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Influence of type of uniform aromatic amide units on segmented copolyetheresteramides

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Abstract

Segmented copolymers with aromatic bisesterdiamides of uniform length and poly(tetramethyleneoxide) (PTMO) soft segments were synthesized. The following aromatic diamines were used for the bisesterdiamides: *p*-phenylenediamine, *o*-tolidine, 4,4′-diaminodiphenylmethane and *m*-phenylenediamine. The concentration of the bisesterdiamide unit the copolymer ranged from 14 to 19 wt%, depending on the type of bisesterdiamide. The amount of solvent (NMP) needed for the solution/melt polymerization is reduced in this direction. Copolymers with a bisesterdiamide based on *p*-phenylenediamine are fast crystallizing and the bisesterdiamide crystallize nearly completely. As a result, the glass transition temperature is low (−65°C), the melting temperature high is (190°C) and the rubbery plateau is temperature independent. By lowering the structural regularity of the aromatic diamine, the melting temperature and crystallinity were reduced, however, the elasticity increased. In the rubbery modulus–elasticity relationship the type of uniform aromatic bisesterdiamide had little effect. Apart from the polymer based on *p*-phenylenediamine, the polymers were transparent. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Segmented copolymers; Copolyetheresteramides; Bisesterdiamides

1. Introduction

In previous publications it was shown that the segmented copolymer TΦT-(PTMO$_{1000}$/DMT)$_{2000}$ (Fig. 1) possesses very interesting properties for thermoplastic elastomer applications (TPE) as well as for the application as a highly elastic textile fiber [1–3]. The polymer has a low T_g of −65°C, a high melting temperature of 188°C and a nearly temperature independent shear rubbery modulus of about 10 MPa. The strain at break is exceptionally high, at least 1400% combined with a relatively high tensile strength of about 10–30 MPa. The elastic recovery after applied deformation is very good.

This unique combination of properties was attributed to the uniform TΦT crystalline units. Several investigators already concluded that monodisperse hard segments yield fast crystallizing polymers with a very well phase separated morphology [4–7]. In polymers with a good phase separation, most of the hard segments are present in the crystalline phase, offering the possibility to make dimensionally stable polymers with a low hard segment content. The low hard segment content and consequently high soft segment content makes the polymers very elastic. Rigid hard segments, such as the TΦT segments provide a high melting temperature and thus dimensional stability at high temperatures. As was already shown in before, (PTMO$_{1000}$/DMT)$_{2000}$ soft segments yield polymers with an improved low temperature flexibility compared to regular PTMO$_{2000}$ segments, due to the reduced PTMO melting temperature and crystallinity [1].

A major disadvantage of the TΦT–PTMO copolymers is that they can only be synthesized in the presence of a rather large amount of solvent, i.e. NMP. The maximum polymerization temperature is 250°C due to the thermal instability of PTMO [8]. The melting temperature of TΦT-dimethyl is much higher, 371°C and TΦT-dimethyl hardly dissolves in PTMO. Therefore, the use of a solvent during the polymerization cannot be avoided. It would be interesting to find hard segments with similar polymer properties as TΦT units give, but with a lower melting temperature of the starting bisesterdiamide to allow a melt polymerization. Changing the structure of the aromatic diamide segment could also be a way to avoid the typical yellow aramid color of the TΦT–PTMO copolymers which might be negative for certain applications, for instance, elastic fibers for textile uses.

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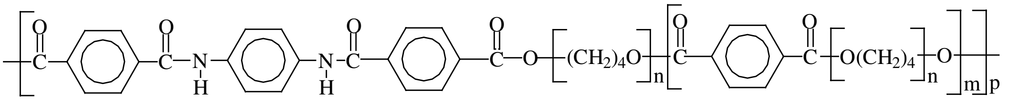

Fig. 1. Structure of TΦT-($PTMO_{1000}$/DMT)$_{2000}$ segmented copolymers.

Gaymans et al. [9] synthesized polyetheresteramides from bisesterdiamides based on 1,4-butanediamine and dimethyl terephthalate which were reacted with PTMO, represented as T4T–PTMO. These polymers are very similar to the TΦT–PTMO copolymers, the only difference being the aliphatic diamine used instead of an aromatic diamine. The melting temperature of T4T-dimethyl is 265°C. A melt polymerization was possible since at 250°C, T4T-dimetyl dissolves a little in PTMO. As soon as the transesterification had started, the solubility of the T4T in PTMO improved. The mechanical properties of T4T–PTMO were almost comparable to TΦT–PTMO. The phase separation was only slightly worse. The melting temperature of the polymers was, however, much lower, for instance, T4T–$PTMO_{2000}$ has a melting temperature of 135°C compared to 191°C for TΦT–$PTMO_{2000}$. T2T–PTMO (based on 1,2-ethanediamine) copolymers synthesized by Mangnus [10] and Bouma [11] have an even lower melting temperature, for instance, the melting temperature of T2T-($PTMO_{1000}$/DMT)$_{2000}$ is 87°C.

From the results described above it is concluded that in order to obtain high melting segmented copolymers with diamide segments, the use of fully aromatic uniform hard segments cannot be avoided. The melting temperature of TΦT-dimethyl is very high, 371°C, making a melt polymerization of TΦT-($PTMO_{1000}$/DMT)$_{2000}$ impossible. The question is whether the type of aromatic diamine can be changed to obtain lower melting aromatic bisesterdiamides, in order to reduce the amount of solvent needed for the polymerization, without changing the thermal and mechanical properties of the polymer too much. In this study the effect of the type of diamine in the aromatic bisesterdiamide on the synthesis and properties of TαT–($PTMO_{1000}$/DMT)$_{2000}$ segmented copolymers (α represents the diamine used) is investigated. Four different diamines were compared (Fig. 2).

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), *p*-phenylenediamine (PPA), *m*-phenylenediamine (MPA), 4,4′-diamino diphenylmethane (MDA), anhydrous methanol and *N*-methyl-2-pyrrolidone (NMP) were purchased from Merck. *o*-Tolidine (TOL) was purchased from Aldrich. Tetraisopropyl orthotitanate ($Ti(i\text{-}OC_3H_7)_4$), obtained from Merck, was diluted in anhydrous *m*-xylene (0.05 M), obtained from Fluka. Methyl(4-chlorocarbonyl)benzoate (MCCB) was obtained from Dalian (No. 2 Organic Chemical Works, P.R.O.C.), Poly(tetramethyleneoxide) (PTMO, $M = 1000$ g/mol) was provided by DuPont and Irganox 1330 (3,3′,3″,5,5′,5″-hexa-tert-butyl-A,A′,A″-(mesitylene-2,4,6-tyriyl)tri-*p*-cresol) was obtained from CIBA. All chemicals were used as-received.

2.2. Synthesis of aromatic bisesterdiamides

The CA index name of TΦT-dimethyl is benzoic acid, 4,4′-[1,4-phenylenebis(iminocarbonyl)]bis-, dimethyl ester, no. 56419-58-0.

As a typical example, the synthesis of TΦT-dimethyl is given. For the synthesis of TmΦT-dimethyl, PPA was replaced by MPA, for TmdaT-dimethyl by MDA and for TtolT-dimethyl by TOL.

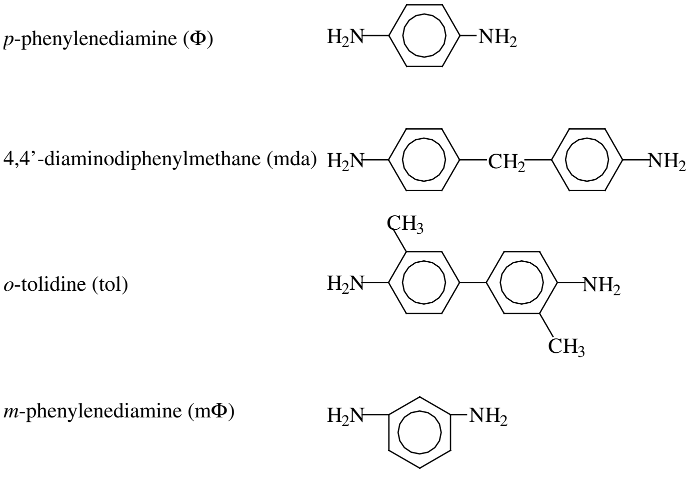

Fig. 2. Different diamines used for bisesterdiamides.

MCCB (61 g, 0.31 mol) was dissolved in 400 ml NMP at room temperature in a 1 l flask, equipped with mechanical stirrer, nitrogen inlet, condenser and calcium chloride tube. PPA (15 g, 0.14 mol), previously dissolved in 200 ml NMP, was added dropwise over a period of 30 min, and methanol (50 ml) was added after a 2 h reaction time. The bisesteramide precipitate and, two hours later the suspension, was filtered off in a soxhlet extraction thimble and washed with hot toluene, and twice with hot acetone. In the case of TmΦT-dimethyl, the product was precipitated with an excess of acetone, prior to washing with toluene and acetone. The product was subsequently dried in a vacuum oven at 70°C.

2.3. Polymerization

The preparation of TΦT-(PTMO$_{1000}$/DMT)$_{2000}$ is shown as an example. The reaction was carried out in a 250 ml stainless steel vessel with a nitrogen inlet and mechanical stirrer. The vessel, containing TΦT-dimethyl (4.32 g, 0.01 mol), PTMO$_{1000}$ (18.8 g, 0.0188 mol), DMT (1.7 g, 0.0088 mol), Irganox 1330 (0.2 g), and 100 ml NMP was heated in an oil bath to 180°C, then the catalyst solution was added (1.8 ml of 0.05 M Ti(i-OC$_3$H$_7$)$_4$ in m-xylene). After 30 min reaction time, the temperature was raised to 250°C and maintained for 2 h. The pressure was then carefully reduced ($P < 20$ mbar) to distill off NMP and then further reduced ($P < 1$ mbar) for 60 min. Finally, the vessel was allowed to slowly cool to room temperature whilst maintaining the low pressure.

For the polymerization with the different bisesterdiamides the following amounts of TαT-dimethyl and NMP were used: TΦT-dimethyl (4.32 g, 0.01 mol) in 100 ml NMP, TmΦT-dimethyl (4.32 g, 0.01 mol) in 20 ml NMP, TmdaT-dimethyl (5.22 g, 0.01 mol) in 30 ml NMP and TtolT-dimethyl (5.36 g, 0.01 mol) in 40 ml NMP.

2.4. NMR

^{1}H NMR spectra were recorded on a Bruker AC 250 - spectrometer at 250.1 MHz, with deuterated trifluoroacetic acid (TFA-d) being used as a solvent without an internal standard. TΦT-dimethyl does not dissolve in TFA and therefore deuterated sulfuric acid (D$_2$SO$_4$) was used as the solvent without internal standard for TΦT-dimethyl.

2.5. DSC

DSC spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. 2-5 mg of dried bisesterdiamide sample was heated at a rate of 20°C/min. The onset of the melting peak was used as the melting temperature, the peak area was used to calculate the melt enthalpy.

2.6. Viscometry

The inherent viscosity of the polymers at a concentration of 0.1 g/dl in a 1/1 (molar ratio) mixture of phenol/1,1,2,2-tetrachloroethane at 25°C, was determined using a capillary Ubbelohde 1B.

2.7. FTIR

Infrared transmission spectra were recorded using a Biorad FTS-60. Samples of bisesterdiamide or polymer were mixed with KBr and tablets were pressed.

2.8. DMA

Samples for the DMA test ($70 \times 9 \times 2$ mm^3) were prepared on an Arburg H manual injection molding machine. The barrel temperature of the injection molding machine was set at 50°C above the melting temperature of the polymer, while the mold temperature was kept at room temperature.

Using a Myrenne ATM3 torsion pendulum at a frequency of approximately 1 Hz the values of the storage modulus G' and the loss modulus G'' as a function of the temperature were measured. Dried samples were first cooled to -100°C and subsequently heated at a rate of 1°C/min with the maximum of the loss modulus being taken as the glass transition temperature. The flow temperature was defined as the temperature where the storage modulus reached 1 MPa.

2.9. Tensile testing

Samples for the tensile tests were prepared by melt extruding the polymers into threads on a 4cc DSM res RD11H-1009025-4 corotating twin screw mini extruder. The extruder temperature was set at 60°C above the flow temperature of the polymers, while the screw speed was kept constant at 30 rpm. The threads were winded at a speed range from 20–50 m/min. The titer (expressed in tex $= 10^{-6}$kg/m) of the threads was measured by carefully weighing 1 m of thread. The density of the polymers was determined in hexane and turned out to be approximately 1 g/cm [3].

Tensile tests were carried out on a Zwick Z020 universal tensile machine equipped with a 10 N load cell, the strain being measured as the clamp displacement. Stress–strain curves were obtained at a strain rate of 250 mm/min, the starting clamp distance being 25 mm. The tensile set was determined by applying a 300% cyclic strain at a strain rate of 200 mm/min, the starting clamp distance being 50 mm. The strain in the second cycle, where the force becomes positive again, was taken as the residual strain. The tensile set (TS$_{300\%}$) was defined as:

$$\mathrm{TS}_{300\%} = \frac{\text{residual strain}}{300} 100\% \tag{1}$$

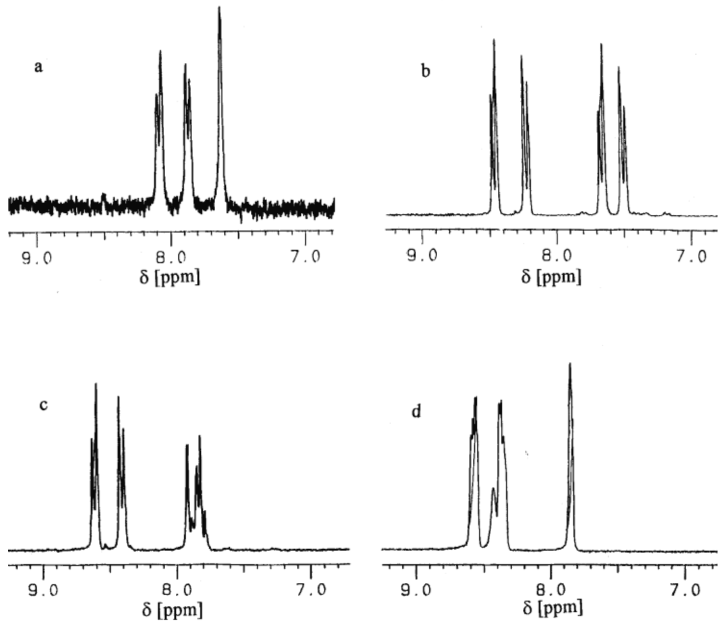

Fig. 3. ^{1}H NMR scan of aromatic peaks of bisesterdiamides: (a) T*Φ*T-dimethyl (D_2SO_4); (b) TmdaT-dimethyl (TFA-d); (c) TtolT-dimethyl (TFA-d); (d) Tm*Φ*T-dimethyl (TFA-d).

2.10. Stress relaxation

Samples (injection molded test bars) for the stress relaxation experiments were similar to those used for DMA. Stress relaxation was measured on a Zwick Z020 universal tensile machine equipped with a 500 N load cell, the strain being measured as the clamp displacement with a starting clamp distance of 40 mm. The samples were strained to 25 or 100% within 5 s at room temperature. The decay of the stress was measured during 30 min. As a measure of the stress relaxation ($SR_{x\%}$), the absolute value of the slope of the line, obtained from the stress plotted versus the logarithm of time, was used (Eq. (2))

$$SR_{x\%} = \frac{|\Delta\sigma_{x\%}|}{\Delta \log t} \tag{2}$$

2.11. Compression set

A piece of an injection molded test bar, similar to those

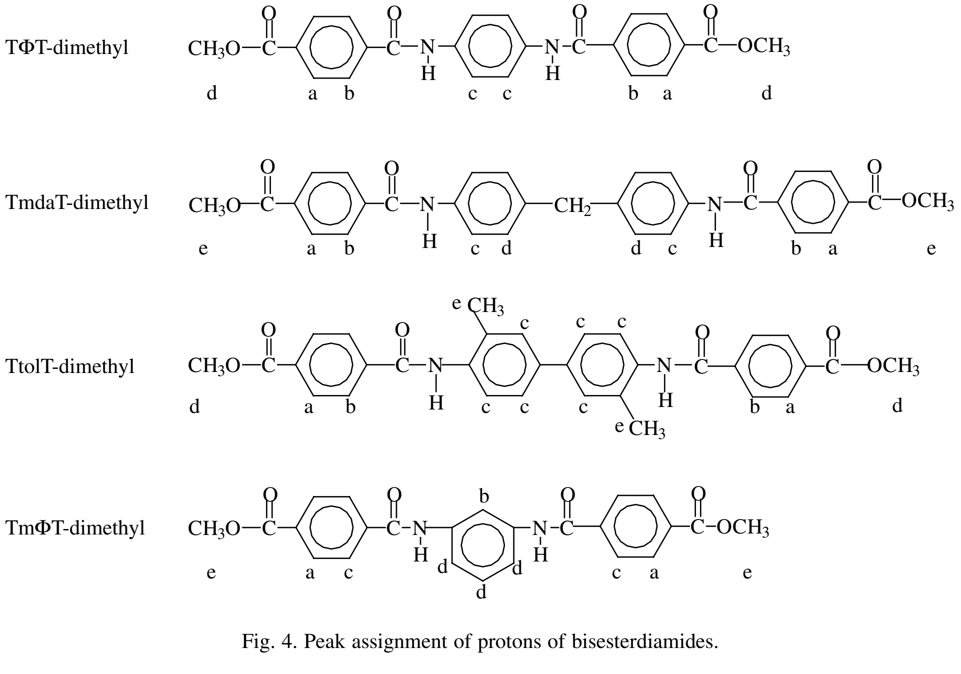

Fig. 4. Peak assignment of protons of bisesterdiamides.

Table 1
Chemical shifts δ of protons of bisesterdiamides

Compound	Peak	Chemical shift δ (ppm)	Type	Description	Integral
TΦT-dimethyl	a	8.0–8.1	Doublet	Terephthalic **H**, ester side	1
Solvent: D_2SO_4	b	7.8–7.9	Doublet	Terephthalic **H**, amide side	1
	c	7.6	Singlet	Aromatic PPA **H**	1
	c′	7.5	Singlet	Free aromatic PPA **H**	
	d	4.3	Singlet	**CH**$_3$ peak	1.5
TmdaT-dimethyl	a	8.4–8.5	Doublet	Terephthalic **H**, ester side	1
Solvent: TFA-d	b	8.2–8.3	Doublet	Terephthalic **H**, amide side	1
	c	7.6–7.7	Doublet	Aromatic MDA **H**, amide side	1
	c′	7.5	Singlet	Free aromatic MDA **H**, amide side	
	d	7.4–7.5	Doublet	Aromatic MDA **H**, CH$_2$-side	1
	e	4.3	Singlet	**CH**$_3$ peak	2
	f	4.2	Singlet	**CH**$_2$ peak	0.67
TtolT-dimethyl	a	8.5–8.6	Doublet	Terephthalic **H**, ester side	1
Solvent: TFA-d	b	8.2–8.3	Doublet	Terephthalic **H**, amide side	1
	c	7.7–8.0	Multiplet	Aromatic TOL **H**	1.5
	c′	7.6	Multiplet	Free aromatic TOL **H**	
	d	4.3	Singlet	**CH**$_3$ peak	1.5
	e	2.6	Singlet	TOL **CH**$_3$ peak	1.5
TmΦT-dimethyl	a	8.5–8.6	Doublet	Terephthalic **H**, ester side	1
solvent: TFA-d	b	8.4	Singlet	Aromatic MPA **H**	0.25
	c	8.3–8.4	Doublet	Terephthalic **H**, amide side	1
	d	7.8	Singlet	Aromatic MPA **H**	0.75
	d′	7.7	Singlet	Free aromatic MPA **H**	
	e	4.3	Singlet	**CH**$_3$ peak	1.5

used for DMA was placed between two steel plates and compressed to 1 mm (≈55% compression). After 24 h at room temperature or at 70°C, the compression was released at room temperature. One hour later, the thickness of the sample was measured. The compression set was defined as:

$$\text{Compression set} = \frac{d_0 - d_2}{d_0 - d_1} 100\% \tag{3}$$

where d_0 is the thickness before compression (mm), d_1 the thickness during compression (mm), and d_2 is the thickness 1 h after release of compression (mm).

3. Results and discussion

Segmented copolymers with crystallizable aromatic bistesterdiamide units and amorphous $(\text{PTMO}_{1000}/\text{DMT})_{2000}$ segments were synthesized. The concentration of the bisesterdiamide in the copolymer ranged from 14 to 19 wt%, depending on the type of bisesterdiamide. The dynamic mechanical properties, tensile properties and elastic properties were studied. The bisesterdiamides are abbreviated as TαT-dimethyl, in which α represents the diamine.

Table 2
Results from bisesterdiamide syntheses

Bisesterdiamide	Yield (%)	Purity (%)	T_m (°C)	ΔH_m (J/g)
TΦT-dimethyl	86	96	371	241
TmdaT-dimethyl	48	98	314	133
TtolT-dimethyl	78	98	318	84
TmΦT-dimethyl	80	98	314	145

3.1. Bisesterdiamide synthesis

The bisesterdiamides were synthesized from the mono acid chloride methyl(4-chlorocarbonyl)benzoate and an aromatic diamine. The purity of the compounds was determined with ^{1}H-NMR. In Fig. 3a–d, enlargements of the aromatic region of the ^{1}-NMR scans of the different bisesterdiamides are given. Fig. 4 shows the peak assignment of the different protons of the bisesterdiamides and in Table 1 the chemical shifts of the different protons are given.

The purity of the bisesterdiamides is very important as it affects the uniformity of the crystalline lamellae. The chemical shifts of the proton atoms of the phenyl rings depend on the substitution by amide and ester groups. The ratio between terephthalic proton on the amide side and the aromatic amide protons are taken as a measure of the purity. The purity is calculated according to Eqs. (4a)–(4d). If Tα is present peak c′ or peak d′.

$$\text{T}\Phi\text{T-dimethyl}: \quad \text{purity} = \left(2 - \frac{\text{b}}{\text{c}}\right) \times 100\% \tag{4a}$$

$$\text{TmdaT-dimethyl}: \quad \text{purity} = \left(2 - \frac{\text{b}}{0.5(\text{c} + \text{d})}\right) \times 100\% \tag{4b}$$

Table 3
DMA and FTIR results of TαT-(PTMO$_{1000}$/DMT)$_{2000}$ segmented copolymers (ν: stretch vibration of NH in polymer and in TαT-dimethyl (hard); y: yellow; c: colorless; t: transparent)

Hard segment	Soft segment length (g/mol)	TαT (wt%)	Color	η_{inh} (dl/g)	T_g (°C)	T_{fl} (°C)	$T_{fl}-T_m^{hard}$ (°C)	G'(25°C) (MPa)	$\nu_{NH}^{polymer}$ (cm^{-1})	ν_{NH}^{hard} (cm^{-1})
TΦT	2026	14	y,t	2.00	−65	189	182	11	3442	3341
TmdaT	1985	19	c,t	2.22	−65	148	202	8	3422	3324
TtolT	1987	19	c,t	2.03	−67	125	166	7	3442	3376
TmΦT	1997	14	c,t	1.95	−65	112	193	6	3445	3324

$$\text{TtolT-dimethyl}: \ \text{purity} = \left(2 - \frac{\text{b}}{0.67\text{c}}\right) \times 100\% \qquad (4c)$$

$$\text{Tm}\Phi\text{T-dimethyl}: \ \text{purity} = \left(2 - \frac{\text{c}}{\text{b}+\text{d}}\right) \times 100\% \qquad (4d)$$

In Table 2 the results of the syntheses of the different aromatic bisesterdiamides are given.

The yield of the reaction is mainly influenced by the solubility of the product in NMP, the reaction solvent. The solubility increases in the following direction: TΦT-dimethyl < TtolT-dimethyl < TmdaT-dimethyl < TmΦT-dimethyl. TΦT-dimethyl precipitated easily, while TmΦT-dimethyl did not precipitate at all during reaction. Therefore an excess of acetone was added at the end of the TmΦT-dimethyl reaction to collect the product. The yield of TmdaT-dimethyl and TtolT-dimethyl can be increased by also adding acetone at the end of the reaction. All the compounds were pure (purity >96%, within the accuracy of NMR).

The melting temperature of TΦT-dimethyl is higher than of the other bisesterdiamides. The melting enthalpy of TtolT-dimethyl is significantly lower than of TmΦT-dimethyl and TmdaT-dimethyl, while the melting temperatures of these three compounds are comparable. Since $T_m = \Delta H_m/\Delta S_m$, the melting entropy of TtolT-dimethyl must also be lower than of TmΦT-dimethyl and TdmaT-dimethyl. Probably, the methyl side groups of TtolT-dimethyl limit the rotation possibilities of the molecules in the melt, resulting in a relatively low entropy in the melt and consequently a low ΔS_m.

3.2. Polymerization

The polymers were synthesized from the aromatic bisesterdiamides, dimethyl terephthalate and PTMO$_{1000}$. The polymerization consists of a transesterification, followed by a polycondensation. For the transesterification a solvent (NMP) was needed because of the high melting temperatures of the aromatic bisesterdiamides (314–371°C), combined with the maximum reaction temperature of 250°C due to thermal instability of PTMO above this temperature [8]. To prevent degradation of PTMO during polymerization and subsequent melt processing Irganox 1330 was added as a stabilizer (1 wt%). The amount of solvent (NMP) needed for the transesterification was drastically lowered going from TΦT- (25 ml/g), TtolT- (10 ml/g), TmdaT- (7.5 ml/g) to TmΦT-dimethyl (5 ml/g). Unfortunately, the use of some solvent could not be avoided yet. During the transesterification, methanol was formed and stripped off. At the end of the transesterification, the melting temperature of the reaction mixture was reduced below 250°C and therefore, the NMP was distilled off at low vacuum (<20 mbar). Than the pressure was reduced further to carry out the polycondensation in the melt. During the polycondensation, more methanol was distilled off and high molecular weight polymers were formed. The soft segment length (PTMO$_{1000}$/DMT) was checked with ^{1}NMR, according to the method given in a previous publication [1]. All the polymers were colorless and transparent, except for the polymer containing TΦT, which was transparent and gold–yellow, the typical aramid color.

3.3. Thermal properties

In Table 3, the soft segment lengths, inherent viscosities, DMA results and the stretch vibration of the amide NH of the polymers and of the bisesterdiamides are shown. The inherent viscosity of the polymers was high, over 1.9 dl/g, indicating that the molecular weights were also high. With DSC no melting and crystallization peaks were found. The DMA results, however, clearly show the presence of a crystalline bisesterdiamide phase. The crystallinity in these polymers is at most 13% (TαT wt%), which is quite low. As the polyether phase does not crystallize, the lamellar thickness is the length of the aramid unit, approximately 2 nm.

The strength of the hydrogen bond of the amide was investigated with infrared spectroscopy. In general, a reduction of amide association leads to an increase of the N–H stretch frequency [13]. The stretch vibration frequency of the amide was comparable for all the polymers ($\approx$3440 cm^{-1}), suggesting that the different amide units have the same –NH···OC– distance in the polymers. The frequency of the amide units in the polymers was, however, higher than for the separate bisesterdiamides, which indicates that the packing of the amide units is worse when they are incorporated in the polymers than in the pure bisesterdiamides. The NH stretch frequency of TtolT-dimethyl is somewhat higher than of the other bisesterdiamides, therefore it can be concluded that the hydrogen bonds in TtolT-dimethyl are a little longer than in the other

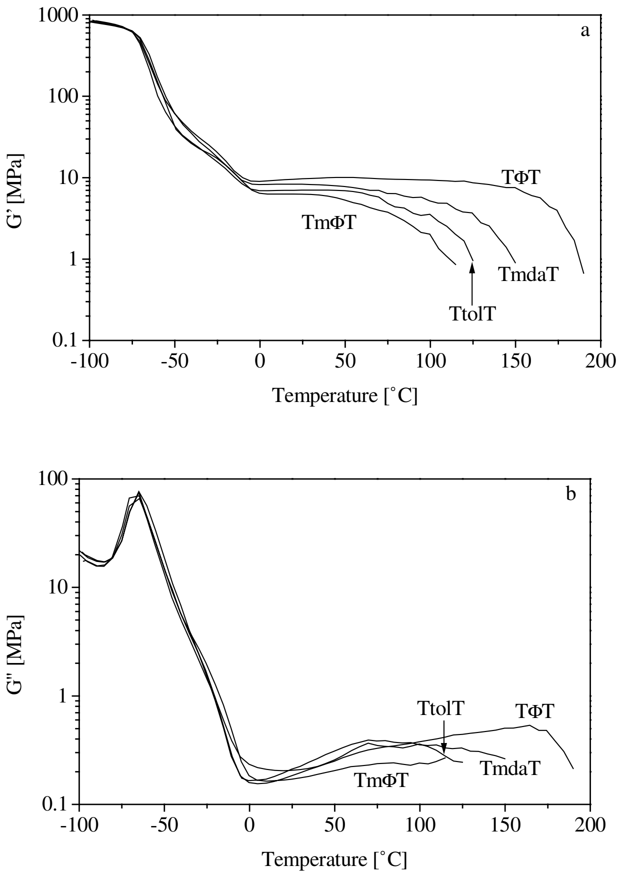

Fig. 5. (a) Storage modulus (G') versus temperature and (b) loss modulus (G'') versus temperature of TαT-(PTMO$_{1000}$/DMT)$_{2000}$ segmented copolymers.

bisesterdiamides. This can be explained by the steric hindrance of the methyl groups on the phenyl rings of the diamine, limiting the association of the molecules.

In Fig. 5a and b, the storage modulus (G') and loss modulus (G'') of the polymers versus temperature are shown.

Fig. 5 shows a low and sharp glass transition temperature of −65°C, for all the polymers. Apparently, the phase separation between the uniform amide hard segments and the PTMO based soft segments is very good and independent of the type of aromatic diamine used. As shown before, the (PTMO$_{1000}$/DMT)$_{2000}$ segments hardly crystallize [1]. Normally, linear PTMO segments with a molecular weight above 1000 g/mol are known to crystallize just around room temperature [8]. PTMO crystallinity in these polymers is visible as a shoulder that appears in the drop of the modulus at the glass transition. In Fig. 5a such a shoulder is still present, but it is very small and lies below zero degrees Celsius. Replacing PTMO$_{2000}$ by (PTMO$_{1000}$/DMT)$_{2000}$ thus gives polymers with an excellent low temperature flexibility. By looking carefully at Fig. 5b, a second maximum in the loss modulus (G'') is observed at a temperature of about 70–100°C, especially for the TtolT copolymer and also for the TmdaT copolymer. This suggests that in these polymers some glassy hard domains exits, next to the crystalline hard domains. The morphology of these polymers is therefore more complicated: instead of a two-phase material (crystalline hard segments and amorphous soft segments) a three phase morphology exists: crystalline hard segments, glassy hard segments and amorphous soft segments. A crystalline PTMO phase is hardly present.

The modulus in the rubbery plateau (G'(25°C) declines going from TΦT > TmdaT > TtolT > TmΦT from 11 to 6 MPa, suggesting a decrease in hard segment crystallization. Incomplete hard segment crystallization, normally leads to an increase of the T_g of the amorphous phase since amorphous hard segments that are miscible with the PTMO phase, reduce the PTMO mobility. However, an increase of the T_g with varying hard segments was not observed. Maybe, the non-crystalline hard segments are (partly) immiscible with the PTMO segments and assemble to form glassy domains within the PTMO amorphous phase. The second maximum in the G'' near 70–100°C confirms the formation of glassy hard domains.

The flow temperature, which indicates the onset of melting, decreases from 189°C to 112°C with varying hard segment. Generally, the melting temperature of the bisesterdiamides is lowered when they are incorporated in a polymer. This decrease is explained by the solvent effect as described in a previous publication [12,14].

3.4. Tensile properties

In general, segmented copolymers such as copolyetheresters or polyurethanes possess a high tensile strain comparable to chemically crosslinked rubbers ranging from 500–800%. Their tensile stress is higher than of chemically crosslinked rubbers, i.e. 20–50 MPa for copolyetheresters and polyurethanes and 10–30 MPa for chemically crosslinked rubbers [15].

In Table 4 an overview of the tensile properties of the segmented copolyetheresteramides, described in this study is given. The tensile properties were studied on melt extruded threads. During extrusion and winding process, some orientation might have occurred, but this effect is under the used conditions minimal [3].

All polymer possess an extremely high strain of break (λ_b) of at least 13 (1200%), much higher than usual for segmented copolymers. This was attributed to the thin amide lamellae which are more easily deformed than thick lamellae [2]. The molecular weight of the polymer has a strong effect on the strain of break as well as the fracture stress (Table 4). The fracture stress depends too on whether the polyether phase strain hardens [2]. The fracture stresses of the polymers are high, except for the polymer with TtolT. This last result is as yet unexplained, but is thought to be due to the high extrusion temperature of this material.

In the studied polymers the G' modulus and the yield stress varied with the type of diamide which is thought to be due to difference in crystallinity. In the TΦT–PTMO polymers the crystallinity has an effect on both the modulus

Table 4
Tensile properties of melt extruded threads of TαT-(PTMO$_{1000}$/DMT)$_{2000}$ copolymers (σ_b: yield stress, σ_b: fracture stress, λ_b: fracture strain)

Hard segment	TαT (wt%)	η_{inh} (dl/g)	G'(25°C) (MPa)[a]	σ_y (MPa)	σ_b (MPa)	λ_b
TΦT	14	1.10	12	6.0	31	14.8
TΦT	14	1.83	11	6.0	37	15.3
TΦT	14	2.20	10	5.9	51	18.3
TmdaT	19	2.19	8	4.5	54	17.2
TtolT	19	1.58	7	4.0	13	16.8
TmΦT	14	1.93	6	3.6	38	13.2

[a] Measured with DMA on injection molded test bars.

Table 5
Elastic properties: Stress relaxation (SR) at 25 and 100% strain, compression set (55%) at room temperature and 70°C, tensile set after 300% strain

Hard segment	η_{inh} (dl/g)	SR$_{25\%}$	SR$_{100\%}$	Compression set, 55%, $T_{20°C}$ (%)	Compression set, 55%, $T_{70°C}$ (%)	Tensile set, 300% (%)
TΦT	2.00	0.22	0.47	22	42	25
TmdaT	2.22	0.22	0.41	26	54	21
TtolT	2.03	0.21	0.27	32	60	33
TmΦT	1.95	0.17	0.29	23	62	16

and the yield stress and in these polymers a linear relationship is observed between the log modulus and yield stress (Fig. 6) [2]. Our polymers seem to follow this relationship too. This suggest that the crystallinity of the aramide unit is dependant on the type of diamine used.

3.5. Elastic properties

Besides a high tensile strain and relatively high tensile stress, one of the most interesting mechanical properties of segmented copolymers is their elasticity, i.e. their elastic response to large deformations. For applications as a thermoplastic elastomer (TPE), the materials must be able to resist strains up to 100%, with the lowest permanent deformation possible. As a measure of this type of elasticity, the stress relaxation and the compression set were determined. The results are shown in Table 5. In an ideal elastomer, no stress relaxation occurs, because there is no plastic deformation. Generally, a lower stress relaxation corresponds with a lower permanent deformation [16]. The stress relaxation was defined as the absolute value of the slope of the line plotting the stress versus the logarithm of time ($\sigma - \log t$ plot) at a certain strain (25 and 100%). The compression set was defined in such a way that a low residual deformation results in a low compression set.

For the stress relaxation at 25% strain, which is near the yield strain, no differences in our polymers were observed. At 100% strain, which is well above the yield point, a decrease of the stress relaxation with the yield stress was found. The less crystalline material is more elastic.

The compression set of 55% compression at room temperature is almost independent of the type of hard segment. Only the compression set of the polymer containing TtdaT is somewhat higher than of the rest of the polymers. At 70°C, the polymer with TΦT had the lowest compression set. If the compression sets are compared to the rubbery plateaus in Fig. 5a, it is clear that for all the polymers, except for the polymer with TΦT, the dimensional stability is already decreasing at 70°C. This explains the relatively low compression set value of TΦT-(PTMO$_{1000}$/DMT)$_{2000}$ at 70°C compared to the other polymers.

For the application as a textile elastic fiber, the residual deformation at high deformation (i.e. 300%) is an important parameter. In Table 5 the set after 300% tensile deformation of melt extruded threads is given (TS$_{300\%}$). In Fig. 7 the tensile set is plotted versus the logarithm of the shear rubbery modulus for the TαT-(PTMO$_{1000}$/DMT)$_{2000}$ series and for TΦT-(PTMO$_{1000}$/DMT) series with increasing soft segment length.

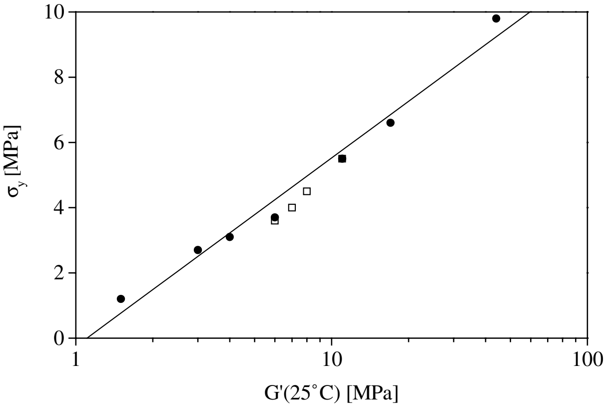

Fig. 6. Yield stress versus the logarithm of the shear rubbery modulus for (□) TαT-(PTMO$_{1000}$/DMT)$_{2000}$ and (●) TΦT-(PTMO$_{1000}$/DMT) segmented copolymers, values from Ref. [2].

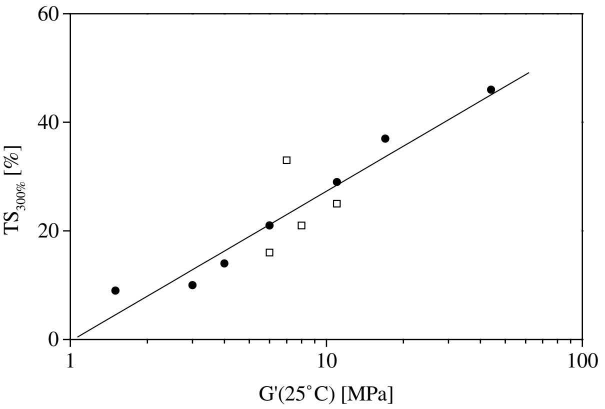

Fig. 7. Tensile set after 300% strain as function of the logarithm of the shear rubbery modulus for (□) TαT-(PTMO$_{1000}$/DMT)$_{2000}$ and (●) TΦT-(PTMO$_{1000}$/DMT), values from Ref. [2].

A linear trend between the tensile set and logarithm of the shear rubbery modulus for the TΦT-PTMO$_{1000}$/DMT copolymers exists. The decrease of the tensile set with decreasing modulus is explained by a decrease in the TΦT content and hence decrease in crystallinity. The tensile set values of TαT-(PTMO$_{1000}$/DMT)$_{2000}$ seem to follow the trend of the TΦT containing polymers. The changes in the tensile set values with modulus between the different TαT-(PTMO$_{1000}$/DMT)$_{2000}$ copolymers are hence explained by differences in crystallinity. (TmdaT-(PTMO$_{1000}$/DMT)$_{2000}$ has a comparable rubbery modulus as TΦT-(PTMO$_{1000}$/DMT)$_{3000}$ ($G(25°C) = 8$ and 6 MPA respectively) and their elastic properties, such as stress relaxation, compression set and tensile set are also comparable. The advantages of the TmdaT polymers over TΦT polymers are the reduced amount of solvent needed for the polymerization (7.5 versus 25 ml/g) and the color, polymers with TmdaT are white/colorless, while polymers with TΦT are gold–yellow. The disadvantage, however, is the lower flow temperature of TmdaT-(PTMO$_{1000}$/DMT)$_{2000}$ (148°C) compared to TΦT-(PTMO$_{1000}$/DMT)$_{3000}$ (172°C).

4. Conclusion

Different aromatic diamines (α) have been incorporated into TαT-(PTMO$_{1000}$/DMT)$_{2000}$ segmented copolymers. The TαT content in the copolymers was only 14–19 wt%. The amount of solvent needed for the polymerization was reduced strongly by replacing *p*-phenylenediamine with *o*-tolidine, 4,4-$'$diaminodiphenylmethane or *m*-phenylenediamine. The typical gold–yellow aramid color was also avoided in this way. Although the glass transition temperature of the PTMO phase was not affected by the type of diamine used, the melting temperature and crystallinity were reduced. TΦT–PTMO copolymers possess a two phase morphology: a crystalline TΦT-phase and an amorphous PTMO phase. The other TαT copolymers seemed to have a more complicated morphology: beside a crystalline phase consisting of very thin TαT crystalline lamellae (approximately 2 nm) and an amorphous PTMO phase, there were glassy TαT domains present. The rubbery modulus varied with different hard segments between 6–11 MPa, suggesting different degrees of crystallinity. The tensile stress of the polymers was not affected by the type of hard segment used, but mainly by the molecular weight of the polymers and the strain induced crystallization of the PTMO phase. The fracture strain of the polymers was always high, as a result of the uniform hard segments. The yield stress varied with the different diamines, probably due to differences in crystallinity. Differences in recovery after applied deformation appear above the yield strain and the recovery improves if the modulus is decreased. At 70°C, however, the polymers with a lower melting temperature already showed a reduction in dimensional stability and consequently a high compression set. TmdaT-dimethyl could be an alternative for TΦT-dimethyl. Less solvent is needed for the polymerization and the polymers are colorless. The melting temperature of polymers containing TmdaT units is not lowered too much compared to TΦT containing polymers, while the modulus is lowered and consequently the elasticity is improved.

References

[1] Niesten MCEJ, Ten Brinke JW, Gaymans RJ. Polymer (submitted).
[2] Niesten MCEJ, Gaymans RJ. Polymer (in press).
[3] Niesten MCEJ, Krijgsman J, Gaymans RJ. Chem Fibers Int 2000;50(3):256–60.
[4] Harrell LL. Macromolecules 1969;2(6):607–12.
[5] Ng HN, Allegrazza AE, Seymour RW, Cooper SL. Polymer 1973;14:255–61.
[6] Eisenbach CD, Baumgartner M, Gunter G. In: Lal L, Mark JE, editors. Advances in elastomer and rubber elasticity, Proceedings Symposium, vol. 51. New York: Plenum Press, 1985.
[7] Miller JA, Shaow BL, Hwang KKS, Wu KS, Gibson PE, Cooper SL. Macromolecules 1985;18(1):32–44.
[8] Dreyfuss P, Dreyfuss MP, Pruckmayr G. In: Mark, Bikales, Overberger, Menges, editors. Encyclopedia of polymer science and engineering, vol. 16. New York: Wiley, 1989. p. 649–76.
[9] Gaymans RJ, de Haan JL. Polymer 1993;34(20):4360–4.
[10] Mangnus R. Terephthalamide-PTMO segmented copolymers with a uniform block length, Twaio report, University of Twente, 1992.
[11] Bouma K, Wester G, Gaymans RJ. J Appl Sci (in press).
[12] Niesten MCEJ, Feijen J, Gaymans RJ. Polymer 2000 (in press).
[13] Skrovanek DJ, Howe SE, Painter PC, Coleman MM. Macromolecules 1985;18(9):1676–83.
[14] Flory PJ. Trans Faraday Soc 1955;51:848–57.
[15] Grady BP, Cooper SL. In: Mark JE, Erman B, Eirich FR, editors. Science and technology of rubber. San Diego, CA: Academic Press, 1978 (chap. 13).
[16] Kubát J, Rigdahl M. In: Browstow W, Corneliussen RD, editors. Munich: Hanser, 1986 (chap. 4).