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Thermoplastic polyester elastomers based on long-chain crystallizable aliphatic hard segments†

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A plant-oil derived long-chain (C_{23}) α,ω-dicarboxylic acid and the corresponding diol provide entirely aliphatic hard segments in segmented thermoplastic polyester elastomers, with poly(tetramethylene glycol) (PTMG) or carbohydrate-based poly(trimethylene glycol) (PPDO) soft segments. Physical crosslinking is provided by their polyethylene-like crystallinity. Compared to materials derived from mid-chain (C_{12}) analogs, thermal properties are significantly enhanced, with melting points up to 96 °C. These novel materials feature high ductility values in combination with a good elastomeric behavior.

Introduction

Thermoplastic elastomers (TPEs) combine the processing and recyclable characteristics of thermoplastics with the flexibility and ductility of elastomers.[1] They have found widespread applications in *e.g.* electronics, clothing, adhesives and automotive components. Unlike classical vulcanized rubbers they do not possess permanent chemical, but reversible physical crosslinks *via* crystallites. Morphologically, most TPEs are multiphase systems, with one or more types of hard phases and an elastomeric soft phase. Besides blending one possible approach to obtain such microstructures is block copolymerization. Widely used representatives of such block copolymers are styrenic ABA triblock copolymers, such as poly(styrene-*b*-butadiene-*b*-styrene) (SBS) or poly(styrene-*b*-isoprene-*b*-styrene) (SIS) from anionic polymerizations.[2] Recently, analogs based partly or entirely on renewable feedstocks have also been developed.[3] Additionally, AB diblock or ABA triblock copolymers can be synthesized using atom transfer radical polymerization (ATRP).[4] In all these approaches polymerizations are performed in a sequential manner, adding a second monomer after one block has been grown. However, TPEs can also be generated by chain growth polymerization in a single step as illustrated by multiblock copolymers obtained *via* chain-shutting ethylene/1-olefin insertion polymerizations.[5,6]

TPEs are also accessible *via* classical step-growth polymerization of difunctional monomers. For example, thermoplastic polyester elastomers consisting of amorphous poly(tetramethylene glycol) soft phases and crystalline poly(butylene terephthalate) hard segments are applied widely.[7] In these TPEs physical crosslinking is provided by crystallizable aromatic polyester hard segments. Utilization of aliphatic hard segments in such polycondensates – that is exploiting polyethylene-like crystallinity for physical cross-linking – has been prohibited by a lack of access to the required monomers. However, α,ω-difunctional linear long-chain compounds have recently become available from common seed oils or algae oils[8] *via* biotechnological[9] or chemical catalytic routes such as metathesis[10] or isomerizing alkoxycarbonylation.[11] The long methylene sequences originating from complete incorporation of the entire fatty acid chain in these monomers impart a polyethylene-like solid state structure in all-aliphatic polyesters, polycarbonates and polyacetals.[12] We now demonstrate the utility of long-chain aliphatic dicarboxylic acids and diols for the generation of all-aliphatic thermoplastic polyester elastomers.

Results and discussion

Polymer composition and molecular weights

As a diacid component erucic acid-based dimethyl-1,23-tricosanedioate was employed, together with 1,23-tricosanediol generated from the diester *via* catalytic hydrogenation. Dihydroxy-terminated poly(tetramethylene glycol) (PTMG) and poly(trimethylene glycol) (PPDO), respectively, served as diol macromonomers for the generation of soft blocks. Note that both compounds are available industrially from 1,4-butanediol and 1,3-propanediol, respectively, derived from renewable carbohydrate feedstocks.[13,14] Molecular weights of the copolymers obtained amount to M_n 2 to 5×10^4 g mol^{-1} according to end group analysis from ^{1}H NMR spectroscopy. This is qualitatively confirmed by GPC analysis which also shows well behaved molecular weight distributions M_w/M_n around 2 (Table 1). Note that apparent GPC molecular weight *vs.* polystyrene

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Table 1 Polyester–polyether copolymers based on long-chain crystallizable aliphatic hard segments

Entry		mol% polyether diol of total diol	M_n [a] (NMR) [g mol^{-1}]	M_n [b] (GPC) [g mol^{-1}]	M_w/M_n [b]	T_m [c] [°C]	T_c [c] [°C]	Young mod.[e,f] [MPa]	Residual strain[g] [%]
1	TPE-C_{23}PTMG$_{1000}$-73wt%	100% PTMG$_{1000}$	3.8×10^4	10.9×10^4	1.9	40	7/23	n.d.	n.d.
2	TPE-C_{23}PTMG$_{1000}$-62wt%	75% PTMG$_{1000}$	5.0×10^4	11.1×10^4	2.3	44/68[d]	24/44[d]	60	45%
3	TPE-C_{23}PTMG$_{1000}$-48wt%	50% PTMG$_{1000}$	3.4×10^4	10.9×10^4	1.9	87	66	96	41%
4	TPE-C_{23}PTMG$_{1000}$-29wt%	25% PTMG$_{1000}$	5.1×10^4	n.d.	n.d.	96	74	122	100%
5	TPE-C_{23}PTMG$_{2000}$-85wt%	100% PTMG$_{2000}$	4.1×10^4	12.6×10^4	1.9	34	7	n.d.	n.d.
6	TPE-C_{23}PTMG$_{2000}$-77wt%	75% PTMG$_{2000}$	4.0×10^4	8.9×10^4	1.9	30/63[d]	3/37[d]	34	36%
7	TPE-C_{23}PTMG$_{2000}$-65wt%	50% PTMG$_{2000}$	3.8×10^4	11.4×10^4	2.0	23/86[d]	−3/64[d]	38	30%
8	TPE-C_{23}PTMG$_{2000}$-45wt%	25% PTMG$_{2000}$	5.6×10^4	n.d.	n.d.	93	71	78	45%
9	TPE-C_{23}PPDO$_{1000}$-73wt%	100% PPDO$_{1000}$	5.2×10^4	7.1×10^4	1.8	39[d]	25[d]	n.d.	n.d.
10	TPE-C_{23}PPDO$_{1000}$-62wt%	75% PPDO$_{1000}$	2.8×10^4	6.1×10^4	2.0	45/78[d]	38/54[d]	43	39%
11	TPE-C_{23}PPDO$_{1000}$-48wt%	50% PPDO$_{1000}$	2.4×10^4	5.9×10^4	1.8	89	69	50	24%
12	TPE-C_{23}PPDO$_{1000}$-29wt%	25% PPDO$_{1000}$	2.0×10^4	n.d.	n.d.	95	79	125	57%
13	TPE-C_{23}PPDO$_{2000}$-85wt%	100% PPDO$_{2000}$	3.7×10^4	6.7×10^4	1.9	7/24[d]	−7/10[d]	n.d.	n.d.
14	TPE-C_{23}PPDO$_{2000}$-77wt%	75% PPDO$_{2000}$	2.9×10^4	6.4×10^4	1.9	36/77[d]	28/49[d]	11	35%
15	TPE-C_{23}PPDO$_{2000}$-65wt%	50% PPDO$_{2000}$	1.9×10^4	4.3×10^4	2.2	86	67	28	15%
16	TPE-C_{23}PPDO$_{2000}$-45wt%	25% PPDO$_{2000}$	3.0×10^4	n.d.	n.d.	94	78	79	27%

[a] Determined by end-group analysis from ^{1}H NMR spectroscopy. [b] Determined by GPC in THF at 50 °C *versus* polystyrene standards. [c] Determined by DSC with a heating/cooling rate of 10 K min^{-1}. [d] Broad melting and crystallization transitions observed. [e] Tensile tests according to ISO 527/1-2, specimen type 5A prepared by injection molding. [f] Crosshead speed 1 mm min^{-1}. [g] Determined from hysteresis experiments after 10 cycles at an elongation of 100% with a crosshead speed of 50 mm min^{-1}.

standards typically overestimate molecular weights for polymers with hydrocarbon segments.

Thermal properties

Polycondensation of stoichiometric amounts of dimethyl-1,23-trisocanedioate together with only PTMG or PPDO, respectively, yields polyester–polyether copolymers with low melting temperatures of about 40 °C for PTMG and PPDO with a number average molecular weight of about 1000 g mol^{-1} (PTMG$_{1000}$ and PPDO$_{1000}$) and 34 °C or 24 °C for the corresponding polycondensate with PTMG$_{2000}$ or PPDO$_{2000}$ respectively (Table 1, entries 1, 5, 9 and 13. The content of the soft diol in these polymers is 73 and 85 wt%, respectively). The thermal properties of these polymers basically reflect the polyether soft phase as the number of methylene units of the long-chain dicarboxylic component alone is not sufficient to provide significant crystalline domains. In order to increase the portion of the crystalline hard phase, the polyether diol macromonomer was partially replaced by the long-chain aliphatic diol, resulting in significantly increased melt and crystallization temperatures with increasing content of 1,23-tricosanediol (Table 1).

The DSC thermograms obtained for these polymers feature an additional melt peak for the crystalline hard segments, which dominates entirely at a content of the 'soft' polyether-diol of less than 50 wt% (Fig. 1 and S1–S3†). This peak melting temperature of the hard segment (63 °C to 96 °C for PTMG copolymers and 77 °C to 95 °C for PPDO copolymers) is depressed with increasing polyether content. Such a behavior is also observed for TPEs based on crystalline poly(butylene terephthalate) hard segments and poly(tetramethylene glycol) soft phases[15] and can be attributed to the larger amount of crystal imperfections due to the altered microstructure and the consequently less favorable crystallization conditions. Note that for the PPDO containing polymers also a glass transition of the soft block was observable by DSC at *ca.* T_g −65 °C.

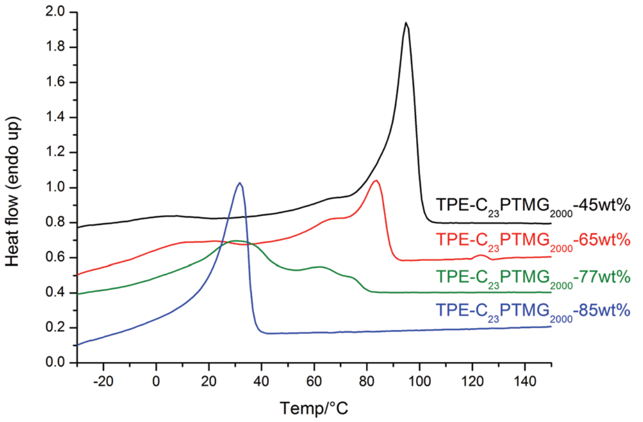

Fig. 1 DSC thermograms (second heating) of polyester–polyether copolymers based on PTMG$_{2000}$.

Mechanical properties

Tensile tests (Table 1) were performed on specimens prepared by piston injection molding. Polymers with relatively low contents of the soft polyether phase behave like semi-rigid thermoplastics, with limited elongation at break (ε_b < 200%) and irreversible deformation (*cf.* entries 4 and 12 with 29 wt% of PTMG$_{1000}$ or PPDO$_{1000}$). However, at higher contents elastomeric behavior is observed, with satisfactory recovery and ε_b up to >1100% (entry 10, Fig. S6†). Young moduli generally decrease with an increasing content of polyether soft segment for all polymer series, as expected (Fig. S7†). At identical

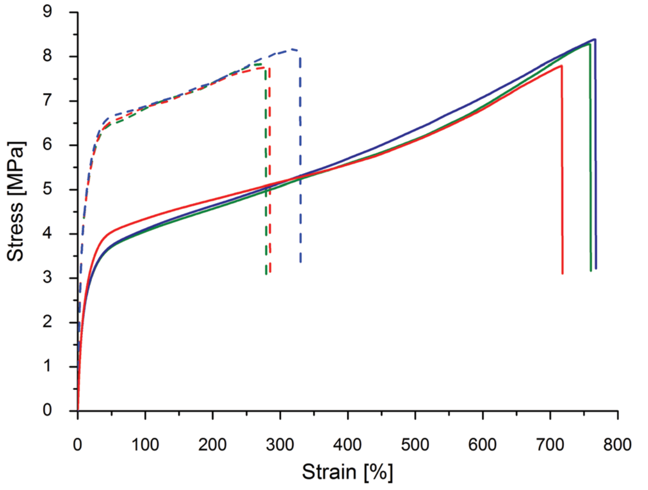

Fig. 2 Stress–strain curves of polyester–polyether copolymers TPE-$C_{23}PTMG_{2000}$-65wt% (dashed line) and TPE-$C_{23}PPDO_{2000}$-65wt% (solid line). Crosshead speed 500 mm min^{-1}.

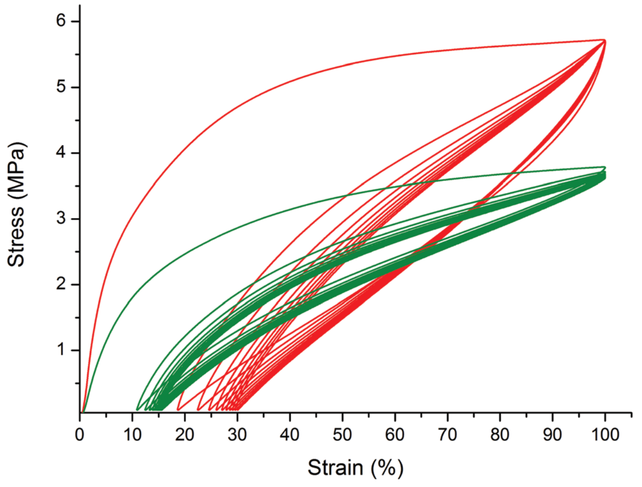

Fig. 3 Stress–strain curves from cyclic tensile tests with a constant strain of 100% for polyester–polyether copolymer TPE-$C_{23}PTMG_{2000}$-65wt% (red) and TPE-$C_{23}PPDO_{2000}$-65wt% (green) (10 cycles) (10 cycles at a crosshead speed of 50 mm min^{-1}).

copolyester mass compositions and chain lengths of the polyether segments (1000 *vs.* 2000 g mol^{-1}), PPDO-copolymers tend to have lower Young's moduli and higher elongations at break *vs.* their PTMG-analogs (also *cf.* Fig. 2).

In order to assess the elastic properties of these new materials cyclic hysteresis tests were performed. Test specimens were repeatedly exposed to consecutive cycles of loading and unloading to a constant strain of 100% (Table 1). Upon cyclic repetition with up to 100 cycles, after the first few cycles, where the residual deformation gradually increases, all TPEs exhibit a virtually constant level of recovery. This behavior is typical for TPEs[1] and can be ascribed to the alignment of the polymer microstructure.[16] After an initial change in morphology, a largely constant structure is adopted and hysteresis is observed (providing the repeated deformation is kept in the same order). For the segmented block copolymers studied here the residual strain (*i.e.* permanent set) after 10 cycles ranges between 30% and 100% for PTMG copolymers and between 15% and 57% for PPDO copolymers (Fig. 3). For both series, copolymers with 50 mol% (of total diol) of polyether soft diol show the smallest residual strain, indicating this to be an optimum ratio of hard and soft segment. Copolymers containing polyether segments of a number average molecular weight of 2000 g mol^{-1} show better elastomeric behavior than the corresponding copolymers with polyether segments of 1000 g mol^{-1}.

Comparison to copolymers based on mid-chain (C_{12}) analogs

In order to further assess the effect of the long hydrocarbon chain of the aliphatic hard segments, polyester–polyether copolymers based on the mid-chain aliphatic monomers dodecanedioic acid and dodecanediol with a comparable weight fraction of polyether diols were prepared (TPE-$C_{12}PTMG_{2000}$-62wt% and TPE-$C_{12}PPDO_{2000}$-62wt%, Table S1†). Considering their chain microstructures, the most relevant difference will be that the shortest 'hard block', *i.e.* an isolated diacid repeat unit, is already twice as large for the long-chain monomer based polyester (C_{23}) *vs.* its mid-chain analog (C_{12}). A statistical consideration of block length distributions (Fig. S14†) shows that these constitute only a relatively small portion of the aliphatic blocks in the polymer composition discussed. Overall, block length distributions are similar at the polymer composition of interest, apart from a slightly higher heterogeneity of the mid-chain polyester due to the large range of block length relevant here.

DSC analysis of TPE-$C_{12}PTMG_{2000}$-62wt% and TPE-$C_{12}PPDO_{2000}$-62wt% showed melting points of 66 °C and 62 °C, respectively, that is 20 °C lower than for their long-chain analogs (Tables 1 and S1†). This can be attributed to a lowering of the cohesion energy by additional ester groups incorporated in the crystalline domains, and larger amount of crystal imperfections caused by the additional ester groups interrupting the crystallizable hydrocarbon chains of the hard segments and the consequent less favorable crystallization conditions.

Mechanical analysis of TPE-$C_{12}PTMG_{2000}$-62wt% and TPE-$C_{12}PPDO_{2000}$-62wt% showed that the lower chain-length of the monomers for the aliphatic hard segment does not result in dramatically different mechanical properties. TPE-$C_{12}PPDO_{2000}$-62wt% exhibited a slightly higher residual strain of 22% and a significantly lower elongation at break (ε_b 240%) than TPE-$C_{23}PPDO_{2000}$-65wt% with ε_b = 750% (Tables 1 and S2; Fig. S8, S9, S12 and S13†).

Experimental

Materials

Toluene was distilled from sodium under inert gas atmosphere. Titanium(IV) tetrabutoxide and dodecane-1,12-diol

(>99%) were supplied by Sigma-Aldrich and *N*,*N*′-di-2-naphthyl-1,4-phenylenediamine (>96%) and dimethyl dodecanedioate (>99%) were purchased from TCI Europe. Poly(tetramethylene glycol) with a number average molecular mass of M_n = 1000 purchased from Sigma-Aldrich and poly(tetramethylene glycol) with a number average molecular mass of M_n = 2000 kindly donated by BASF SE, as well as poly(trimethylene glycol) with a number average molecular mass of M_n = 1000 and 2000 respectively kindly donated by Allessa GmbH were all degassed prior to use. Dimethyl-1,23-tricosanedioate[12d] and tricosane-1,23-diol[12d] were prepared from methyl erucate according to previously reported literature procedures.

Characterization

NMR spectra were recorded on a Varian Inova 400, a Bruker Avance 400 and on a Bruker Avance DRX 600 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-d_2 at 130 °C.

DSC analyses were performed on a Netzsch Phoenix 204 F1 instrument with a heating and cooling rate, respectively, of 10 K min^{-1} in a temperature range of −50 to 160 °C. Data reported are from second heating cycles.

Gel permeation chromatography (GPC) measurements were carried out on a Polymer Laboratories PL-GPC 50 with two PLgel 5 μm MIXED-C columns in THF at 50 °C against polystyrene standards with refractive index detection.

Tensile testing was performed on dogbone-shaped sample bars (75 × 12.5 × 2 mm^3; ISO 527-2, type 5A) which were prepared using a HAAKE Minijet II (Thermo Scientific) piston injection molder. After preconditioning the samples overnight tensile tests were performed on a Zwick Z005 and Zwick 1446 Retroline tC II instrument according to ISO 527 (crosshead speed 50 mm min^{-1} or 500 mm min^{-1}, with a determination of the Young modulus at a crosshead speed of 1 mm min^{-1}). The Zwick test Xpert software version 11.0 was used to collect and analyse the data. Young's modulus, yield stress, yield strain, tensile stress at break and tensile strain at break were obtained by averaging the data from several test specimens.

Cyclic hysteresis tests on dogbone-shaped sample bars (75 × 12.5 × 2 mm^3; ISO 527-2, type 5A) of polyester–polyether copolymers were performed on a Zwick 1446 Retroline tC II instrument. The test specimens were repeatedly exposed to consecutive cycles of loading and unloading to a constant strain of 100% with a constant crosshead speed of 50 mm min^{-1}. The recovery was measured by observing the residual strain after 10 cycles.

General polymerization procedure

Polycondensations were performed under inert gas atmosphere in a 100 mL two-necked Schlenk tube, heated with an aluminum block. The temperature was controlled by a thermocouple in the block. The polymerization mixture was mechanically stirred by a helical agitator. After weighing in the desired amount of monomers (the amount of dimethyl-1,23-tricosanedioate was set to 10 mmol) and 0.05 mol% of *N*,*N*′-di-2-naphthyl-1,4-phenylenediamine, the mixture was degassed and heated to 120 °C. Then, 0.6 mL of a 0.028 M solution of $Ti(OBu)_4$ in toluene was added and the temperature was increased by 10 K every 45 minutes. At a temperature of 180 °C vacuum was applied to remove volatiles. The mixture was then stirred overnight at 200 °C under vacuum.

Conclusions

In summary, polycondensation of dimethyl-1,23-tricosanedioate and 1,23-tricosanediol with diol-terminated PTMG or PPDO yields polyester–polyether copolymers with molecular weights up to M_n 6 × 10^4 g mol^{-1}. The long-chain aliphatic segments provide physical crosslinking that imparts elastomeric behavior to these thermoplastic materials. A particularly high recovery was observed at *ca.* 65 wt% (50 mol% of the total diols employed) of $PTMG_{2000}$ or $PPDO_{2000}$ soft segments, respectively. Compared to mid-chain analogs based on C_{12} aliphatic monomers, melting points are significantly enhanced. This is practically relevant, as the latter materials based on traditional mid-chain monomers appear prone to a softening and loss of their elastomeric properties upon temperature variations within ambient conditions. These novel thermoplastic elastomers rely on the concept of a full incorporation of the entire length of plant oil fatty acids. Also the soft segments are derived from renewable carbohydrate feedstocks.

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