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Synthesis and properties of segmented copolymers containing short aramid hard segments and aliphatic polyester or polycarbonate soft segments

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Abstract

Segmented copolymers based on poly(ethylene adipate) or poly(hexamethylene carbonate) soft segments and short terephthalamide or 2,6-naphthalenedicarboxamide hard segments were prepared by a condensation polymerisation in solution. The polymers were characterised by NMR, IR, GPC, DSC, DMTA and tensile tests. A comparison of several soft segments revealed that the polyester soft segment led to materials with relatively poor elastic recovery, whereas the polymers possessing short aramid hard segments and polycarbonate soft segments showed high elongations at break (820–940%) and good tensile set values (38%).

Keywords: Thermoplastic elastomer; Polyether; Polycarbonate

1. Introduction

Thermoplastic elastomers have increased in importance over the last decades as alternatives to crosslinked rubber. The main advantages of thermoplastic elastomers are: (i) ease of processing, (ii) fast processing times, and (iii) potential for recycling. Segmented (multi-block) copolymers can possess elastic properties provided that the segments are suitably chosen. Thermoplastic polyurethanes (TPUs) are typical examples of this class of elastomers. They are composed of an amorphous and flexible soft segment (usually an aliphatic polyether or polyester of intermediate length) that alternates with a crystalline hard segment consisting of a high-melting oligourethane [1]. Soft and hard segment are incompatible and phase-separate on a microscopic scale. The soft segment is responsible for the rubbery flexibility of the polymer at and above room temperature. Hydrogen bonds between urethane groups of the hard segments impart physical crosslinks between neighbouring polymer chains, and they remain intact almost up to the melting temperature of the polymer. For an elastic material the soft segment has to be above its glass temperature, while the ultimate service temperature range is limited by the melting temperature of the hard segment or, more precisely, the flow temperature of the polymer. The many applications of TPUs include spandex stretch fibres that are made by polymerising a medium-sized poly(tetrahydrofuran)-diol (PTMO) of a number-average molar mass M_n typically around 2000 g mol^{-1} with an aromatic diisocyanate (e.g., 4,4′-diphenylmethane diisocyanate) and 1,4-butanediol, a chain extender that joins two adjacent hard segments together, in a roughly 1:2:1 molar ratio.

While urethane chemistry is hard to beat in price and processing advantages, there are a number of concerns about the health risks associated with diisocyanate monomers and prepolymers, as well as their decomposition products. Most syntheses of polyurethanes for non-biomedical applications rely on aromatic diisocyanates as starting materials, which are a health hazard in their own right [2,3] since thermal degradation of the polymer as well as hydrolysis of the isocyanates invariably lead to electron-rich aromatic amines, many of which are known or suspected carcinogens [4]. There is a strong incentive to

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look at alternative types of hard segments that impart similar, if not improved, mechanical properties and do not depend on isocyanates as chemical precursors.

One option is to replace the urethanes in the hard segment by amide groups. Aromatic amides are particularly attractive in this respect. They induce homogeneous and fast crystallisation, especially when the hard segments have a uniform size [5–7]. In addition, they show good phase separation, high fracture strain and toughness, and high thermal stability [8–10]. While routes have been published which are sensitive to moisture [11–13] or rely once again on isocyanates [14,15], one of the most promising syntheses so far has been reported by Gaymans and co-workers [5–10]. Transesterification of aromatic diester-diamides and PTMO in the melt at 250 °C gives high-molar-mass polymers provided that the polyether soft segment does not degrade at high temperature. The route is also less suited to polyester soft segments, which are susceptible to cleavage in the presence of a transesterification catalyst.

A wide range of soft segments of different length and type is commercially available that allow the properties of the elastomer to be altered [16]. The majority of TPUs contain polyether soft segments derived from PTMO or poly(propylene glycol). TPUs made from aliphatic polyesters, mostly poly(ethylene adipate) or poly(butylene adipate), have some advantages over PTMO as they render the elastomer resistant to oil and high temperature [1]. Although hydrolysis of ester groups, particularly in the presence of acid, is a drawback in some applications, it also provides an opportunity for making polyester TPUs potentially biodegradable. Aliphatic polycarbonates possess a similar resistance to hydrolysis and oxidation, and they are equally attractive as biodegradable and biocompatible materials [1,17].

We have recently described the properties of segmented multiblock copolymers such as **P1** that contain polyether soft segments and short aramid hard segments (Fig. 1). The synthetic route avoids the use of carcinogenic aromatic amines and does leave ester bonds intact [18]. Here we discuss the synthesis and properties of thermoplastic elastomers containing short aramid hard segments while poly(ethylene adipate) **T1** or poly(hexamethylene carbonate) **T2** serve as soft segments (Fig. 2). Comparison of the elastic properties will be made between these polymers and elastomer **P1** to illustrate the influence of the different types of soft segment.

2. Experimental

2.1. Materials

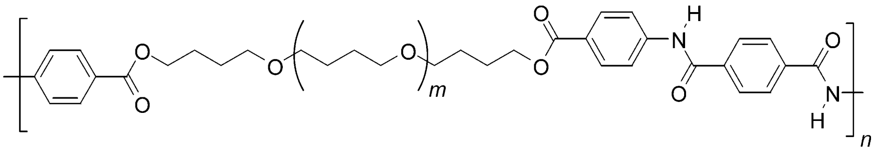
4-Nitrobenzoyl chloride, anhydrous *N*,*N*-dimethylacetamide (DMAc) and poly(hexamethylene carbonate)-diol (M_n 2000 g mol^{-1}) were purchased from Aldrich. Terephthaloyl chloride (**M1**), triethylamine, iron and chlorotrimethylsilane were obtained from Lancaster, toluene and methanol from Fisher Chemicals, and acetic acid from Fisons. Lupraphen 8100, a poly(ethylene adipate)-diol with an M_n of 2000 g mol^{-1}, was provided by Elastogran. 2,6-Naphthalenedicarbonyl chloride (**M2**) was prepared as described previously [18].

2.2. Preparation of telechelic diamines

2.2.1. Poly(hexamethylene carbonate) α,ω-bis(4-aminobenzoate) (*T2*)

Triethylamine (8.0 mL, 60 mmol) was added to a solution of poly(hexamethylene carbonate) (M_n 2000 g mol^{-1}, 50.1 g, 25.1 mmol) in toluene (500 mL), left to rest for about 10 min, and then heated to 50 °C. A solution of 4-nitrobenzoyl chloride (8.76 g, 52.3 mmol) in toluene (250 mL) was added dropwise over 30 min, and the mixture was refluxed for 26 h. The reaction mixture was allowed to cool to room temperature and filtered to remove the precipitate (triethylammonium chloride). The filtrate was washed with a 5% aqueous $NaHCO_3$ solution (ca. 500 mL), the toluene phase was separated and concentrated on a rotary evaporator (40 °C/40 mbar). Drying in vacuum (120 °C/0.2 mbar) gave 54.1 g (94%) of nitrobenzoyl end-capped poly(hexamethylene carbonate) in the form of a light yellow, waxy residue.

A 2 L three-necked round-bottomed flask (fitted with a dropping funnel, a condenser, and a mechanical stirrer) was charged with iron powder (26 g, 460 mmol), toluene (120 mL), water (48 mL) and acetic acid (1.25 mL). The resulting slurry was refluxed until an emulsion had formed. A solution of the nitrobenzoyl end-capped poly(hexamethylene carbonate) (52.0 g, 22.6 mmol) in toluene (120 mL) was added dropwise over 30 min and refluxing continued for 12 h. The mixture was then neutralised with $NaHCO_3$ and filtered whilst hot. The filtrate was washed with water (2×500 mL), the toluene phase was separated and concentrated on a rotary evaporator (40 °C/40 mbar). Drying in vacuum (120 °C/0.2 mbar) gave 45.0 g (89%) of a waxy,



P1

Fig. 1. Structure of polymer **P1**.

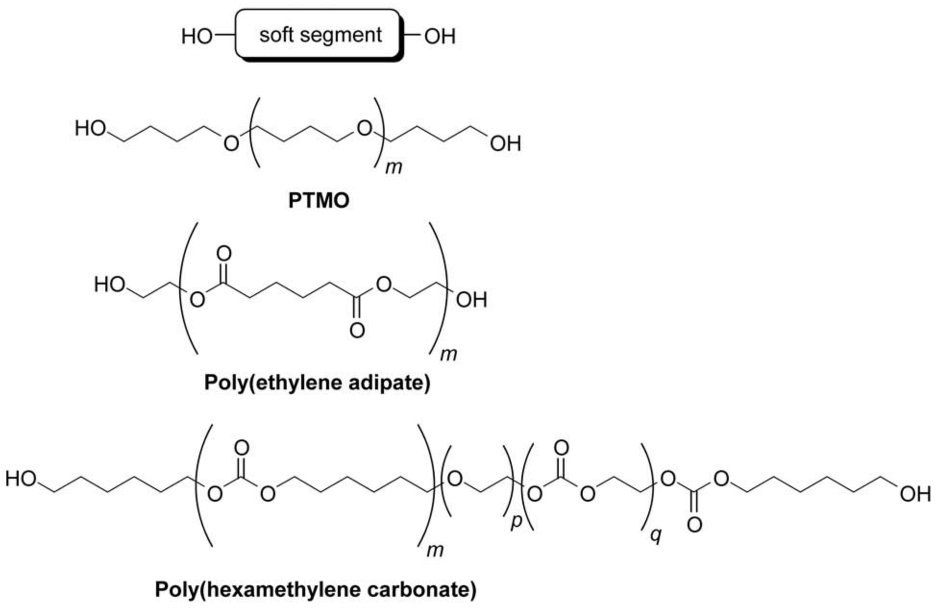


Fig. 2. Structures of the three soft segments studied in the paper (diol precursors).

dark orange residue of **T2**. ^{1}H NMR (400 MHz, $CDCl_3$): see Fig. 6. ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.2, 28.4, 67.6 (aliphatic CH_2, major signals), 25.6, 29.3, 64.0, 66.7, 68.2, 68.8, 70.5, 71.1 (aliphatic CH_2, minor signals), 113.5, 131.4 (aromatic CH, major signals), 131.5 (aromatic CH, minor signal), 119.5, 150.9 (ipso-C), 155.2 (carbonate C=O), 166.5 (aromatic ester C=O).

2.2.2. *Poly(ethylene adipate) α,ω-bis(4-aminobenzoate) (**T1**)*

Telechelic **T1** was prepared analogously in two steps from poly(ethylene adipate)-diol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (br t, ca. 50H, $CH_2CH_2CO_2$), 2.35 (br t, ca. 50H, $CH_2CH_2CO_2$), 4.14 (br. s, 4H, NH_2), 4.25 (s, 8H), 4.26 (s, ca. 36H, OCH_2), 4.38 and 4.44 (m, probably AA′BB′, 2×4H, $ArCO_2CH_2CH_2O$), 6.63 and 7.83 (AA′XX′, 2×4H, aromatic H). Integration of the end group and polymer backbone signals gave an average degree of polymerisation m of 12.5 ± 0.3. ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.0, 33.5, 62.0 (aliphatic CH_2), 113.5, 131.6 (aromatic CH), 118.7, 151.2 (ipso-C), 166.2 (aromatic ester C=O), 172.9 (aliphatic ester C=O).

2.3. *Typical polymerisation procedure*

A solution of **T2** (2.62 g, 1.17 mmol) in anhydrous DMAc (10 mL) was placed in a round-bottomed flask that was sealed with a septum cap and cooled with an ice-water bath. Chlorotrimethylsilane (0.45 mL, 3.6 mmol) was added with a gastight syringe through the septum cap and stirred for 15 min at 0 °C, followed by the dropwise addition of a solution of terephthaloyl chloride **M1** (0.238 g, 1.17 mmol) in dry DMAc (5 mL). Stirring was continued at 20 °C for 22 h until the solution became highly viscous and dark yellow. The polymer was then precipitated into methanol (400 mL), collected by suction filtration, and thoroughly dried in vacuum (120 °C/0.2 mbar) to give 2.25 g (81%) of **PC1** as a colourless solid.

2.4. *NMR*

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 or DPX400.

2.5. *MALDI-TOF MS*

Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectra were obtained in reflectron mode on a Bruker Daltonics (Bremen) Reflex IV instrument equipped with a 337 nm nitrogen laser. The resolution, FWHM, was ca. 20,000 under optimal conditions. The spectrometer was calibrated with poly(ethylene glycol) ($M+Na^+$ peaks) in the mass range of 600–4000 Da, which gave a mass accuracy of ±0.02% throughout the whole m/z range. 2,5-Dihydroxybenzoic acid (DHB) or 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) [19] served as matrix (Fig. 3). Samples were prepared by mixing chloroform solutions of the polymer (50 μL) and matrix (50 μL, concentration ca. 50 mg/mL) with saturated methanolic $NaBF_4$ (10 μL) in a typical ratio of 1:50:2 (w/w/w, polymer/matrix/$NaBF_4$); 1 μL of this solution was dropped onto the target and the solvent was allowed to evaporate. Spectra were averaged over 50–200 laser shots (pulse length 3 ns).

2.6. *GPC*

Gel-permeation chromatography (GPC) was carried out

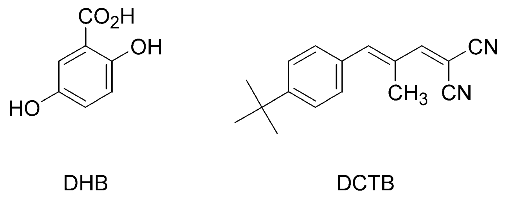


Fig. 3. Structures of DHB and DCTB.

with a Waters 590 programmable HPLC pump, a Waters 410 differential refractometer and a Waters 745B data module. Molar mass averages were determined using a Polymer Laboratories 5 μ mixed-C column (calibrated with polystyrene standards; tetrahydrofuran flow rate 1.0 mL min^{-1}, $T = 35$ °C).

2.7. DSC

Differential scanning calorimetry (DSC) traces were recorded on a Thermal Advantage DSC 2010. Samples consisted of typically 10–12 mg of polymer and were cut from cast films (as used for tensile tests). The DSC samples were heated at a rate of 20 °C min^{-1} under a constant flow of nitrogen.

2.8. DMTA

Samples for dynamic mechanical thermal analysis (DMTA) were prepared by casting polymer films from DMAc. A TA Instruments 2980 was used in tensile mode with the frequency set to 3 Hz. All samples were cooled below the glass transition temperature, then heated at a rate of 2 °C min^{-1}.

2.9. Tensile tests

Elongation at break and tensile set were measured with an Instron Model 1026. Samples were prepared by casting a film from a solution of the polymer in DMAc into a teflon form. The solvent was allowed to evaporate freely, and the film was then dried in an oven at 60 °C and ambient pressure for three days. Rectangular test samples (typical size: 90 mm long, 20 mm wide, and 0.5 mm thick) were cut from good quality films. Recovery experiments were performed at room temperature by stretching a sample to 300% of its original length at a speed of 50 mm min^{-1}, and then reversing the speed. The tensile set was calculated from the following equation [15]:

$$TS_{300\%} = 100\%(L_2 - L_0)/(L_1 - L_0) \quad (1)$$

where L_0 is the original gauge length, L_1 the length at 300% extension, and L_2 the final length after recovery.

3. Results and discussion

3.1. Preparation and characterisation of telechelic precursors

The starting materials were commercial poly(ethylene adipate)-diol and poly(hexamethylene carbonate)-diol. We chose telechelics with an M_n of 2000 g mol^{-1}, since this M_n had already been found to give the best elastic properties in polymers with short aramid hard segments and PTMO soft segments [5–7,18]; it also facilitated comparison between the three types of soft segment. Our polymerisation route required the OH end groups of the telechelic diol to be converted into α,ω-aminobenzoate esters (Fig. 4). Each telechelic was therefore esterified with 4-nitrobenzoyl chloride, and the aromatic nitro groups were then reduced with iron powder in a weakly acidic toluene/water solvent mixture to provide the required telechelic α,ω-bis(aminobenzoate). All modified telechelics were thoroughly dried prior to use and analysed by NMR and MALDI-TOF mass spectrometry.

The MALDI-TOF mass spectrum of polyester **T1** shows a dominant series of peaks separated by 172 Da, the mass of an ethylene adipate repeat unit (Fig. 5). The distribution is broad and distorted towards lower masses, which is not

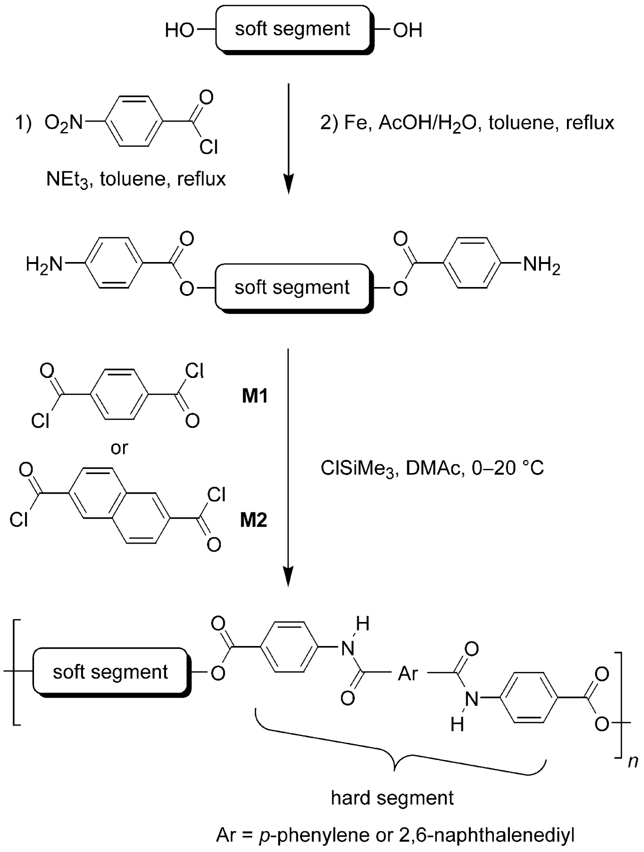
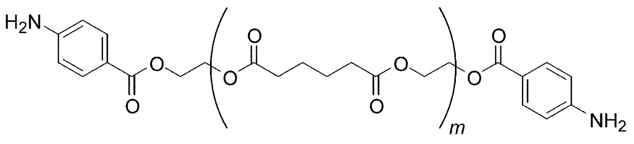


Fig. 4. Reaction scheme for the modification of the telechelic diol precursors and their subsequent polymerisation.



T1

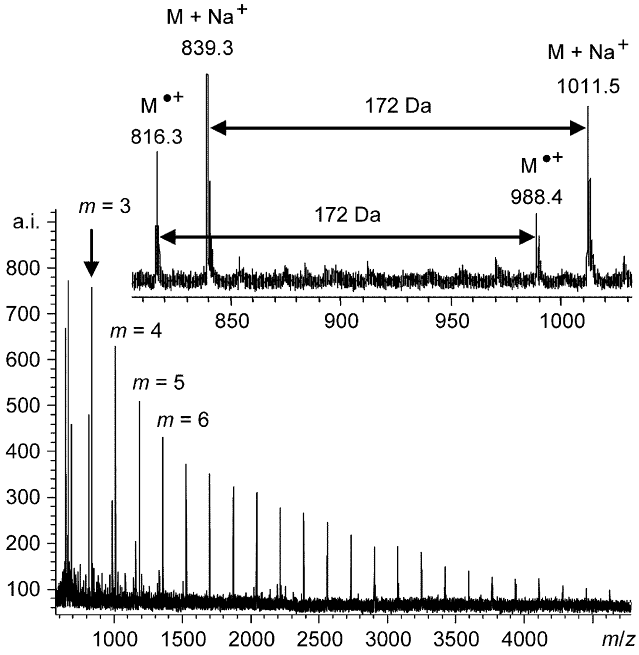


Fig. 5. MALDI-TOF mass spectrum (DCTB matrix) of telechelic **T1** (a.i., arbitrary intensity). The inset shows a minor peak series at lower *m*/*z* values that stems from M^+ species.

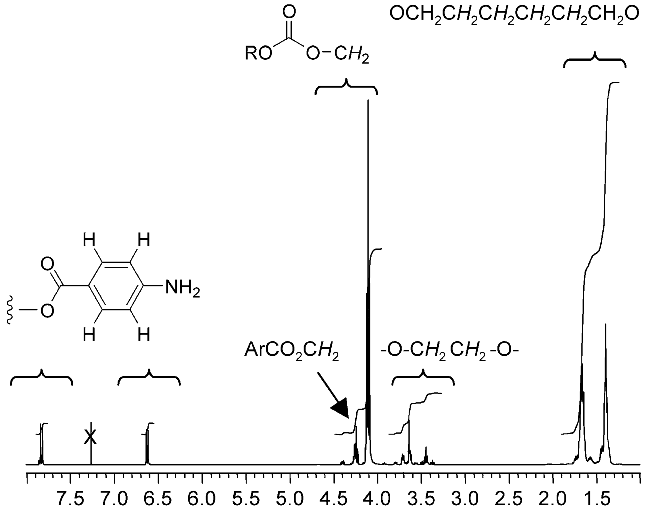
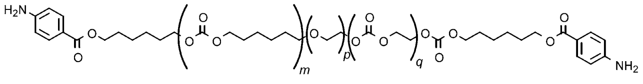


Fig. 6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of telechelic **T2**.

unusual for a mass spectrum run in the reflectron mode. The latter was chosen because its mass resolution allows monofunctional impurities to be easily detected and identified in end-functionalised telechelics [20]. A closer look reveals that the main series is composed of $[M+Na^+]$ ions, where M stands for any *n*-mer of the modified telechelic. A second, less intense series belongs to $M^{\cdot+}$ radical cations and results from the ability of the matrix DCTB (Fig. 3) to ionise a molecule by abstracting an electron. No other ions were observed with DCTB as matrix—unlike the more commonly used DHB (Fig. 3) that gave rise to $[M+Na^+]$ and $[M+H^+]$ ion peaks as well as additional mass peaks arising probably from decomposition under MALDI-TOF conditions.

Whereas the analysis of the NMR spectrum of the modified polyester **T1** was relatively straightforward (see Experimental), polycarbonate **T2** showed several NMR signals in addition to those expected for a simple poly(hexamethylene carbonate) backbone (Fig. 6). Two recent papers have already discussed in detail the various side reactions that commonly occur during the preparation of such polycarbonate-diols [21,22]. Poly(hexamethylene carbonate)-diol is the product of a condensation polymerisation of 1,6-hexanediol and ethylene carbonate in the presence of a transesterification catalyst, and the byproduct ethylene glycol is continuously removed by distillation from the reaction mixture. The resulting polymer contains OH end groups and predominantly hexamethylene carbonate repeat units. Depending on conditions, ethylene carbonate is occasionally incorporated into the polymer backbone. The ^{1}H NMR spectrum of **T2** shows a multiplet at $\delta_H=4.25$ belonging mainly to the $ArCO_2CH_2$ ester end group of the telechelic and, to some extent, to ethylene carbonate (O–CH_2CH_2–OCO–) repeat units. The most prominent side reaction involves partial decarboxylation of an added ethylene carbonate at the end of the growing polycarbonate-diol chain [21,22], which results in the incorporation of ethylene oxide units. In the ^{1}H NMR spectrum of the polymer, these unsymmetrically substituted –OCH_2CH_2O– units are easily spotted as a complex signal group at δ_H 3.3–3.8. From integrating the NMR signals it could be estimated that about 25 mol% of ethylene oxide units and less than 7 mol% of ethylene carbonate were found in the poly(hexamethylene carbonate) backbone.

The complex structure of polycarbonate **T2** is reflected in the MALDI-TOF mass spectrum of the telechelic (Fig. 7(a)). An enlargement of the lower *m*/*z* range, where resolution was still high, was then scrutinised more closely (Fig. 7(b)). The main series (labelled by an A) belongs to the telechelic with aminobenzoate groups at both ends and exclusively hexamethylene carbonate repeat units in between. The mass difference between two peaks of the same series is 144 Da and corresponds to the mass of a hexamethylene carbonate repeat unit. Most other ion peaks are separated from the A series by mass increments of 44 Da, the mass of an ethylene oxide (OCH_2CH_2) unit, or multiples thereof. The peaks marked as B_1, B_2, B_3 refer to molecules with one, two, three etc. ethylene oxide units inserted randomly into the poly(hexamethylene carbonate) backbone. Since the mass of an ethylene carbonate (OCH_2-CH_2OCO, 88 Da) happens to be twice as large as the mass of an ethylene oxide unit (44 Da), it is not possible to decide



T2

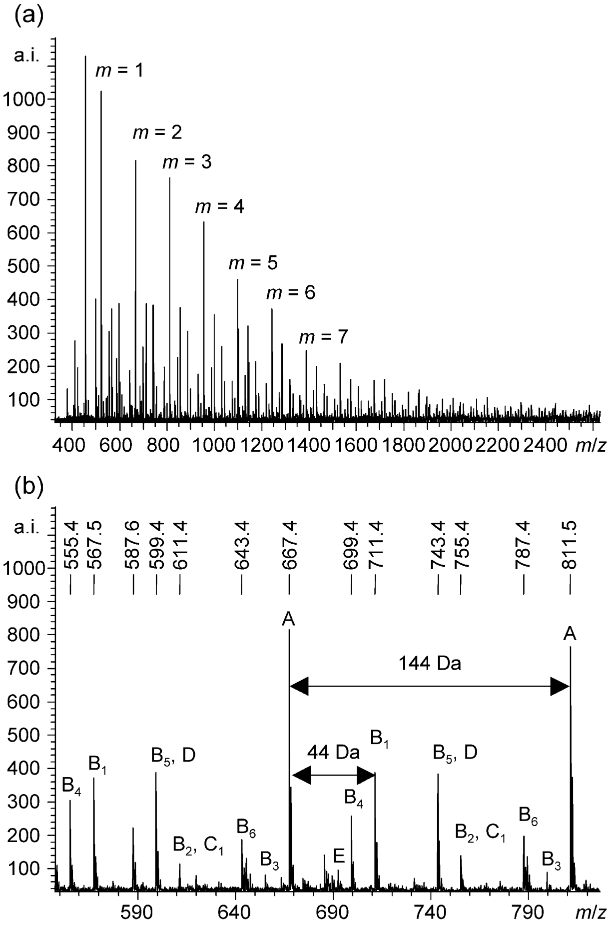


Fig. 7. (a) MALDI-TOF mass spectrum (DHB matrix) of telechelic **T2** and (b) expansion of the region between *m/z* 550 and 820.

which of the two units is actually present in the polymer. For example, B_2 could contain either two ethylene oxides or just a single ethylene carbonate unit (C_1). However, the ^{1}H NMR data suggests that ethylene oxide units are dominating. Although it is tempting to assign the ion peaks at *m/z* 599 and 743 to a cyclic polycarbonate (D), this assignment is less likely because only the cyclic dimer and trimer were observed to a noticeable extent in the MALDI-TOF mass spectrum of the precursor polycarbonate-diol. From a practical point of view, it is important that monofunctional impurities are absent since they interfere in a subsequent condensation polymerisation and are responsible for lowering the degree of polymerisation. The most likely impurity of this type is a modified poly(hexamethylene carbonate) with just a single aminobenzoate end group, originating from incomplete esterification of the telechelic diol. Its ion peak would be expected at *m/z* 692 (E), but it is virtually absent in the MALDI-TOF mass spectrum.

3.2. Polymerisation

The polymerisation method was adapted from an aramid polymer synthesis reported initially by Imai and later developed further by Kricheldorf [23,24]. Based on the condensation of a diacid chloride with an *N*,*N*′-bis(trimethylsilylated) aromatic diamine, silylation activates aromatic amines so that they react fast and quantitatively with acid chlorides, even at −15 °C. A drawback of this method is that the silylated intermediates are highly sensitive towards moisture. Problems with hydrolysis can, however, be conveniently circumvented by making the silylated intermediates in situ in the presence of excess chlorotrimethylsilane [25]. We therefore treated the telechelic diamines **T1** and **T2** with $ClSiMe_3$ prior to the addition of terephthaloyl chloride (comonomer **M1**) or 2,6-naphthalenedicarbonyl chloride (comonomer **M2**). Polymerisation occurred readily at 0–20 °C and led to a rise in viscosity within a few hours (Fig. 4). The polymers were isolated by precipitation and, according to GPC analysis, possessed number-average molar masses M_n in the range of 49–81 kg mol^{-1} (Table 1). All new polymers were subsequently characterised by ^{1}H NMR, DSC, DMTA, tensile tests and IR.

3.3. Thermal properties: DSC and DMTA

As expected for phase-separated polymers, DSC measurements revealed a glass-transition temperature T_g for the soft segment as well as a melting temperature T_m for the hard segment (Table 1). Glass transitions were observed around −35 °C and were almost independent of the type of soft or hard segment. None of the DSC traces revealed any evidence of soft segment crystallisation (Fig. 8). The melting of the hard segments occurred in the range of 150–224 °C, with the two polycarbonates having melting temperatures well above those of the corresponding polyesters. Furthermore, polymers **PC2** and **PE2** (both containing naphthalene-2,6-dicarboxamide hard segments)

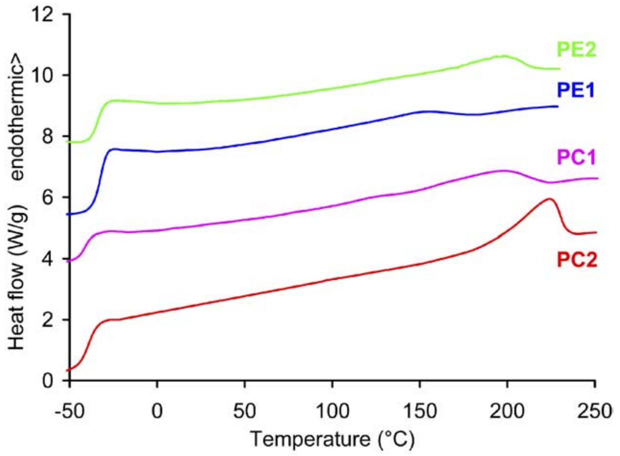


Fig. 8. DSC traces (second heating).

Table 1
Characteristic data

Polymer	Telechelic (M_n)	Diacid chloride	T_g (°C)[a]	T_m (°C)[a]	M_n[b] (kg mol^{-1})	M_w/M_n	Elongation at break (%)	TS_{300} (%)
PE1	Polyester 2000 (**T1**)	**M1**	−32	152	81	1.6	480	67
PE2	Polyester 2000 (**T1**)	**M2**	−35	197	49	1.3	600	75
PC1	Polycarbonate 2000 (**T2**)	**M1**	−41	197	68	1.4	940	43
PC2	Polycarbonate 2000 (**T2**)	**M2**	−40	224	63	1.7	820	33
P1	PTMO 2000	**M1**	−73	212[c]	69	2.0	1180	29

[a] Determined by DSC; second heating.
[b] Determined by GPC (THF, polystyrene standards).
[c] **P1** showed an additional endotherm at +6 °C owing to the melting of the PTMO soft segment.

melted not only at a higher temperature than their terephthalamide analogues but they also gave rise to slightly sharper melting endotherms.

Results of DMTA measurements are shown in Fig. 9. The storage modulus vs. temperature curves have rubbery plateaus typical for thermoplastic elastomers. Above T_g, the modulus drops sharply by two orders of magnitude and then remains almost constant from −10 °C to 50–80 °C for the polyesters and up to over 100 °C for the polycarbonates before the modulus starts to decrease again. Neither the polyester nor the polycarbonate soft segments crystallise so that the onset of the rubbery plateau region is already observed around −10 °C.

3.4. Tensile tests

Elongations at break for films made from polyesters **PE1** and **PE2** were lower than for polycarbonates **PC1** and **PC2** (Table 1), and even the latter still remained below those of related elastomers such as **P1**, which contained a polyether (PTMO) soft segments [5–10,18]. Table 1 also lists the tensile set for each polymer, which were obtained after stretching a sample by 300% at room temperature and then allowing it to relax. This standard test for elastic recovery gave tensile set values of 43% and 33% for polycarbonate elastomers **PC1** and **PC2**, respectively, which was much better than the recovery of the polyesters. The incorporation of a polyester soft segment evidently led to mechanical properties that were noticeably inferior than the two related polymers based on a polycarbonate soft segment.

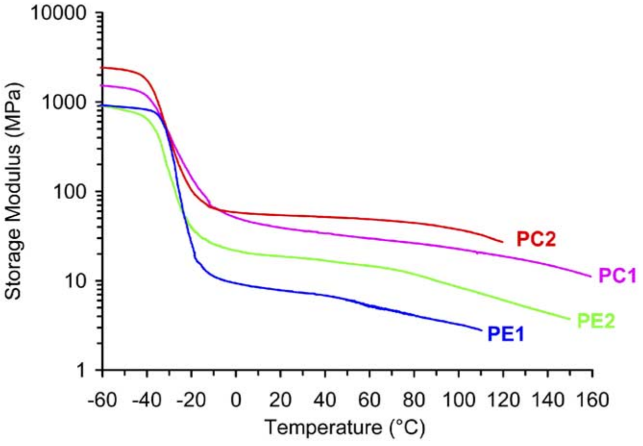


Fig. 9. Dynamic mechanical analysis of polymers **PE1/PE2** and **PC1/PC2**: semilogarithmic plot of storage modulus vs. temperature.

3.5. IR

Hydrogen bonding interactions in these polymers could be studied conveniently by infrared spectroscopy. The NH stretch region is shown in Fig. 10. Polymers **PE2** and **PC2** with their naphthalene-2,6-dicarboxamide-derived hard segments had relatively sharp NH stretches, indicating strong hydrogen bonding in small and well-dispersed domain sizes. In comparison, the NH stretches of polymers **PE1** and **PC1** (both containing terephthalamide hard segments) were noticeably broader.

The C=O stretch region, shown in Fig. 11, is dominated by a strong band for the carbonate (1744 cm^{-1}) or aliphatic ester carbonyl group (1738 cm^{-1}). Two smaller peaks at 1698 cm^{-1} and 1668 cm^{-1} are characteristic for an

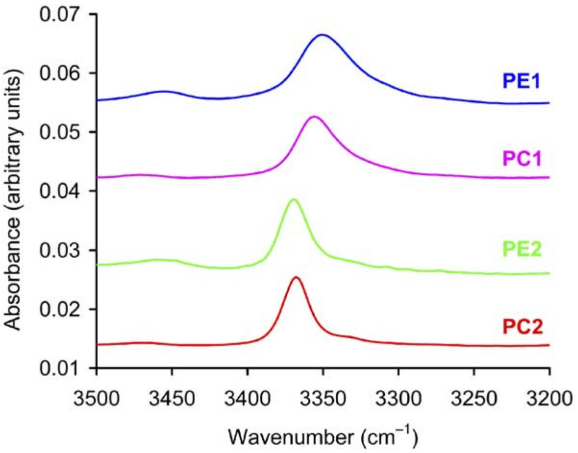


Fig. 10. IR spectra of polymers **PE1–PC2**: N–H stretching region.

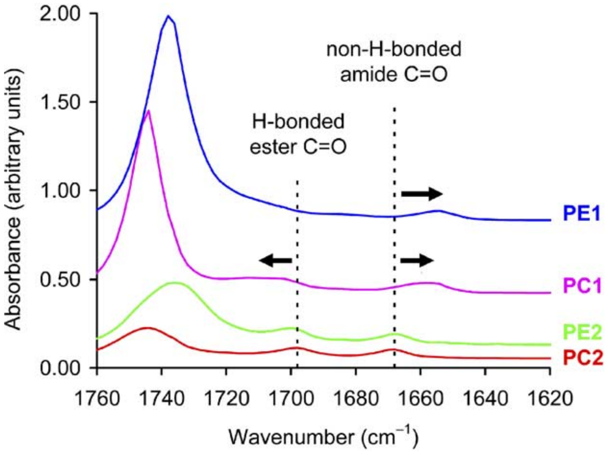


Fig. 11. IR spectra of polymers **PE1**–**PC2**: C=O stretching region.

H-bonded aromatic ester and a non-hydrogen-bonded aromatic amide C=O, both of which form part of the hard segment [18]. The observation of these IR peaks for **PE2** and **PC2** suggests that the naphthalene-2,6-carboxamide unit favours hydrogen bonds between the amide NH and the ester carbonyl group of nearby hard segments [18]. The corresponding amide carbonyl stretches are shifted in **PE1** (1654 cm^{-1}) and **PC1** (1658 cm^{-1}), attesting that a considerable proportion of terephthalamide C=O groups are instead involved in hydrogen bonding.

Our data suggests that at least the naphthalenedicarboxamides are more selective hydrogen-bond donors and have a preference for H-bonding between hard segment NH and C=O groups. The IR data remains inconclusive whether or not H-bonding occurred between the amide NH of the hard segment and carbonyl groups of the soft segment; such hydrogen bonds would increase phase mixing between hard and soft segments. It should be noted that TPUs containing aliphatic polycarbonates as soft segments show strong hydrogen bonds between the more polar carbonate group and the urea/urethane NH, which tend to increase phase mixing and ultimately result in a decrease in the mechanical strength of the TPU [26]. The absence of such deleterious effects on mechanical properties in polycarbonates **PC1** and **PC2** lead us to the conclusion that amide hard segments are not as much involved in hydrogen bonds between hard segment NH and soft segment ester/carbonate C=O groups.

3.6. Influence of the choice of soft and hard segment on elastic properties

At this point it is instructive to compare thermoplastic elastomers having the same aramid (terephthalamide) hard segment but a different soft segment, viz. aliphatic polyester, polycarbonate or polyether (PTMO). The choice of soft segment affects the thermal properties of the polymers, with the T_m of the polymer decreasing in the order PTMO-based elastomer **P1** (212 °C) > polycarbonate **PC1** (197 °C) > polyester **PE1** (152 °C). The low melting temperature of **PE1** was accompanied by a small and broad DSC melting peak. Increased phase mixing is the most likely reason for the poor elastic properties of the polyester.

The storage and loss moduli as a function of temperature are represented in Fig. 12 for the three polymers **PE1**, **PC2** and **P1**. Each polymer shows a maximum in the loss modulus around the glass transition temperature. The temperature-dependence of the storage modulus is typical for thermoplastic elastomers. Below T_g, each polymer has a storage modulus of about 1–2 GPa. Upon heating above T_g, the modulus drops sharply to a rubbery plateau. PTMO-based elastomer **P1** possesses a partially crystalline poly(tetrahydrofuran) soft segment that melts at around 5 °C [18] and, consequently, the onset of its rubbery plateau moves to about +10 °C, well above the T_g (−75 °C) of the polymer. As might be expected, the modulus at room temperature depends on the type of the soft segment. The two polymers with PTMO or poly(ethylene adipate) soft segments possessed a slightly lower rubbery modulus than their analogue **PC1** containing aliphatic polycarbonate soft segments.

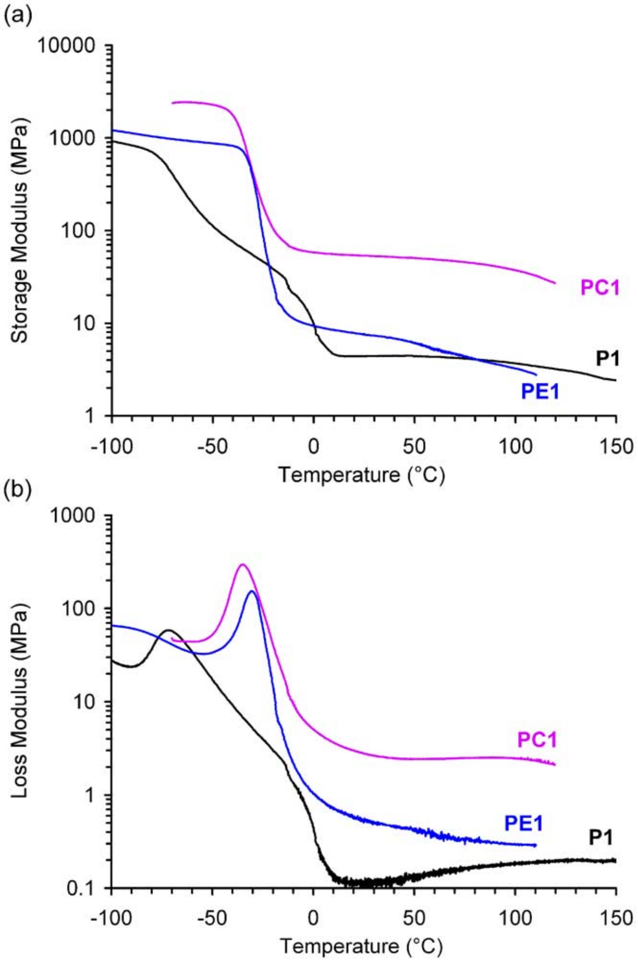


Fig. 12. Temperature dependence of (a) storage modulus and (b) loss modulus for PTMO-based elastomer **P1**, polyester **PE1** and polycarbonate **PC1**.

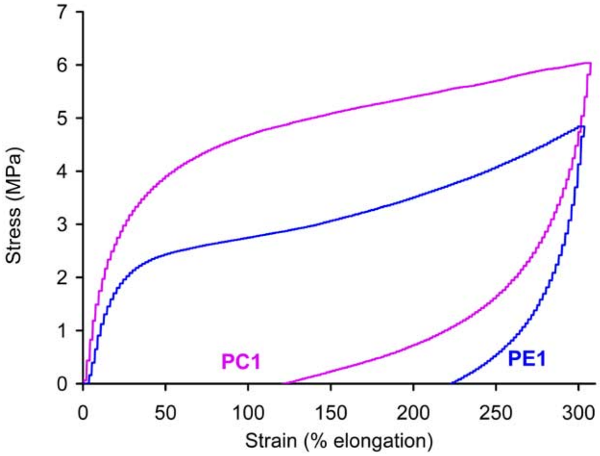


Fig. 13. Stress–strain hysteresis test for polymers **PE1** and **PC1**.

Despite the higher room-temperature modulus of the polycarbonate elastomer, polycarbonate **PC1** displayed good recovery and its tensile set almost competed with that of PTMO-based **P1**. A cyclic tensile test illustrates the superior recovery of elastic energy for polycarbonate **PC1** when compared with polyester **PE1** (Fig. 13).

When the two hard segments are compared instead, the strengthening effect of the naphthalenedicarboxamide over the terephthalamide hard segment is immediately apparent [18]. Polymers with naphthalenedicarboxamide hard segments possess a higher melting temperature than their terephthalamide analogues, stronger hydrogen bonds between amide NH and aromatic ester C=O, a slightly increased room temperature modulus, and a wider temperature range across the rubbery plateau.

4. Conclusions

The new elastomers described here behaved differently from TPUs with the same soft segments. Whereas TPUs with poly(hexamethylene carbonate) soft segments suffer from a high degree of phase mixing that accounts for a deterioration of their elastic properties [27], the replacement of the urethane hard segment by short aramid units led to good elastic recovery when an aliphatic polycarbonate served as soft segment. Surprisingly and unlike the corresponding TPU analogues [1], the combination of short aramid hard segments and poly(ethylene adipate) soft segments gave rather disappointing mechanical properties. The reason for this is as yet unclear.

Polycarbonates **PC1** and **PC2** possessed promising tensile set and elongation at break values. The two polymers are the first examples of thermoplastic elastomers with short aramid hard segments and potentially biodegradable or biocompatible soft segments. Their overall performance was only slightly inferior to analogous PTMO-based polymers (such as **P1**) and a considerable improvement over polymers **PE1** and **PE2** that relied on poly(ethylene adipate) soft segments.

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