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Segmented copolyetheresteraramids with extended poly(tetramethyleneoxide) segments

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Abstract

Segmented copolymers with crystallizable uniform *p*-phenyleneterephthalamide ester units and soft poly(tetramethyleneoxide) (PTMO) segments were synthesized by polycondensation. Long PTMO (>1000 g/mol) segments are known to crystallize around room temperature which reduces the low temperature flexibility of the copolymers. The PTMO crystallization was reduced by incorporating chemical irregularity. $PTMO_{1000-9000}$ segments having a reduced tendency to crystallize are formed by extending $PTMO_{650}$ or $PTMO_{1000}$ with dimethyl terephthalate or dimethyl isophthalate. Furthermore modified PTMO segments (PTMOm: 15 wt% of methyl side groups) were used. The thermal and dynamic mechanical properties of the copolymers were studied with DSC and DMA, respectively. In addition, the PTMO crystallization was studied with synchrotron WAXS measurements. PTMOm segments melt about 20°C lower than PTMO. $PTMO_{1000}$, DMT and DMI extended $PTMO_{1000}$ and PTMOm strain crystallize reversibly, while $PTMO_{1400}$ and longer strain crystallize irreversibly. Reversible strain-induced crystallization of the PTMO phase gives the polymers a relatively high tensile strength combined with a good recovery from tensile deformation. The glass transition temperature of the polymers is not increased by incorporation of the stiff terephthalic or isophthalic units in the PTMO phase. The *p*-phenyleneterephthalamide ester units crystallize fast and nearly completely due to their uniform length. Even at a concentration of only 3 wt% of *p*-phenyleneterephthalamide ester units dimensionally stable polymers with a relatively high melting temperature were formed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Segmented copolymers; Poly(tetramethyleneoxide); Copolyetheresteramides

1. Introduction

The properties of segmented copolymers with poly(tetramethyleneoxide) (PTMO) soft segments are affected by the length of the PTMO segment [1]. PTMO segments of 1000 g/mol or shorter are amorphous, while PTMO segments longer than 1000 g/mol crystallize just around room temperature [2], limiting the low temperature flexibility and elasticity of the copolymer. PTMO crystallization increases upon straining (strain-induced crystallization), resulting in strain hardening. Polymers showing strain hardening have an upturn in the stress–strain curve and a relatively high tensile strength. In a previous publication [7], it was shown that TΦT–PTMO segmented copolymers (Fig. 1) with long PTMO segments (M > 1000 g/mol) possess a low and temperature independent modulus over a wide temperature range. A low modulus is interesting for applications in which a high elasticity is desirable. At low temperatures (−30–20°C), however, the modulus of TΦT–PTMO copolymers with PTMO segments longer than 1000 g/mol was increased due to PTMO crystallization in this temperature range.

Morbitzer and Hespe [3] reported that crystallization of the polyol (polyesters or polyethers) in polyurethane elastomers could be surpressed by incorporating sufficient chemical irregularity, for instance by using copolyesters or by incorporating bulky diphenylmethane-4,4′-diisocyanate (MDI) units in the polyol. Abhiraman [4] surpressed the crystallization of poly(oxyethyleneglycol) by building in hydantoin moieties. Greene et al.[5,6] reported the use of copolymers of tetrahydrofuran and 3-methyltetrahydrofuran as soft segments (PTMO, PTMOm) for segmented copolymers. It was claimed that incorporation of 3–20 mol% of PTMOm gives segmented copolymers with improved tensile set values without loss of the tensile strength compared to polymers with only PTMO soft segments.

The aim of this study is to synthesize segmented

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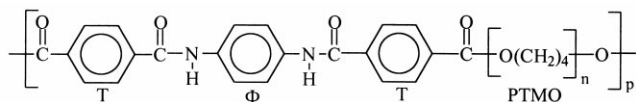[1] Present address: Hutsman Polyurethanes, Everberg, Belgium.

Fig. 1. Structure of TΦT–PTMO segmented copolymers.

copolyetheresteramides with long PTMO based soft segments being elastic even below room temperature while still possessing a high tensile strength through strain hardening. For this purpose TΦT based polymers with different types of PTMO were synthesized. Four different types of PTMO are compared: PTMO, PTMO extended with dimethyl terephthalate (PTMO/DMT), PTMO extended with dimethyl isophthalate (PTMO/DMI) and modified PTMO (PTMOm, PTMO containing 15 wt% of methyl side groups) (Fig. 2). Extending PTMO with DMT or DMI is a way to make long PTMO blocks from short PTMO segments.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), Dimethyl isophthalate (DMI) and N-methyl-2-pyrrolidone (NMP) were purchased from Merck. Tetraisopropyl orthotitanate u(Ti(i-OC$_3$H$_7$)$_4$), obtained from Merck, was diluted in anhydrous *m*-xylene (0.05 M), obtained from Fluka. TΦT-dimethyl (the dimethyl ester of TΦT) was synthesized as described in in a previous publication [7]. Poly(tetramethyleneoxide) ((PTMO, $M = 250 - 2900$ g/mol) was provided by DuPont and modified PTMO (PTMOm, PTMO containing 15 wt% of methyl side groups $M = 2000$ g/mol) from Mitsui. 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. Polymerization

All polymers were synthesized according to route I described in a previous publication [7]. TΦT-dimethyl was synthesized according to route II of the TΦT-dimethyl synthesis described in a previous publication [7]. 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$_7$)$_4$). 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.

2.3. NMR

^{1}H NMR spectra of the polymers were recorded on a Bruker AC 250 spectrometer at 250.1 MHz. Deuterated trifluoroacetic acid (TFA-d) was used as a solvent without an internal standard.

2.4. 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 sample was heated at a rate of 20°C/min. The first cooling and second heating scan were used to determine the melting and crystallization peaks of the polymers. For the melt-extruded threads, the first heating scan was used to determine the melting peak. The peak maximum or minimum was used as the melting or crystallization temperature, respectively, the peak area as the enthalpy.

2.5. 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 Ubbelhode 1B.

2.6. 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, with the mold temperature being held 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 then 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.

2.7. Synchrotron WAXS

Synchrotron WAXS measurements were performed on unoriented melt extruded polymer threads during straining at a straining rate of 10^{-2} s^{-1} at the ESRF in Grenoble (France) on ID11. The wavelength of the beam was 0.1 nm. Every 30 s a measurement was done with an exposure time of 10 s.
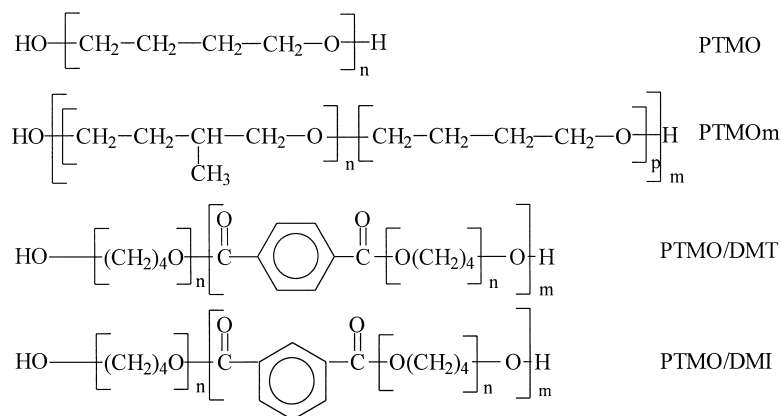
Fig. 2. Structure of different types of PTMO.

3. Results and discussion

3.1. Introduction

Polymers with different types of PTMO based soft segments were synthesized according to polymerization route I described in a previous publication [7]. Four different types of PTMO are compared: PTMO, PTMO extended with dimethyl terephthalate (PTMO/DMT), PTMO extended with dimethyl isophthalate (PTMO/DMI) and modified PTMO (PTMOm). Extending PTMO with DMT or DMI is a way to make longer PTMO blocks from short PTMO segments. The structure of the different segments is given in Fig. 2.

All the polymers possess a homogeneous melt during the polycondensation. PBT–PTMO copolymers are known to melt phase during polymerization at certain polymer compositions [8]. Melt phasing will inhibit the formation of high molecular weight polymers. In Fig. 3, melt phasing
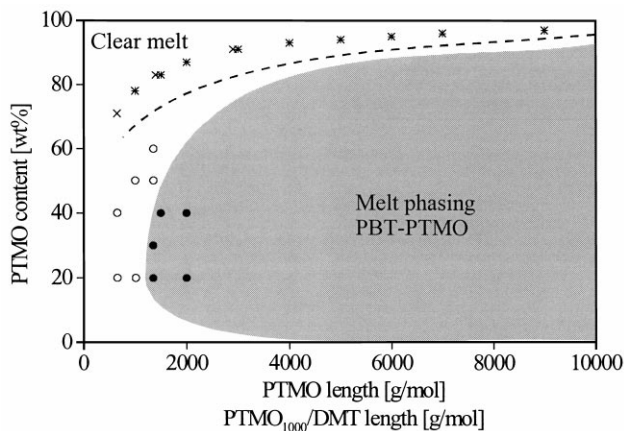

Fig. 3. Melt phasing in polycondensations as function of PTMO or (PTMO$_{1000}$/DMT) content and length for: (●,○) PBT–PTMO [8]; (x) TΦT–PTMO; (*) TΦT–(PTMO$_{1000}$/DMT), the melt phasing region of PBT–PTMO is indicated, the dotted line indicates the expected melt phasing transition of TΦT–PTMO and TΦT–PTMO$_{1000}$/DMT) copolymers.

of PBT–PTMO polycondensations as a function of the PTMO content and length is shown. In PBT–PTMO copolymers melt phasing is enhanced by decreasing the PTMO content and increasing the PTMO length. In these systems, increasing the PTMO content while keeping the PTMO length constant results in an increase of the PBT segment length. Longer PBT segments melt phase at a lower concentration than short PBT segments. The TΦT units are of uniform thickness and cannot become longer. During the polycondensation of TΦT–PTMO copolymers a homogeneous melt was obtained at all compositions. Apparently, the PTMO content in TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) copolymers is always high enough to avoid melt phasing and consequently high molecular weight PTMO segments can be used without melt phasing to occur. Using uniform TΦT crystallizable units, PTMO$_{1000}$/DMT segments up to a molecular weight of 9000 g/mol can be built into the polymer without the problem of melt phasing. To illustrate this, the points of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) are included in Fig. 3. The melt phasing region of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) probably lies at a somewhat different polymer composition compared to PBT–PTMO, indicated by the dotted line.

3.2. Determination of PTMO length in copolymers

For convenience, the PTMO molecular weight is used as a measure of the PTMO length. In other words, a PTMO length of, for instance, 1000 g/mol originates from PTMO segments with a molecular weight of 1000 g/mol. The length of the PTMO segments follows that of the starting commercial PTMO and PTMOm.

Since DMT and DMI are always incorporated between two PTMO segments, the average soft segment length was calculated according to Eq. (1)

$$M_{\text{soft}} = nM_{-(CH_2)_4O-} + (n-1)M_{\text{terephthalic/isophthalic}} \text{ [g/mol]}$$

(1)

In this formula, n represents the number of $-(CH_2)_4O-$

Fig. 4. Aromatic region of ^{1}H NMR spectra of: (a) TΦT–(PTMO$_{1000}$/DMT); (b) TΦT–(PTMO$_{1000}$/DMI).

repeat units in a PTMO segment and *M* the molecular weight of a $-(CH_2)_4O-$ unit, a terephthalic unit or an isophthalic unit. The assumptions are made that the trans-esterification rate of all the ester groups is equal. The calculated soft segment length is an average soft segment length. It is expected that the soft segment length distribution will hardly affect the polymer properties [9]. During polymerization, some DMT or DMI might have sublimed. This will lower the molecular weight (η_{inh}) of the polymer due to a lack of stoichiometry and it will affect the average soft segment length. The amount of DMT or DMI incorporated in the polymers was checked with ^{1}H NMR by looking at the integral ratio of the TΦT aromatic peaks and the terephthalic or isophthalic aromatic peaks. In Fig. 4, the aromatic region of the ^{1}H NMR spectra of: (a) a DMT containing polymer; and (b) a DMI containing polymer are given. In high molecular weight polymers the end groups are not visible with ^{1}H NMR. Therefore, the length of DMT extended PTMO and DMI extended PTMO was calculated from the molar ratio between TΦT and the

terephthalic or isophthalic groups in the copolymers, according to Eq. (2a and b)

$$M_{PTMO/DMT} = \frac{I_b}{I_a} M_{terephthalic} + \left(\frac{I_b}{I_a} + 1 \right) M_{PTMO} \text{ [g/mol]}$$

(2a)

$$M_{PTMO/DMT} = \frac{I_{a+b+f}}{I_c} M_{isophthalic} + \left(\frac{I_{a+b+f}}{I_c} + 1 \right)$$
$$\times M_{PTMO} \text{ [g/mol]}$$

(2b)

In this formula, *I* represents the integral of a peak and *M* the molecular weight of PTMO, terephthalic or isophthalic groups in the polymer. It turned out that the pre-calculated (Eq. (1)) soft segment lengths agreed well with the soft segment lengths calculated via Eq. (2a and b). Hence, it is concluded that DMT and DMI hardly sublimes during the reaction and are built in the copolymers in the pre-calculated amounts.

Table 1
DSC and DMA properties of TΦT–(PTMO based segment)$_{2000}$(subscript s refers to soft segment)

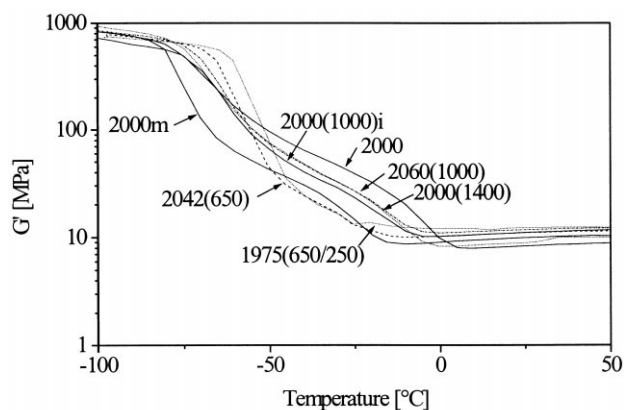| PTMO type	η_{inh} (dl/g)	$T_{m,s}$ (°C)	$\Delta H_{m,s}$ (J/g)	$T_{c,s}$ (°C)	$\Delta H_{c,s}$ (J/g)	T_g (°C)	T_{fl} (°C)	G'(25°C) (MPa)
PTMO$_{2000}$	2.50	0	17	−39	−13	−65	191	9
PTMO$_{2000m}$	2.38	−20	11	–	–	−75	193	10
(PTMO$_{1400}$/DMT)$_{2018}$	2.34	−6	16	−42	−7	−67	194	12
(PTMO$_{1000}$/DMT)$_{2060}$	2.13	−10	14	−48	−5	−65	188	12
(PTMO$_{650}$/DMT)$_{2042}$	1.84	–	–	–	–	−65	198	11
(PTMO$_{650/250}$/DMT)$_{1975}$[a]	1.35	–	–	–	–	−61	200	12
(PTMO$_{1000}$/DMI)$_{2043}$	1.61	−8	8	−46	−6	−65	189	11

[a] 1/1 molar mixture of PTMO$_{650}$ and PTMO$_{250}$.

Fig. 5. Enlargement of the region around T_g of the shear storage modulus versus temperature for TΦT–(PTMO based segments)$_{2000}$.

3.3. Influence of the PTMO structure on the PTMO crystallinity

A series of polymers with different PTMO based soft segments having a constant soft segment length of 2000 g/mol was synthesized (Fig. 2). In Table 1, the DSC and DMA properties of these polymers are given. In the first place, Table 1 clearly shows that the shear rubbery modulus ($G'(25°C)$) and the flow temperature (T_{fl}, the onset of melting) are hardly affected by the type of PTMO based soft segment used. The glass transition temperature of the polymers is in most cases $-65°C$ and it is not influenced by incorporating stiff terephthalic or isophthalic units in the PTMO phase. The methyl-side groups of PTMO$_{2000m}$ decrease the T_g to $-75°C$.

The melting temperature, melting enthalpy and crystallization enthalpy of the PTMO phase ($T_{m,s}$, $\Delta H_{m,s}$, $\Delta H_{c,s}$) are reduced going from PTMO$_{2000}$ to DMT extended PTMO$_{1400}$, PTMO$_{1000}$, PTMO$_{650}$ and PTMO$_{650/250}$. The reduction of PTMO crystallinity is illustrated in a shear modulus (G') versus temperature plot (Fig. 5). PTMO crystallinity is

visible as a shoulder that appears in the drop of the modulus just after the glass transition temperature and below room temperature. The polymer with PTMO$_{2000}$ possesses the largest shoulder and hence has the highest PTMO crystallinity. The PTMO crystallinity is reduced using DMT extended PTMO. DMT extended PTMO$_{650}$ and DMT extended PTMO$_{652/250}$ are hardly crystalline. The crystallinity of DMI extended PTMO$_{1000}$ is comparable to (PTMO$_{1000}$/DMT)$_{2000}$ or maybe slightly lower. In Fig. 5, the curve of PTMO$_{2000m}$ is horizontally shifted to lower temperatures compared to PTMO$_{2000}$. PTMO$_{2000m}$ melts about 20°C lower than PTMO$_{2000}$, which was also measured with DSC. Consequently, the low temperature flexibility of polymers with PTMO$_{2000m}$ is improved compared to polymers with PTMO$_{2000}$ since the rubbery plateau starts at a lower temperature. The crystallinity ($\Delta H_{m,s}$) of PTMO$_{2000m}$ is lowered somewhat compared to PTMO$_{2000}$.

To conclude, polymers with DMT or DMI extended PTMO show a reduced crystallinity and consequently an improved low temperature flexibility compared to polymers with PTMO. PTMOm is crystalline below 0°C, melting at a lower temperature than PTMO and therefore induces an improved low temperature flexibility.

3.4. The effect of strain on the PTMO melting temperature

Strain-induced crystallization of the PTMO phase yields polymers with a high tensile strength. Strain-induced crystallization can negatively influence the elasticity, especially if the crystallization starts at strains below 300% strain. The PTMO crystallinity caused by straining was studied with DSC and WAXS. In Fig. 6, a DSC diagram of unoriented and oriented (1000% pre-strained) melt extruded threads of TΦT–PTMO$_{1000}$ and TΦT–PTMO$_{2000}$ are shown. The PTMO melting peaks are indicated by arrows. On orienting TΦT–PTMO$_{2000}$, the PTMO melting temperature peak sharpens and shifts to a higher temperature ($-3 \rightarrow 45°C$). The increase of the melting temperature

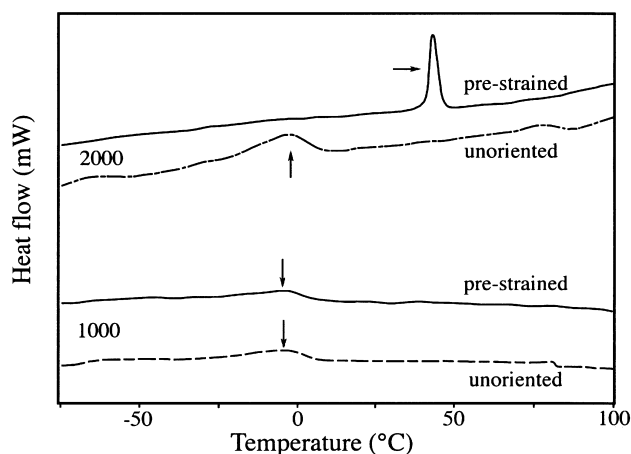Fig. 6. PTMO melting peaks of unoriented and 1000% pre-strained TΦT–PTMO$_{1000}$ and TΦT–PTMO$_{2000}$.
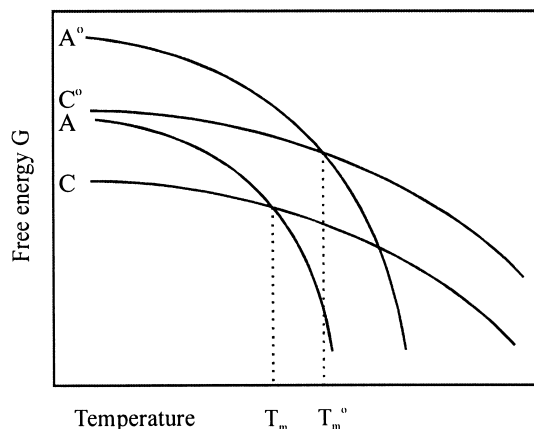

Fig. 7. Schematic representation of increase of melting temperature upon straining due to changes in the free energy G of the crystalline (C) and amorphous (A) PTMO phases, superscript ° means oriented.
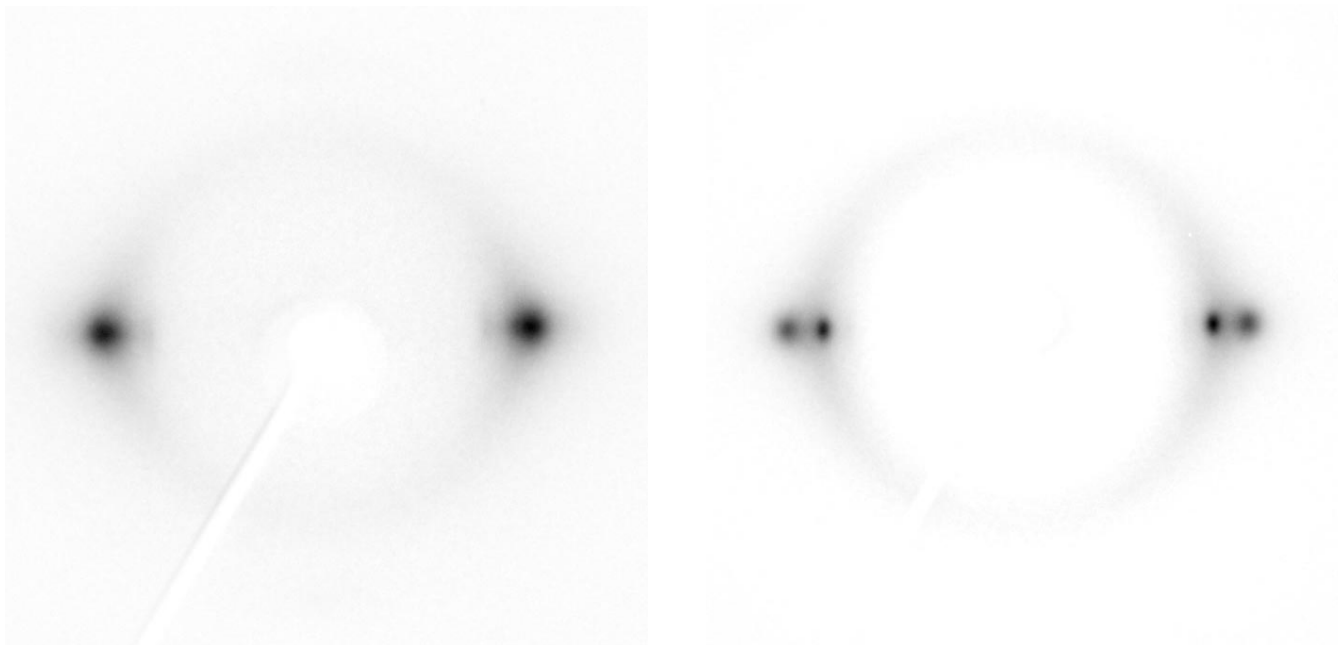
Fig. 8. Synchrotron WAXS pictures of TΦT–PTMO$_{1000}$ (left) and TΦT–PTMO$_{2000}$ (right) at 1000% strain, black dots originate from PTMO crystallinity.

due to straining is caused by changes in the free energy of the crystalline and amorphous phase [10,11]. Schematically, this phenomenon is illustrated in Fig. 7. The melting temperature is at the intersection point of the free energy of the crystalline phase (C) and amorphous phase (A). If the polyether phase in the segmented copolymer is oriented as a result of straining both the free energy of the crystalline (C$'$) and the amorphous phase (A$'$) increases and as a result of this the melting temperature. One should bear in mind that in these segmented copolymers the orientation of the polyether does not relax on melting as the structure is fixed by the crystalline aramid phase. After releasing the strain, the melting temperature is lowered again, but as long as the increased melting temperature during straining is far above room temperature, the melting temperature of the oriented and unstrained PTMO will remain above room temperature.

The PTMO$_{1000}$ melting peak is broad and below 0°C, no difference between the melting peak of the unoriented and the oriented sample is observed (Fig. 6). This suggests that the melting temperature of strain-induced crystallized PTMO$_{1000}$ is just above room temperature during straining. Hence, after releasing the strain the melting temperature shifts to a temperature below room temperature and consequently the strain-induced PTMO crystals melt. Synchrotron WAXS measurements of TΦT–PTMO$_{1000}$ threads taken during straining, clearly show the presence of a PTMO$_{1000}$ crystalline phase, although less crystalline than TΦT–PTMO$_{2000}$, at 1000% strain (Fig. 8). From these observations, it is concluded that PTMO$_{1000}$ undergoes reversible strain-induced crystallization, i.e. it crystallizes during straining, but melts when the strain is released. This phenomenon is also observed for some rubbers such as *cis*-

polybutadiene and *cis*-polyisoprene [12,13]. In Table 2, the values for T_m and ΔH_m of several unoriented and oriented polymers is given. Of all these polymers synchrotron WAXS measurements during straining were done (not shown, compare Fig. 8). PTMO segments of 1400 g/mol and longer strain crystallize irreversibly. All PTMO$_{1000}$ based soft segments and PTMO$_{2000m}$ undergo reversible strain-induced crystallization.

3.5. Thermal properties of TΦT–(PTMO$_{1000}$/DMT) copolymers

To compare the thermal properties of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) copolymers a series of polymers with PTMO$_{1000}$/DMT soft segments was synthesized. The soft segment length was varied from 1000 to 9000 g/mol. In Table 3, the properties of the TΦT–(PTMO$_{1000}$/DMT) and TΦT–PTMO copolymers are given. TΦT–(PTMO$_{1000}$/DMT)$_{2000}$ copolymers with TΦT contents below 17 wt% are transparent, suggesting that the TΦT crystallites are smaller than the wavelength of visible light in all directions (<50 nm). Similar polymers with non-extended PTMO are not transparent due to the presence of the relatively large PTMO crystals.

In Fig. 9, the shear storage modulus (G') versus temperature is given for TΦT–(PTMO$_{1000}$/DMT). For all the polymers the drop of the modulus at the T_g is very sharp and independent of the soft segment length, suggesting that the TΦT concentration in the amorphous polyether phase is negligible. The nearly temperature independent rubbery modulus and the sharp flow transition are explained by the uniform TΦT segment that form perfect crystals which melt in a narrow

Table 2
T_m and ΔH_m of unoriented and oriented (1000% pre-strained) polymer threads

Polymer	Unoriented		After straining 1000%	
	$T_{m,s}$ (°C)	$\Delta H_{m,s}$ (J/g)	$T_{m,s}$ (°C)	$\Delta H_{m,s}$ (J/g)
TΦT–PTMO$_{1000}$	–	–	–	–
TΦT–PTMO$_{1400}$	−8	14	40	13
TΦT–PTMO$_{2000}$	−3	27	43	28
TΦT–PTMO$_{2900}$	−2	24	47	43
TΦT–PTMO$_{2000m}$	−25	12	−18	13
TΦT–(PTMO$_{1000}$/DMT)$_{2060}$	−5	17	−4	13
TΦT–(PTMO$_{1000}$/DMT)$_{2982}$	−3	19	1	26
TΦT–(PTMO$_{1000}$/DMI)$_{2055}$	−9	15	−6	13
TΦT–(PTMO$_{1000}$/DMI)$_{3140}$	−1	24	3	24

temperature range. Even at a soft segment length of 9000 g/mol, corresponding to only 3 wt% TΦT, a relatively large rubbery plateau is formed. Apparently, the TΦT segments crystallize very easily and nearly complete, even at low concentrations. To compare the thermal properties of TΦT–(PTMO$_{1000}$/DMT) and TΦT–PTMO, the T_{fl}, T_g and $T_{m,s}$ are plotted versus the soft segment length for these two series of polymers in Fig. 10. From Fig. 10, it is very clear that incorporating DMT in the amorphous PTMO phase does not increase the T_g. The T_{fl} does decrease with increasing soft segment length, and thus decreasing TΦT content. The melting temperature depression of the TΦT-segments upon copolymerization with soft segments is explained by the solvent effect as desribed by Flory [14]. The melting temperature of crystalline PTMO increases with increasing PTMO length. Generally, the melting temperature of a polymer increases with the crystalline size (lamellar size)[15]. Longer PTMO segments have an improved long-range order, facilitating the formation of larger crystals. No PTMO melting peak for TΦT–PTMO$_{1000}$ was observed with DSC, neither any PTMO crystalline transi-

tion in the DMA. DMT extended PTMO$_{1000}$, however, starts to show DSC melting peaks and a crystalline PTMO transition in DMA at soft segment lengths of 2000 g/mol and longer. The melting temperature and enthalpy are lower compared to non-extended PTMO of similar length. These results suggest that PTMO$_{1000}$ is somewhat crystalline, but at low PTMO contents this crystallinity is too low to observe with DSC and DMA.

The logarithm of the shear rubbery modulus ($G'(25°C)$) increases with increasing TΦT content and again no difference between PTMO and DMT extended PTMO$_{1000}$ was observed (Fig. 11). This increase is attributed to an increase in TΦT crystallinity and consequently the physical cross-link density, making the polymers stiffer in the rubbery plateau.

With DMT extended PTMO$_{1000}$ it is possible to make segmented copolymers with poorly crystallizable long soft segments and thus low modulus materials with good low temperature flexibility. For instance, the shear storage modulus of TΦT–(PTMO$_{1000}$/DMT)$_{3000}$ is only 6 MPa with a rubbery plateau starting at 0°C, while for TΦT–PTMO$_{2900}$ the rubbery plateau starts at 15°C.

Table 3
Thermal properties of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) (subscript s refers to soft segment)

	TΦT-content (wt%)	η_{inh} (dl/g)	$T_{m,s}$ (°C)	$\Delta H_{m,s}$ (J/g)	$T_{c,s}$ (°C)	$\Delta H_{c,s}$ (J/g)	T_g (°C)	T_{fl} (°C)	$G'(25°C)$ (MPa)
M(PTMO) (g/mol)									
650	29	1.40	–	–	–	–	−58	247	118
1000	22	1.57	–	–	–	–	−69	216	44
1400	17	1.92	−8	12	−46	−6	−70	198	15
2000	13	2.50	0	17	−39	−13	−65	191	9
2900	9	2.54	9	30	−31	−22	−70	170	6
M(PTMO$_{1000}$/DMT) (g/mol)									
1532	16	1.70	–	–	–	–	−66	201	17
2060	13	2.13	−10	14	−48	−5	−65	188	11
2982	9	2.29	−3	20	−44	−6	−65	172	6
4022	7	2.09	3	24	−36	−16	−65	155	4
5030	6	1.93	6	22	−29	−19	−66	140	3
7024	4	1.31	8	29	−25	−22	−65	119	2
9005	3	1.67	8	28	−26	−20	−65	102	1.5
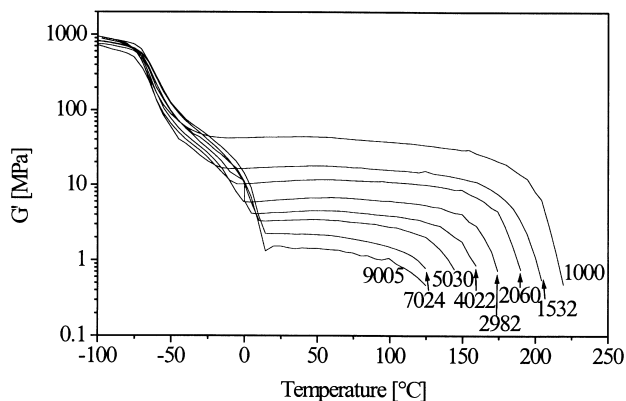
Fig. 9. Shear storage modulus versus temperature for TΦT–(PTMO$_{1000}$/DMT).

Fig. 11. Logarithm of the shear rubbery modulus versus TΦT content for TΦT–PTMO (■) and TΦT–(PTMO$_{1000}$/DMT) (○).

4. Conclusions

Segmented copolymers with uniform aramid units (TΦT) and PTMO based soft segments were synthesized. PTMO segments of 1000 g/mol and longer crystallize in a temperature range of -30–$20°C$. This crystallization can be reduced by changing the PTMO structure. DMT extended PTMO and DMI extended PTMO have a reduced crystallinity and melting temperature compared to PTMO itself. DMT extended PTMO$_{650}$ and DMT extended PTMO$_{650/250}$ are completely amorphous. DMI extended PTMO has a comparable or a somewhat lower crystallinity compared to DMT extended PTMO.

PTMO$_{1000}$ based soft segments strain-crystallize reversibly. This could be interesting to combine high elasticity (no strain-induced crystallization below 300% strain) with a relatively high tensile strength (strain-induced crystallization above 300% strain). The PTMO$_{2000m}$ crystalline phase melts $20°C$ lower than PTMO$_{2000}$ and hence has an improved low temperature flexibility. Strain-induced crystallization of PTMO$_{2000m}$ is also reversible. Strain-induced crystallization of PTMO$_{2000}$ is irreversible, the melting transition sharpens
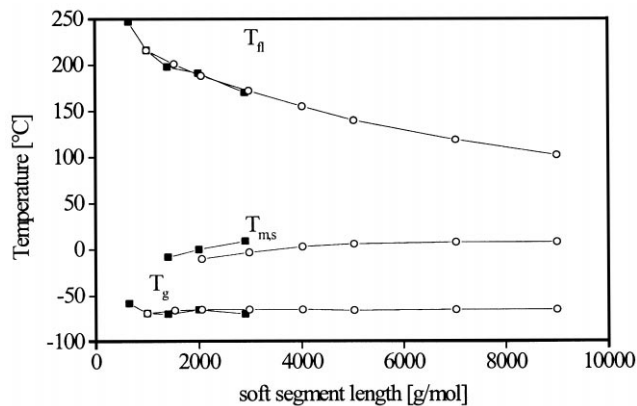
and shifts from 0 to $43°C$ after straining. This increase of the melting temperature is explained by differences in the free energy of the amorphous and crystalline PTMO phase in the unoriented and oriented state. Incorporating terephthalic or isophthalic units in the PTMO phase does non increase the T_g, it remains constant at $-65°C$. The methyl side groups in TΦT–PTMO$_{2000m}$ lower the T_g from $-65°C$ (T_g of TΦT–PTMO$_{2000}$) to $-75°C$. The flow temperature and rubbery modulus are not affected by the structure of PTMO. By varying the PTMO$_{1000}$/DMT soft segment length from 1000 to 9000 g/mol, the modulus decreased from 44–1.5 MPa and the flow temperature from 216 to $102°C$. Very low concentrations of TΦT (3 wt%) are able to crystallize and form polymers with a relatively large temperature independent rubbery plateau and high melting temperature of $102°C$, suggesting that the TΦT segments crystallize easily. At TΦT contents below 17 wt%, the TΦT–(PTMO$_{1000}$/DMT) copolymers are transparent, indicating that the TΦT crystallites are small.

Fig. 10. T_{fl}, T_g and $T_{m,s}$ for TΦT–(PTMO$_{1000}$/DMT) (○) and TΦT–PTMO (■).

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