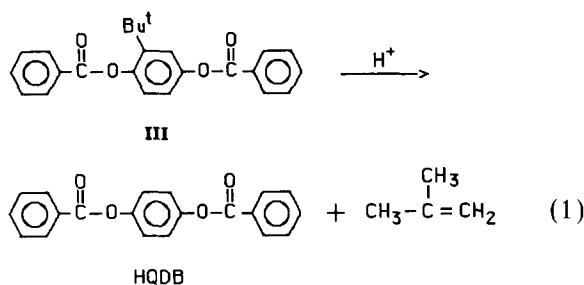
The treatment of the model compound (III) with triflic acid was performed in a round-bottomed flask containing III (1.0 g) and triflic acid (5 ml). The model compound readily dissolved, forming a dark brown solution. After stirring at 40°C under a stream of nitrogen for a fixed time, the mixture was poured into chloroform (50–60 ml) to extract any HQDB produced, then washed with dilute sodium hydroxide and water successively to remove triflic acid. The chloroform layer was separated and dried with anhydrous magnesium sulphate. The chloroform was distilled off under reduced pressure. At the end of distillation a crude product (HQDB) was obtained, which was recrystallized from ethanol and dried at 60°C in a vacuum oven overnight. In addition, a by-product was produced when the treatment was conducted for a longer period of time. This by-product was found on the top of the separated aqueous layer after standing overnight. It was collected and purified before further analysis.

Treatment of the copolymer with triflic acid was carried out in a carefully dried atmosphere. After weighing the polymer powder (0.5 g) into a flask, the system was built up and dried by flaming under vacuum. Nitrogen passed through phosphorus pentoxide was then used to release the vacuum established. Triflic acid (4 ml) plus its anhydride (10% by volume) was transferred to the flask through a septum with a syringe. After the required reaction time, sodium-dried diethyl ether (25 ml) was injected into the flask, upon which precipitation occurred. The precipitate was filtered off and thoroughly washed with acetone and water, followed by drying at 60°C in a vacuum oven overnight.

RESULTS AND DISCUSSION

Model compound studies

It is known that dealkylation of aromatic compounds can occur in the presence of Friedel–Crafts catalysts. In the present work, preliminary experiments showed that zinc chloride, ferric chloride, p-toluenesulphonic acid and polyphosphoric acid (PPA) were effective in eliminating t-butyl substituents from the model compound (III). The effect of PPA was further studied in detail, and the results are summarized in *Table 1*; the desired cleavage reaction occurred under the more severe conditions as follows:

The starting material (III), however, was also detected in each experiment after the reaction. This means that only partial de-t-butylation took place under these conditions. In addition, side-reactions occurred during the treatment, as confirmed by the detection of by-products such as t-butylhydroquinone (TBHQ) and benzoic acid (BA). The nature of these by-products suggests that they were produced by hydrolysis of III. Chemical analysis by titration confirmed that the PPA used was a tetramer. The water consumed may originate from dehydration of PPA at high temperatures due to condensation[12]. Without the use of PPA, heating at 320°C for 2 h also led to the removal of the t-butyl groups. Although hydrolysis of III was then eliminated, other high-temperature side-reactions still took place.

A stronger protonic acid should provide a more powerful catalytic effect and help to eliminate the high-temperature side-reactions. Treatment of III with triflic acid, one of the strongest acids known[13], was therefore investigated. The results (*Table 2*) indicate that the desired de-t-butylation reaction of III (equation (1)) occurred at a much lower temperature (40°C) when using triflic acid. In this case, no starting material (III) was detected in the product.

Apart from HQDB, a by-product was also produced when the treatment proceeded for 4 h (*Table 2*). After recrystallization from hot water, the by-product showed a sharp melting transition at 164°C (d.s.c.). Its i.r. spectrum was different both from the product (HQDB) and from the starting material (III), and did not show any evidence for the presence of t-butyl groups. Treatment of the authentic HQDB with triflic acid at room temperature for 6 h gave the same material as the by-product in experiment 2 (*Table 2*), as confirmed by i.r. spectra (*Figure 1*) and melting temperatures. The absence of a strong i.r. absorption around $1630 \, cm^{-1}$, typical of an aromatic ketone carbonyl group in the *ortho* position to a hydroxy group, excluded the possibility of a Fries rearrangement reaction of the debutylated product, which has been reported for other aryl benzoates in triflic acid[14]. This by-product was identified as 4-hydroxyphenyl benzoate (m.p. = $163-164°C^{15}$, $167°C^{11}$), the mono-hydrolysis product of HQDB.

It is concluded that the desired cleavage reaction for the model compound (III) occurred on treatment with triflic acid at 40°C. However, a side-reaction due to the hydrolysis of the debutylated product also took place.

Elimination of t-butyl substituents from the copolymer

Investigations on elimination of the t-butyl substituents from the copolymer (I-co-II) were carried out both by heating at 330°C for 4 h and by treatment with triflic acid under various conditions.

The degree of t-butyl elimination from the treated polymers was primarily evaluated by i.r. spectroscopy; ^{13}C n.m.r. analysis was used for corroboration. For i.r. evaluation, the t-butyl group C–H stretching absorption at $2961 \, cm^{-1}$ (*Figure 2*) was used for the absorbance

Table 1 Treatment of the model compound (III) with polyphosphoric acid[a]

Expt No.	Temp. (°C)	Time (h)	Products[b]			
			HQDB	TBHQ	BA	Other
1	180	1	None	Yes[c]	Yes	None
2	180	2	None	Yes	Yes	None
3	180	4	Yes	Yes	Yes	Yes
4[d]	180	2	Yes	Yes	Yes	Yes
5	250	2	Yes	Yes	Yes	None
6	300	0.5	Yes	Yes	Yes	Yes
7	300	1	Yes	Yes	Yes	Yes
8	300	2	Yes	Yes	Yes	Yes
9	300	4	Yes	Yes	Yes	Yes
10	320	2	Yes	Yes	Yes	Yes
11[e]	320	2	Yes	None	None	Yes

[a] A mixture of model compound (III) with 5 wt% of polyphosphoric acid, unless indicated otherwise, was heated under an atmosphere of nitrogen
[b] Products were identified by t.l.c. and i.r. spectroscopy; 'Other' means the material was detected by t.l.c., but not identified. HQDB = hydroquinone dibenzoate; TBHQ = t-butylhydroquinone; BA = benzoic acid
[c] Detected after the reaction
[d] 150 wt% of polyphosphoric acid was used
[e] No polyphosphoric acid added

Table 2 Treatment of the model compound (III) with triflic acid

Expt No.	Temp. (°C)	Time (h)	Products[a]	
			HQDB	Other
1	40	2	Yes[b]	None
2	40	4	Yes	Yes

[a] Identified by i.r. spectroscopy; HQDB = hydroquinone dibenzoate
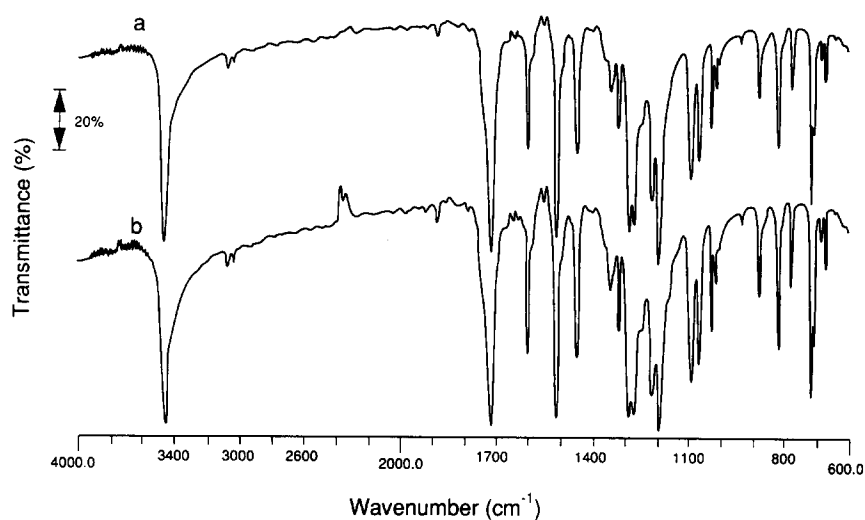[b] Detected after the reaction

Figure 1 I.r. spectra of (a) the by-product obtained in experiment No. 2 (*Table 2*), and (b) the product obtained by treating hydroquinone dibenzoate with triflic acid
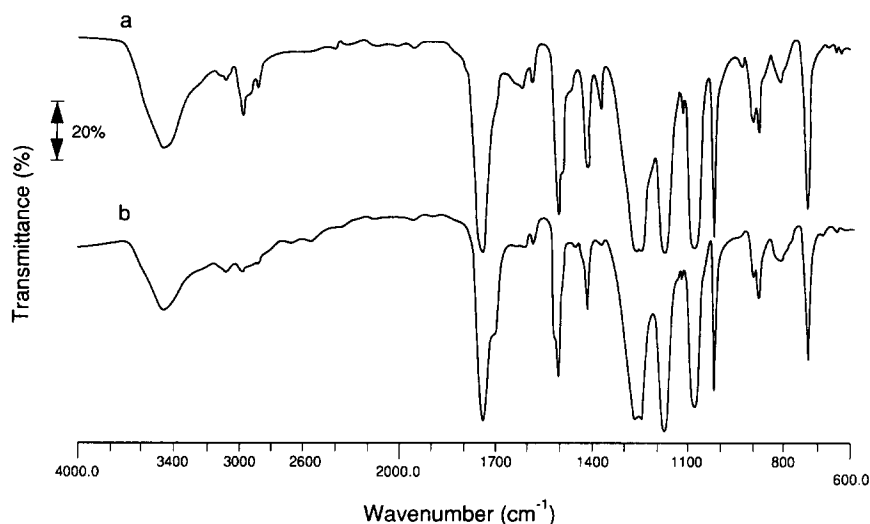

Figure 2 I.r. spectra of (a) copolymer I-co-II ([s] = 50 mol%) and (b) triflic-acid-treated sample (No. 8 in *Table 3*)

measurement because of its greater intensity and better resolution, which gave easier determination of its baseline than for the C–H deformation band at $1366\,cm^{-1}$. All the absorbance values were normalized against absorptions both at $1016\,cm^{-1}$ and at $722\,cm^{-1}$, owing to the relatively stable position and intensity of these two bands when the polymer composition is changed. The linear correlations between the normalized absorbances and t-butyl group content (*Figure 3*) for the series of copolymers previously made[1] indicate that this technique is satisfactory. The difference between absorbance ratios obtained in repeat experiments did not exceed 0.04. The failure of these correlation lines in *Figure 3* to pass through the origin is attributed to the presence of acetoxy groups, which provide additional methyl group absorptions.

Thermal treatment at 330°C had no effect on removal of the t-butyl groups from the copolyester (*Table 3*). When triflic acid was used, however, the t-butyl substituents were eliminated completely at 25°C or higher temperatures. At lower temperatures, only partial removal occurred. The lower the temperature, the fewer t-butyl groups were removed. Solid-state ^{13}C n.m.r.
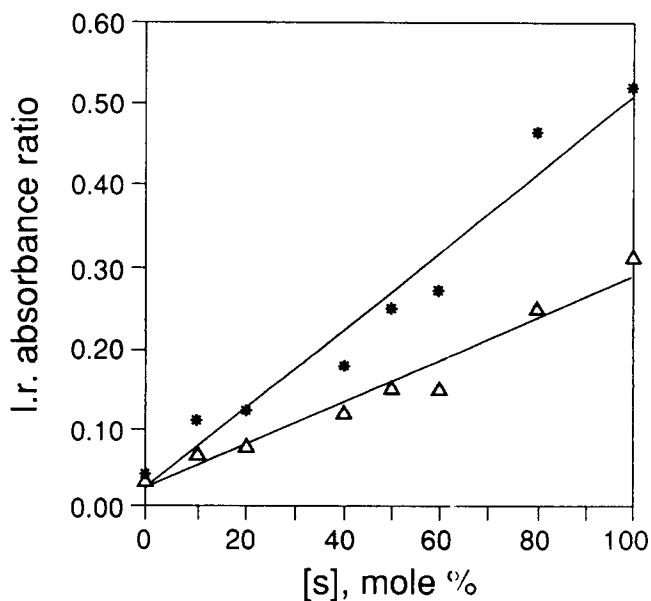

Figure 3 Effect of copolymer (I-co-II) composition on i.r. absorbance ratios: ($*$) $2961/722\,cm^{-1}$; ($\triangle$) $2961/1016\,cm^{-1}$

Table 3 Treatment of the copolymer I-*co*-II ([s] = 50 mol%) with triflic acid

Expt No.	Temp. (°C)	Time (h)	[s] (mol%)[a] 2961/1016	[s] (mol%)[a] 2961/722	[s] (mol%)[a] N.m.r.	H[b] 1698/1016	H[b] 1698/722
1[c]	330	4	51	48	48	None	None
2	40	4	0	0	_[d]	1.03	1.22
3	40	2	0	0	_[d]	0.75	0.98
4	40	1	0	0	_[d]	0.50	0.59
5	25	4	0	0	_[d]	0.45	0.57
6	25	2	0	0	_[d]	0.35	0.45
7	20	2	6	5	_[d]	0.31	0.41
8	10	2	12	10	16	0.17	0.23
9	0	6	15	13	_[d]	0.10	0.15
10	0	4	12	12	16	_[e]	_[e]

[a] [s] is the molar per cent of unit II in the polymer, determined by i.r. absorbance ratios 2961/1016 cm^{-1}, etc.
[b] Degree of chain breakdown expressed by i.r. absorbance ratios
[c] Pure thermal treatment, no triflic acid added
[d] Not measured
[e] Too weak to measure

C (C=O)

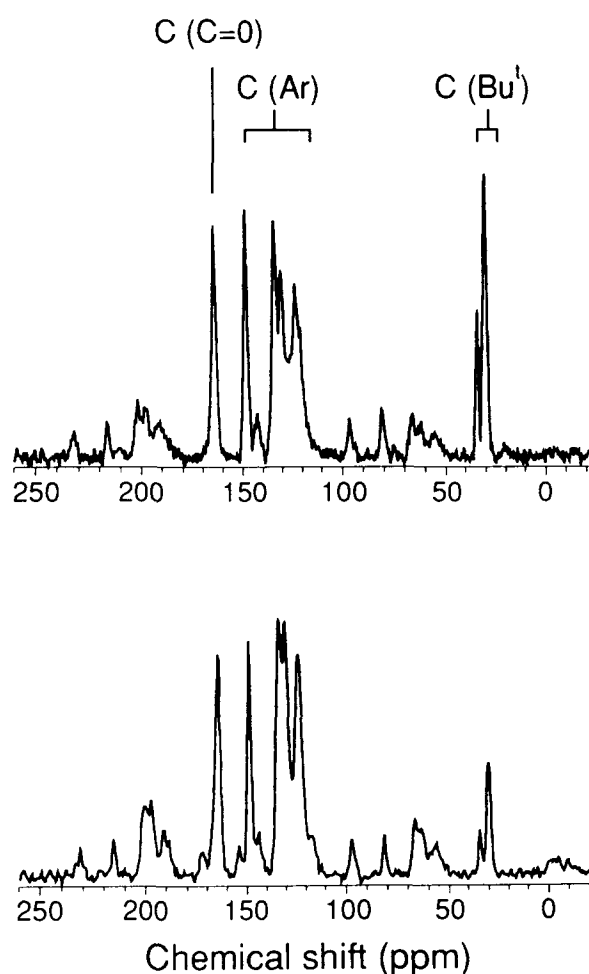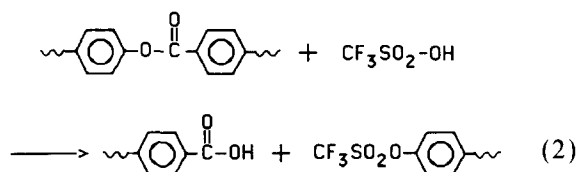C (Ar)   C (Bu^t)

a

b

Chemical shift (ppm)

Figure 4 N.m.r. spectra of (a) copolymer I-*co*-II ([s] = 50 mol%) and (b) triflic-acid-treated sample (No. 8 in *Table 3*)

analysis (*Figure 4*) confirmed the i.r. conclusions as shown in *Table 3*.

Comparison of Nos 9 and 10 (*Table 3*) shows that increasing reaction time at 0°C did not produce a greater loss of the t-butyl groups, as might have been expected. This is attributed to the reversible nature of the t-butyl

cleavage process, as suggested for other Friedel–Crafts debutylation reactions[16]. The debutylation reaction takes place with the formation of a t-butyl cation intermediate[3,17], which is more stable at low temperatures[18]. This increases the probability of its reversing the reaction and reducing the degree of debutylation.

As in the case of the model compound, some hydrolytic breakdown of the ester linkages was revealed by an i.r. absorption at 1698 cm^{-1} attributed to the carbonyl group of carboxylic acids and the appearance of a broad band around 3000–2500 cm^{-1} characteristic of carboxylic acids. Since precautions were taken during the experiments to exclude any moisture, formation of the carboxylic acid is attributed to attack of triflic acid on the chain ester groups, as shown below:

$$\text{~}\langle O \rangle\text{-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-}\langle O \rangle\text{~} + CF_3SO_2\text{-OH}$$

$$\longrightarrow \text{~}\langle O \rangle\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH} + CF_3SO_2O\text{-}\langle O \rangle\text{~} \quad (2)$$

The extent of production of the carboxylic acid was measured using i.r. absorbance ratios 1698/1016 cm^{-1} and 1698/722 cm^{-1}. *Table 3* shows that lower temperatures and shorter reaction times reduce the chain degradation. After 4 h at 0°C, no hydrolysis occurred.

The thermal properties of the triflic-acid-treated samples were examined by hot-stage microscopy, d.s.c. and t.g.a. The large melting endotherm at about 370°C for the starting copolymer was not observed for any of the treated samples. Accordingly, the hot-stage microscopy did not reveal any flow at temperatures up to the onset of decomposition, in contrast to the starting polymer where flow occurred at about 355°C. Typical t.g.a. thermograms of the triflic-acid-treated samples are shown in *Figure 5*. Products in which hydrolysis had occurred showed loss of volatile materials at temperatures below 500°C, but the product in which no hydrolysis was detected showed little loss below 500°C and an enhanced thermal stability.
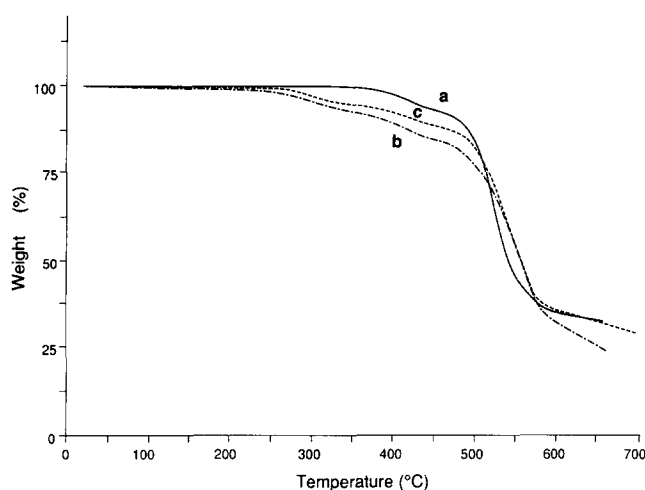
Figure 5 T.g.a. (10°C min^{-1}) curves of (a) copolymer I-*co*-II ([s] = 50 mol%) and triflic-acid-treated samples (b) No. 8 and (c) No. 9 in *Table 3*

CONCLUSIONS

The t-butyl substituents in copolymer I-*co*-II were not preferentially removed by thermal means. However, elimination of the t-butyl groups occurred under the influence of triflic acid at 0–40°C. The elimination process was favoured by higher temperatures, and complete cleavage of the substituents took place above 25°C. However, chain degradation due to the attack of triflic acid also became serious at higher temperatures. Partial removal of the t-butyl groups occurred below 25°C, and the chain degradation was suppressed to a very low extent and eliminated at 0°C. The residual content of repeat unit II after these treatments was about 10–15 mol%.

REFERENCES

1   Voice, A. M., Li, Z. G., McIntyre, J. E. and Tomka, J. G. *Polymer* in press
2   McOmie, J. E. W. and Saleh, S. A. *Tetrahedron* 1973, **29**, 4003
3   Svanholm, U. and Parker, V. D. *J. Chem. Soc., Perkin Trans.* (*1*) 1973, 562
4   Tashiro, M. and Fukata, G. *J. Org. Chem.* 1977, **42**, 1208
5   Tashiro, M., Fukuda, Y. and Yamato, T. *Heterocycles* 1981, **16**(5), 771
6   Olah, G. A., Prakash, G. K. S., Iyer, P. S., Tashiro, M. and Yamato, T. *J. Org. Chem.* 1987, **52**, 1881
7   Risse, W. and Sogah, D. Y. *Macromolecules* 1990, **23**, 4029
8   Risse, W. and Sogah, D. Y. *Polym. Prepr.* 1990, **31**(1), 616
9   Mohanty, D. K., Lin, T. S., Ward, T. C. and McGrath, J. E. *Int. SAMPE Symp. Exp.* 1986, **31**, 945
10 'CRC Handbook of Chemistry and Physics' (Ed. R. C. Weast), 60th Edn, CRC Press, Boca Raton, FL, 1979, C-159
11 Schroeder, J. P. and Bristol, D. W. *J. Org. Chem.* 1973, **38**, 3160
12 Corbridge, D. E. C. 'Phosphorus – An Outline of Its Chemistry, Biochemistry and Technology', 3rd Edn, Elsevier, Amsterdam, 1985
13 Stang, P. J. and White, M. R. *Aldrichimica Acta* 1983, **16**(1), 15
14 Effenberger, F. and Gutmann, R. *Chem. Ber.* 1982, **115**, 1089
15 Kehrmann, F., Sandoz, M. and Monnier, R. *Helv. Chim. Acta* 1921, **4**, 941
16 Olah, G. A. 'Friedel–Crafts Chemistry', Wiley, New York, 1973
17 Olah, G. A. and Mo, Y. K. *J. Org. Chem.* 1973, **38**, 3221
18 March, J. 'Advanced Organic Chemistry', 3rd Edn, Wiley, New York, 1985