Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 45 (2004) 437–446
polymer
www.elsevier.com/locate/polymer

Tensile and elastic properties of thermoplastic elastomers based on PTMO and tetra-amide units

J. Krijgsman[1], R.J. Gaymans*

Laboratory of Polymer Technology, Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Received 13 November 2002; received in revised form 27 October 2003; accepted 11 November 2003

Abstract

The tensile and elastic properties of melt spun threads of segmented copolymers based on T6T6T-dimethyl (5–16 wt%) and $PTMO_{1000}$/DMT of different lengths (3000–10,000 g/mol) are very good. Stress–strain measurements show that extruded threads of these polymers have high fracture strains (>1000%) and little strain hardening. The modulus and yield stress increase with increasing T6T6T content. The modulus decreases with increasing drawing-strain as a result of the breaking up of the crystalline network (strain softening). The compression set and tensile set increase with increasing T6T6T content and are low. The uniformity of T6T6T has little influence on the properties. At a soft segment length of 6000 g/mol a fibre with a tensile set of 5%, flow temperature of 200 °C and rubber modulus of 7 MPa is feasible, which can compete with commercial materials.

Keywords: Elastic fibers; Poly(tetramethylene oxide); Tetra-amide

1. Introduction

Thermoplastic elastomers (TPE's) [1,2] are polymers that show elastomeric behaviour at their service temperature and that can be melt-processed at elevated temperatures. A special kind of thermoplastic elastomers are segmented copolymers or multi-block copolymers that consist of alternating crystallisable hard segments and amorphous soft segments. Especially segmented copolymers with crystallisable units of uniform length were found to crystallise fast and complete [3–6]. Such segmented copolymers may possess good elastic properties.

Segmented copolymers based on T6T6T-dimethyl (two-and-a-half repeating unit of nylon-6,T) [7] crystallisable segments and PTMO (poly(tetramethylene oxide)) or $PTMO_{1000}$/DMT (PTMO of 1000 g/mol extended with dimethyl terephthalate) soft segments (Fig. 1) were found to have very interesting thermal-mechanical and elastic properties [8]. The polymers all have a low glass transition temperature (−60 to −70 °C), a wide and extremely flat rubbery plateau and a sharp melting temperature. The modulus of the rubbery plateau and the flow temperature increase with decreasing PTMO length or increasing T6T6T content as the degree of crystallinity increases. The injection moulded test bars of these copolymers had a light yellow to brown colour and were transparent.

The possible morphology of the T6T6T-($PTMO_{1000}$/DMT) segmented copolymers is schematically drawn in Fig. 2. The crystallisable T6T6T units form threads or ribbons with a high aspect ratio in the amorphous matrix [8–12]. The crystalline lamellae (C) act as physical cross-links and reinforcing filler for the amorphous phase (A). Some crystallisable segments cannot crystallise and are mixed with the amorphous phase (B). As a result the mobility of the amorphous phase decreases and the T_g increases.

Thus far only the thermal-mechanical and elastic properties of test bars of ~2 mm thickness were studied [8]. Melt-spun T6T6T-($PTMO_{1000}$/DMT) fibres are expected to have desirable properties such as high tensile stress and strain and low tensile set. The properties will be compared with that of TΦT-($PTMO_{1000}$/DMT) copolymers [12–15] and commercial elastic materials such as Lycra®. The TΦT segment is a aromatic di-amide segment that corresponds to one-and-a-half repeating unit of poly(*p*-phenylene terephthalamide).

The mechanical and elastic properties of TΦT-($PTMO_{1000}$/DMT) copolymers are good. However, the

---

* Corresponding author. Tel./fax: +31-534-982-970.
E-mail addresses: r.j.gaymans@utwente.nl (R.J. Gaymans), j.krijgsman@kema.nl (J. Krijgsman).

[1] Present address: KEMA Nederland B.V., Arnhem, The Netherlands.

0032-3861/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2003.11.008

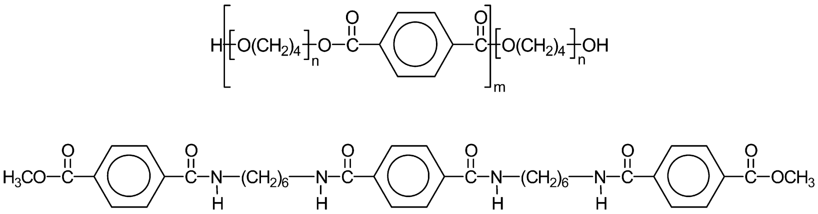

Fig. 1. Structure of PTMO/DMT amorphous segment and T6T6T-dimethyl crystallisable segment.

elasticity is only good at low TΦT content (<5 wt%) and thus at low modulus and melting temperature. The combination of a high melting temperature and high modulus at room temperature (‘non-sticky’ material) with a very low tensile set is not observed for TΦT-($PTMO_{1000}$/DMT) copolymers.

A major disadvantage of Lycra®, a segmented polyether-urethane, is that it is spun from solution (dimethyl formamide or dimethyl acetamide). This spinning process is expensive and environmentally unfriendly. Another disadvantage is the low thermal stability of the polyether-urethane, which makes it difficult to dye, a process that is usually performed at elevated temperatures.

The purpose of this study is to obtain a segmented copolymer that is processable from the melt, with a modulus above 5 MPa at room temperature, a melting temperature above 200 °C and a very low tensile set below 10% that can compete with Lycra®. In this article the structure-property relationships of melt spun threads of T6T6T-($PTMO_{1000}$/DMT) will be discussed.

2. Experimental

2.1. Materials

T6T6T-($PTMO_{1000}$/DMT) copolymers were synthesised by a polycondensation reaction using PTMO (1000 g/mol) extended with DMT and T6T6T-dimethyl [7] as was described before [8].

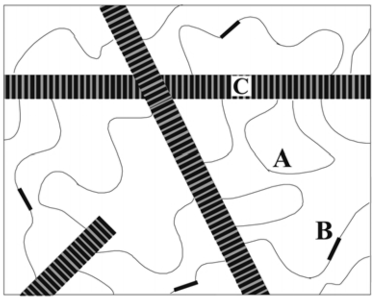

Fig. 2. Schematic representation of the morphology of crystallised segmented copolymers with uniform crystallisable segments: A = amorphous PTMO phase; B = amorphous crystallisable segments; C = crystalline ribbons [8–12].

2.2. Viscometry

The inherent viscosity (η_{inh}) of the polymers was determined with a capillary Ubbelohde type 1B at 25 °C, using a polymer solution with a concentration of 0.1 g/dl in phenol/1,1,2,2-tetrachloroethane (50:50, mol/mol). The inherent viscosity is used as a measure for molecular weight, because the polymers are insoluble in common GPC solvents.

2.3. Sample preparation

Samples for the tensile tests were prepared by melt extruding (melt spinning) the polymers into threads on a 4cc DSM res RD11H-1009025-4 co-rotating twin-screw mini extruder. The extruder temperature was approximately 60 °C above the flow temperature, and the screw speed was 30 rpm. The threads were wound at a speed of 20–40 m/min. The thickness or titer of the threads (expressed in tex = 10^{-6} kg/m) was measured by weighing 1 m of thread. The density of the polymers was approximately 1.0 g/cm^3.

For some experiments the threads were pre-drawn with a Zwick Z020 universal tensile machine with a speed of 250 mm/min up to the desired strain. Then the strain was released with the same speed. The pre-drawn threads were used for further experiments after 1 h relaxation.

2.4. Tensile tests

Tensile tests (at least in 5-fold) on threads and pre-drawn threads were carried out on a Zwick Z020 universal tensile machine equipped with a 10 N load cell. The strain was measured with the clamp displacement. Stress–strain curves were obtained at a strain rate of 250 mm/min with a starting clamp distance of 25 mm. Above 500% strain, necking occurred also within the clamps. Therefore the strain at break was corrected. The amount of necking within the clamps was determined with optical markers on the thread. By this method it can roughly be concluded that at the measured strain is 10% too high at ~1300% and 20% too high at ~1700%.

2.5. Tensile set

The tensile set of threads and pre-drawn threads (at least in 5-fold) was measured on a Zwick Z020 universal tensile machine equipped with a 10 N load cell. The strain was measured with the clamp displacement. The strain rate was 200 mm/min with a starting clamp distance of 50 mm. The tensile set was measured in a cyclic test to 300% strain. The residual strain (strain where the force becomes positive again) in the second cycle was determined. $TS_{300\%}$ was defined as

$$TS_{300\%} = \frac{\text{residual strain}}{300} 100\% \quad (1)$$

2.6. Cyclic tensile tests

Cyclic tensile tests on threads were carried out on a Zwick Z020 universal tensile machine equipped with a 10 N load cell. The strain was measured with the clamp displacement. The strain rate was 200 mm/min with a starting clamp distance of 50 mm. Until 100% strain, the strain was increased by 20% each cycle, followed by a strain increase of 100% for each cycle until the sample broke. There was no dwell time between the steps. The *E*-modulus was redetermined after each load cycle (at least in 5-fold). The *E*-modulus in each cycle was corrected for the change in area of the thread by multiplying with the corresponding straining factor ($= 1 + (\varepsilon/100)$).

3. Results and discussion

Copolymers of T6T6T-dimethyl and PTMO of 1000 g/mol extended with DMT were extruded into threads with a titer of 10–50 tex (mg/m). An inherent viscosity of at least 1.4 dl/g is necessary for melt spinning. When the inherent viscosity is lower the melt strength of the material is not sufficient for spinning. The threads were transparent and had a faint yellow colour.

The tensile and elastic properties of two series of T6T6T-($PTMO_{1000}$/DMT) were studied. In the series 1 uniform T6T6T-dimethyl was used with a $PTMO_{1000}$/DMT length of 3000–10,000 g/mol. In the series 2 T6T6T-dimethyl with a lower uniformity of ~76% (76% T6T6T and 24% $T(6T)_n$ with $n > 2$) was used with a $PTMO_{1000}$/DMT length of 3000–6000 g/mol. This non-uniform T6T6T-dimethyl contains some further reacted units such as T6T6T6T-dimethyl and T6T6T6T6T-dimethyl [7]. These units will form thicker lamellae upon crystallisation and melt at a higher temperature [16].

3.1. Stress–strain behaviour

Stress–strain curves of extruded threads of T6T6T-($PTMO_{1000}$/DMT) with uniform T6T6T (series 1) are given in Fig. 3. The *E*-modulus, yield stress and fracture stress and strain are given in Table 1 (series 1 and 2).

The shear modulus (G') and the tensile modulus (E) both decrease strongly with decreasing T6T6T concentration. For a rubber, with a Poisson ratio of 0.5 the *E*-modulus is three times as high as the G'-modulus [18]. In the values obtained for the E and G' this is not the case. A possible reason for this discrepancy is an error in the thickness of the threads and the determination of E. More research is necessary to fully understand these effects.

The fracture strain and stress are high for all copolymers. The fracture stress of T6T6T-$(PTMO_{1000}/DMT)_{3000}$ is higher than for $PTMO_{1000}$/DMT lengths of 6000–10,000 g/mol. Above 300%, strain hardening—strain-induced crystallisation of PTMO—takes place, which results in a high fracture stress. There is no relationship between the soft segment length or crystalline segment concentration and the fracture stress and strain. Previous research [6] on TΦT-($PTMO_{1000}$/DMT) copolymers showed that with $PTMO_{1000}$/DMT as amorphous segment the fracture stress and strain are mainly dependent on the molecular weight of the copolymer. This can be explained by the fact that longer chains can be oriented further. Therefore the high fracture stress and strain of T6T6T-$(PTMO_{1000}/DMT)_{3000}$ can be ascribed to a molecular weight effect.

In Fig. 4 the stress–strain curves of T6T6T-$(PTMO_{1000}/DMT)_{4000}$ with high (2.3 dl/g) and low (1.4 dl/g) inherent viscosity are compared. The molecular weight has a strong effect on the stress–strain behaviour. The fracture stress and strain and the true fracture stress are much lower at low molecular weight. The yield stresses are comparable, although the yield stress is more pronounced when the molecular weight is lower. The *E*-modulus is higher at lower inherent viscosity (Table 1), which indicates higher crystallinity or a different crystalline structure (higher aspect ratio of the crystalline lamellae).

In Fig. 5 the true fracture stress of the T6T6T-($PTMO_{1000}$/DMT) copolymers of series 1 and 2 compared

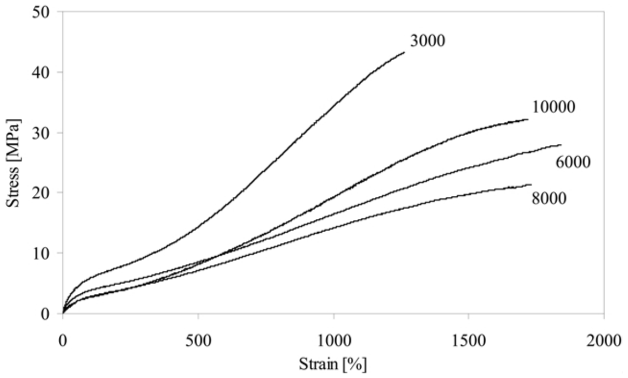

Fig. 3. Stress–strain curves of different T6T6T-($PTMO_{1000}$/DMT) with uniform T6T6T and different $PTMO_{1000}$/DMT lengths as indicated in the figure (series 1).

Table 1
Tensile testing properties of T6T6T-(PTMO$_{1000}$/DMT) copolymers with uniform T6T6T (series 1) and non-uniform T6T6T (series 2)

PTMO$_{1000}$/DMT length (g/mol)	T6T6T content (wt%)	η_{inh} (dl/g)	G (25 °C) (MPa)	E (MPa)	σ_y^{a} (MPa)	σ_b (MPa)	ε_b^{b} (%)	σ_b(true)^c (MPa)
Series 1: uniform								
3000	15.7	3.1	14.5	21	5.2	42	1100	500
4000	12.3	2.3	8.5	18	4.0	20	1150	250
4000	12.3	1.4	18	100	4.1	8	750	70
6000	8.6	2.6	6.8	14	3.4	25	1450	390
8000	6.6	2.2	5.1	12	2.7	20	1400	300
10,000	5.4	2.5	3.3	10	2.0	31	1400	470
Series 2: non-uniform								
3000	15.7	1.4	23.5	95	5.3	24	1100	290
4000	12.3	1.5/1.8^d	14.3	60	4.4	23	1200	300
6000	8.6	1.9/2.1^d	6.9	35	3.3	34	1300	480

Explanation of symbols: η_{inh} = inherent viscosity; G' (25 °C) [8] = rubber modulus at 25 °C of injection moulded test bar; E, σ_y, σ_b, ε_b and σ_b(true) = E-modulus, yield stress, stress at break, strain at break and true stress at break of melt spun threads.

[a] Determined by Considère's method [17].

[b] After correction for necking in the clamps.

[c] σ_b(true) was obtained multiplying σ_b and the straining factor (= $1 + (\varepsilon_b/100)$).

[d] The first number is the inherent viscosity for the G' (25 °C) data [8]; the second number is the inherent viscosity of the polymer that was used for melt spun threads (tensile test data).

to TΦT-(PTMO$_{1000}$/DMT) [12] copolymers is given as function of the inherent viscosity (molecular weight). The true fracture stress increases linearly with increasing inherent viscosity for copolymers based on extended PTMO$_{1000}$/DMT and TΦT or uniform T6T6T. The fracture strength in these materials is thus highly dependent on the molecular weight of these polymers and not on the length of the amorphous segment. The maximum attainable true fracture stresses are high considering that these are very soft materials.

With non-uniform T6T6T the true fracture stress is higher (Fig. 5). TΦT-PTMO copolymers based on regular PTMO of 2000 g/mol and higher were found to have higher true fracture stresses as well [12] (not shown in Fig. 5). This is due to the occurrence of more strain hardening of regular PTMO. Apparently the copolymers based on non-uniform T6T6T and extended PTMO$_{1000}$/DMT strain harden more than those based on uniform T6T6T and extended PTMO$_{1000}$/DMT.

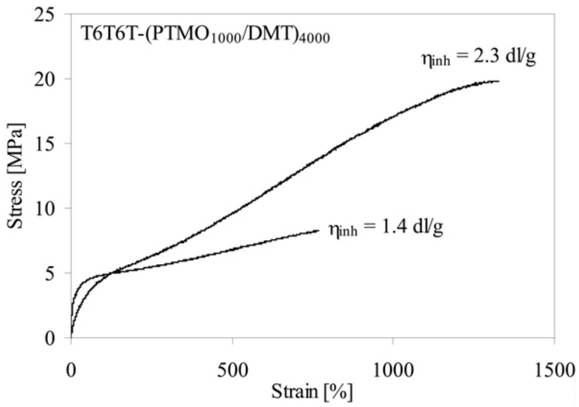

Fig. 4. Stress–strain curves of T6T6T-(PTMO$_{1000}$/DMT)$_{4000}$ with uniform T6T6T and different inherent viscosities.

The stress–strain curves in Figs. 3 and 4 show a yield point, which is indicative for the breaking up of the crystalline structure [2,9]. The yield stress decreases and becomes less pronounced with decreasing hard segment content, because the degree of crystallinity decreases in this direction. In Fig. 6 the yield stress is given as function of the hard segment content for the copolymers of series 1 and 2 compared to TΦT-(PTMO$_{1000}$/DMT) [12] copolymers.

The yield stress of copolymers based on T6T6T (uniform and non-uniform) or TΦT [12] and extended PTMO$_{1000}$/DMT increases linearly with the hard segment content. The type of crystallisable unit has no influence on the yield stress at a certain hard segment content. The height of the yield stress in polyethylene is said to be dependent on both the crystallinity and the lamellar thickness [19–21]. The lamellar thickness within a series of copolymers based on T6T6T or TΦT [12] as crystallisable unit is constant. However, the lamellar thickness of T6T6T is higher than that of TΦT, while the yield stresses are comparable. In these systems the yield stress seem only dependent on the hard segment

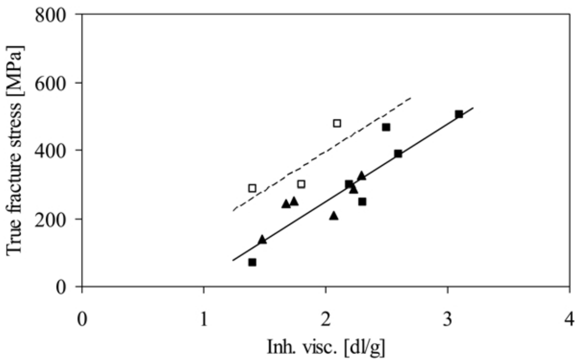

Fig. 5. True fracture stress as function of the inherent viscosity: (■), T6T6T-(PTMO$_{1000}$/DMT), series 1; (□), T6T6T-(PTMO$_{1000}$/DMT), series 2, non-uniform T6T6T; (▲), TΦT-(PTMO$_{1000}$/DMT) [12].

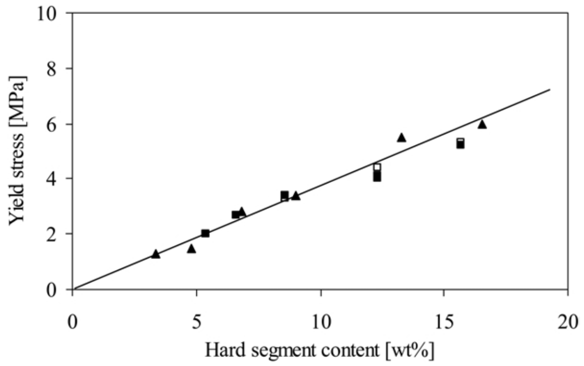

Fig. 6. Yield stress as function of the hard segment content: (■), T6T6T-($PTMO_{1000}$/DMT), series 1; (□), T6T6T-($PTMO_{1000}$/DMT), series 2, non-uniform T6T6T; (▲), TΦT-($PTMO_{1000}$/DMT) [12].

content (degree of crystallinity). This can be explained by the fact that at a certain hard segment content the number of crystalline TΦT ribbons is higher, because the thickness of the TΦT crystalline ribbons is lower. Therefore the cross-section of the sheared TΦT crystalline ribbons is comparable to that of the T6T6T ribbons at a certain hard segment content.

3.1.1. Effect of pre-orientation

By drawing, the crystalline ribbons in the copolymers are broken up and oriented in the straining direction. During breaking up of the crystalline structure the aspect ratio of the crystalline ribbons decreases [12]. During drawing the PTMO phase is oriented, but on releasing the strain the orientation of the PTMO phase is lost for $PTMO_{1000}$/DMT (reversible strain hardening) [13]. The modulus is thus only dependent on the structure and orientation of the crystalline phase. As the crystallites become smaller on orientation they also become more difficult to deform plastically. When a highly drawn thread is stretched a second time, the PTMO phase can more easily be oriented, which results in a higher fracture stress and lower fracture strain with a similar true fracture stress.

The effect of drawing-strain on the tensile and elastic behaviour for T6T6T-($PTMO_{1000}$/DMT)$_{6000}$ copolymers was studied. In Fig. 7 the stress–strain curves of threads of T6T6T-($PTMO_{1000}$/DMT)$_{6000}$ based on non-uniform T6T6T (series 2) after different drawing-strains are given.

When the drawing-strain increases, the modulus decreases, the fracture stress increases and the fracture strain decreases. The true fracture stress, however, is comparable for all samples (only dependent on molecular weight). After drawing, fibres with a low modulus, a high fracture stress and still a high strain at break can be obtained. As the modulus decreases after drawing, shearing of the T6T6T ribbons upon straining is an irreversible process. This type of oriented fibres with stress–strain curves as given in Fig. 7 (500–750% drawing-strain) could also be obtained directly in a commercial fibre spinning process at high spinning speeds in one step [13].

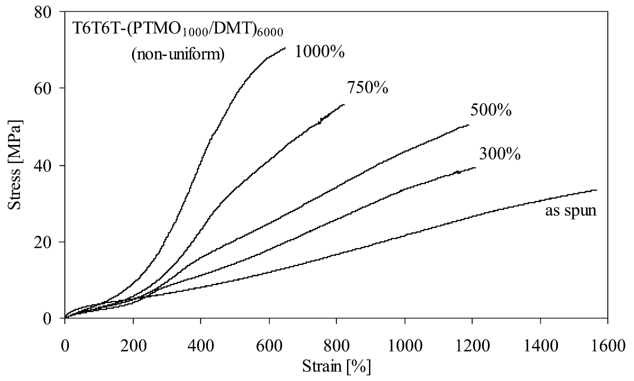

Fig. 7. Stress–strain curves of T6T6T-($PTMO_{1000}$/DMT)$_{6000}$ (non-uniform T6T6T) after drawing; the amount of drawing-strain is given for each line in the figure.

3.2. Strain softening

As was shown in Fig. 7 the modulus decreases after drawing because the crystalline ribbons are broken up and their aspect ratio decreases. As a result their reinforcing effect decreases and the modulus of the copolymers will decrease. On the other hand, upon drawing, orientation of the crystalline ribbons will occur, which results in an increase in modulus. At higher drawing-strains (>500%) strain-induced crystallisation of PTMO can also occur which increases the modulus when it is not able to relax fully upon strain release [12,13].

The influence of drawing-strain on the *E*-modulus for T6T6T-($PTMO_{1000}$/DMT) copolymers was determined in cyclic tensile tests. The *E*-modulus as function of the drawing-strain is given in Fig. 8 for copolymers of series 1. The *E*-modulus in each cycle was corrected for the change in area of the thread by multiplying with the corresponding straining factor.

At low drawing-strains (<40%) there is only a small decrease of the *E*-modulus. At higher drawing-strains (>60%) the decrease is strong and has a linear relationship in a log–log plot. In the first 200% strain (just above the

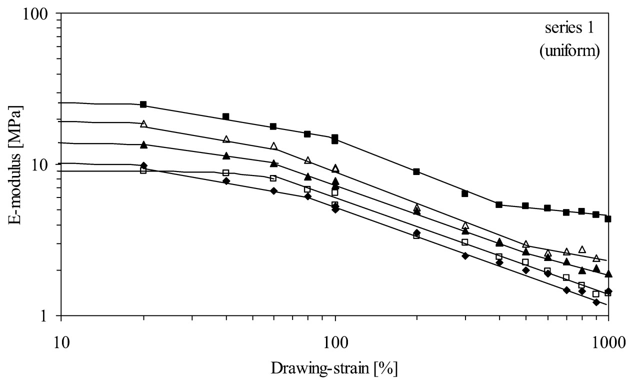

Fig. 8. *E*-modulus as function of the drawing-strain in a cyclic test for T6T6T-($PTMO_{1000}$/DMT) with uniform T6T6T (series 1) and different soft segment lengths: (■), 3000 g/mol; (△), 4000 g/mol; (▲), 6000 g/mol; (□), 8000 g/mol; (◆), 10,000 g/mol.

yield point), the modulus decreases by a factor 3–4 for all five copolymers. The PTMO length or T6T6T content seems to have little effect on this, thus the degree of crystallinity has little effect either. Between 100 and 300% or 300 and 900% strain, the decrease in modulus is comparable, about a factor 2.

The decrease in modulus or strain softening that is observed is caused by disruption of the crystalline ribbon structure upon drawing [21–23]. The modulus decreases because the crystalline structure is broken up and the aspect ratio of the crystallites decreases. When a material is strained a second time the modulus is lower and less stress is needed due to this strain softening [2].

At low strains (<30%) the strain is mainly elastic. No plastic deformation occurs and the modulus is hardly lowered. At higher strains plastic deformation takes place and the modulus decreases as the PTMO phase is broken up. At strains above 500%, the T6T6T phase is further broken up and also strain hardening of the PTMO phase can occur. As a result of strain hardening the modulus will increase [12]. Only for T6T6T-($PTMO_{1000}$/DMT)$_{3000}$ the modulus does not decrease much with increasing strain above 500% strain. This is probably due to the occurrence of some (irreversible) strain hardening of the PTMO phase that partially counteracts the effect of decreasing aspect ratio of the T6T6T crystallites. The stress–strain test on the T6T6T-($PTMO_{1000}$/DMT)$_{3000}$ thread (Fig. 3) also shows more strain hardening than that of threads of the other copolymers. However, the effect of strain hardening is much smaller than for regular PTMO with a length above 2000 or 2900 that show strong strain hardening [12].

Even at very high strains (>1000% up to break) the modulus decreases further, indicating that the process of breaking up of the crystalline ribbons continues up to high strains. It is thought that the crystalline ribbons are broken up further until they reach a square shape (aspect ratio of 1) [12]. Apparently the crystallites still have an aspect ratio above 1 at break.

3.3. Elasticity

The CS and $TS_{300\%}$ of T6T6T-($PTMO_{1000}$/DMT) copolymers with uniform and non-uniform T6T6T segments are given in Table 2. The compression set (CS) at 20 and 70 °C was measured using polymer pieces, cut from the injection moulded bars (data were discussed before [8]).

The compression set at 20 and 70 °C decreases with decreasing T6T6T content, thus with increasing diol length. The compression set (55%, 20 °C) is low for all T6T6T contents and decreases slightly from 10 to 6% when the T6T6T content is decreased from 15.7 to 5.4 wt%. With non-uniform T6T6T the compression set values at 20 °C are comparable. The compression set at 70 °C of T6T6T-($PTMO_{1000}$/DMT) copolymers, is still relatively low. For these copolymers the melting temperature is not reached by far at 70 °C, and thus plastic flow is still suppressed.

For fibre applications the tensile set value is an important property. In Fig. 9 the tensile set is given as a function of the rubber modulus (a) and the reciprocal value of the $PTMO_{1000}$/DMT length; (b) for T6T6T-($PTMO_{1000}$/DMT) with uniform (series 1) and non-uniform T6T6T (series 2) and for TΦT-($PTMO_{1000}$/DMT) [13].

For all copolymer series in Fig. 9 the tensile set decreases with decreasing rubber modulus. When the rubber modulus decreases, the degree of crystallinity decreases. At a lower rubber modulus the hard segment content is lower. A larger part of the strain is taking place in the PTMO phase and there is less plastic deformation possible and therefore the tensile set decreases. The tensile set values for the T6T6T copolymers are low and even lower than for the TΦT system. This is surprisingly as the yield stresses and strain softening behaviour are comparable (Figs. 6 and 8).

The tensile set of all T6T6T-($PTMO_{1000}$/DMT) copolymers is lower than that of TΦT-($PTMO_{1000}$/DMT) at a certain rubber modulus. With T6T6T as crystallisable segment a very low tensile set of only 5–8% can be obtained when the rubber modulus is below 10 MPa. The rubber modulus has only little effect on the tensile set when it is below 10 MPa. When the rubber modulus is above 10 MPa the tensile set increases linearly with increasing rubber modulus. The slope of this line is comparable with that of copolymers based on TΦT as crystallisable unit.

The tensile set as a function of rubber modulus seems a little lower for non-uniform T6T6T (series 2) than for uniform T6T6T (series 1) at a rubber modulus above

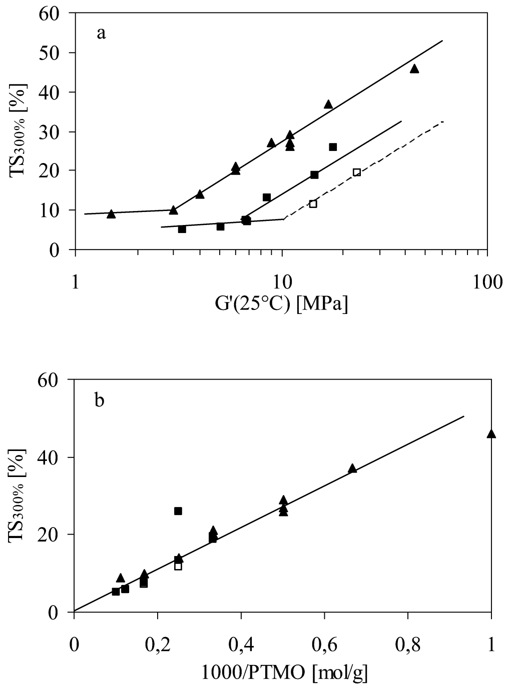

Fig. 9. Tensile set after 300% strain of copolymers with different crystallisable segments as function of (a) the rubber modulus G' at 25 °C and (b) 1000/PTMO: (■), T6T6T-($PTMO_{1000}$/DMT), series 1; (□), T6T6T-($PTMO_{1000}$/DMT), series 2, non-uniform T6T6T; (▲), TΦT-($PTMO_{1000}$/DMT) [13].

Table 2
Compression set [8] and tensile set of T6T6T-($PTMO_{1000}$/DMT) copolymers with uniform (series 1) and non-uniform T6T6T (series 2)

$PTMO_{1000}$/DMT length (g/mol)	T6T6T content (wt%)	η_{inh} (dl/g)	G' (25 °C) (MPa)	$CS_{55\%}$ (20 °C) (%)	$CS_{55\%}$ (70 °C) (%)	$TS_{300\%}$ (%)
Series 1: uniform						
3000	15.7	3.1	14.5	10	32	19
4000	12.3	2.3	8.5	8	34	13
4000	12.3	1.4	18	18	45	26
6000	8.6	2.6	6.8	9	29	7.5
8000	6.6	2.2	5.1	7	34	5.7
10,000	5.4	2.5	3.3	6	33	5.1
Series 2: non-uniform						
3000	15.7	1.4	23.5	12	24	20
4000	12.3	1.5/1.8[a]	14.3	8	21	11
6000	8.6	1.9/2.1[a]	6.9	8	20	7.0

Explanation of symbols: η_{inh} = inherent viscosity; G' (25 °C) = rubber modulus at 25 °C of injection moulded test bar [8]; $CS_{55\%}$ and $TS_{300\%}$ = compression set after 55% compression [8] and tensile set after 300% strain of a melt spun thread.

[a] The first number is the inherent viscosity for the G' (25 °C) and compression set data [8]; the second number is the inherent viscosity of the polymer that was used for extruding into threads (tensile set data).

10 MPa. This could be explained by fact that the copolymers with non-uniform T6T6T have a higher rubber modulus at a constant soft segment length, probably because the crystallinity is higher [8].

In Fig. 9(b) the tensile set is given as a function of the reciprocal value of the $PTMO_{1000}$/DMT length for the T6T6T-($PTMO_{1000}$/DMT) copolymers. The reciprocal value of the soft segment length corresponds to the network density, the number of physical cross-links per chain. The tensile set follows a linear relationship with increasing 1000/PTMO for copolymers with uniform and non-uniform T6T6T. The tensile set values are compared with those of the TΦT-($PTMO_{1000}$/DMT) copolymers [13]. The tensile set values of copolymers based on T6T6T or TΦT as function of 1000/PTMO are the same. The compression set was shown to deviate from such a linear relationship for 1000/PTMO values below 0.4 [8]. Apparently the elasticity under tension is better than under compression at large soft segments lengths.

From Fig. 9(b) it can be concluded that for the tensile set not the crystallinity, but the distance between two crystalline ribbons is important in these copolymers. When the distance between the crystalline ribbons increases, the elasticity increases. This can be explained by the fact that when more PTMO is present between cross-links more deformation is taking place in this PTMO phase.

When a thread with a certain PTMO length for both T6T6T and TΦT is stretched to 300% the fraction of ribbons that is broken up to reach this strain is probably comparable. Also the strain softening factor is independent of the hard segment content (Fig. 8) and type [24]. The fact that the modulus and yield stress at a particular PTMO length are larger for T6T6T than for TΦT does not seem to influence the elasticity. Apparently the deformation of the crystalline phase has no effect on the elasticity.

Therefore it can probably be concluded that the elasticity is mainly dependent on the length of PTMO between two crystalline ribbons and not on the type of crystallisable units for this type of segmented copolymers.

3.3.1. Effect of pre-orientation on tensile set

For the copolymers of series 2 with non-uniform T6T6T the tensile set was also measured as a function of the amount of drawing-strain. A thread that is drawn to 500–750% corresponds to a fibre that is obtained in a commercial process directly after spinning [13]. The results are given in Table 3 and Fig. 10.

After drawing to 300%, the tensile set is somewhat lower than that of an as spun thread. A minimum in tensile set with the drawing-strain is observed for all three polymers. The minimum with T6T6T-($PTMO_{1000}$/DMT)$_{3000}$ is reached after 300% drawing-strain. With T6T6T-($PTMO_{1000}$/DMT)$_{4000}$ and T6T6T-($PTMO_{1000}$/DMT)$_{6000}$ the minimum is at 500% drawing-strain.

Upon drawing, strain softening occurs (Fig. 8) and the modulus drops as the crystalline network is broken up. The crystalline ribbons are broken up into smaller pieces and oriented in the straining direction. This process continues up to high strains. Apparently the aspect ratio has only little

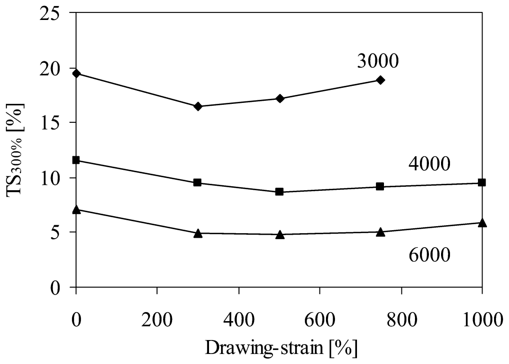

Fig. 10. $TS_{300\%}$ as a function of the drawing-strain for T6T6T-($PTMO_{1000}$/DMT) copolymers with non-uniform T6T6T (series 2) and $PTMO_{1000}$/DMT length as indicated in the figure.

Table 3
Tensile set for T6T6T-(PTMO$_{1000}$/DMT) copolymers with non-uniform T6T6T (series 2), measured in a cyclic tensile test up to 300% strain after spinning (as spun) and different drawing-strains of 300–1000%

PTMO$_{1000}$/DMT length (g/mol)	T6T6T content (wt%)	η_{inh} (dl/g)	TS$_{300\%}$ (%)				
			As spun	300%	500%	750%	1000%
3000	15.7	1.4	19.5	16.5	17.2	18.8	–
4000	12.3	1.8	11.5	9.0	8.7	11.1	12.0
6000	8.6	2.2	7.0	5.0	4.8	5.1	5.8

effect on the tensile set, as it does not change a lot after pre-drawing to 500, 750 or 1000%. It could also be that part of the crystalline ribbons that are broken up upon drawing can recover after stress release, however, the modulus was found to stay low after stress release.

Above 500% strain, strain induced crystallisation of the PTMO phase can take place, as has been observed before [13]. However, with strain induced crystallisation a large increase of the tensile set with increasing drawing-strain is expected as for TΦT-PTMO with PTMO lengths above 2000 g/mol. Therefore strain induced crystallisation of extended PTMO$_{1000}$/DMT is probably reversible [13].

In Fig. 11 the TS$_{300\%}$ for as spun extruded threads and 500% drawn threads is given versus the *E*-modulus of these threads (non-uniform T6T6T, series 2). By drawing the modulus is decreased by a factor 10 for these copolymers, while the TS$_{300\%}$ is decreased only slightly.

The modulus of the extruded thread is high and therefore the granulate of the T6T6T-(PTMO$_{1000}$/DMT) copolymers will not be sticky. For processing this result is important, as it is very inconvenient to have a sticky granulate. After spinning from the melt at high speed, fibres that are comparable with extruded threads at a drawing-strain of 500% can be obtained. These are fibres with a low modulus, high tensile strength and strain and very low tensile set.

The low uniformity of T6T6T in series 2 does not seem to have a negative effect on the properties. With a uniformity of 76% the tensile and elastic properties of T6T6T-(PTMO$_{1000}$/DMT) are comparable with that using uniform T6T6T. It was expected that the properties would be better in the copolymers based on uniform T6T6T [3–6]. Apparently excellent uniformity of T6T6T is not very important. A uniformity of 76% seems sufficient for good properties. As yet the effect of uniformity of T6T6T is not fully understood.

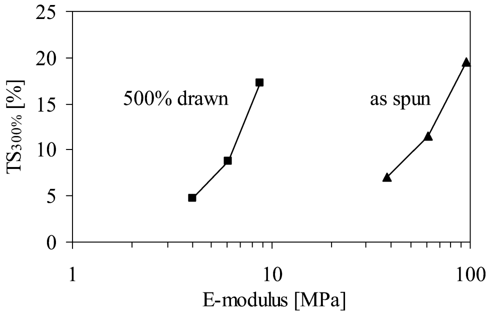

Fig. 11. TS$_{300\%}$ versus *E*-modulus of T6T6T-(PTMO$_{1000}$/DMT) copolymers with non-uniform T6T6T (series 2): (▲), as spun threads; (■), 500% pre-strained threads.

3.4. Comparison with other systems

The T6T6T-(PTMO$_{1000}$/DMT) copolymers that are described in this article are compared with the TΦT-(PTMO$_{1000}$/DMT) copolymers from previous research [12, 13] and several commercial materials [25] in Table 4. In Fig. 12 the tensile set is given as a function of the flow temperature and rubber modulus for the T6T6T-(PTMO$_{1000}$/DMT) copolymers compared to other systems.

The T6T6T and TΦT based segmented copolymers are

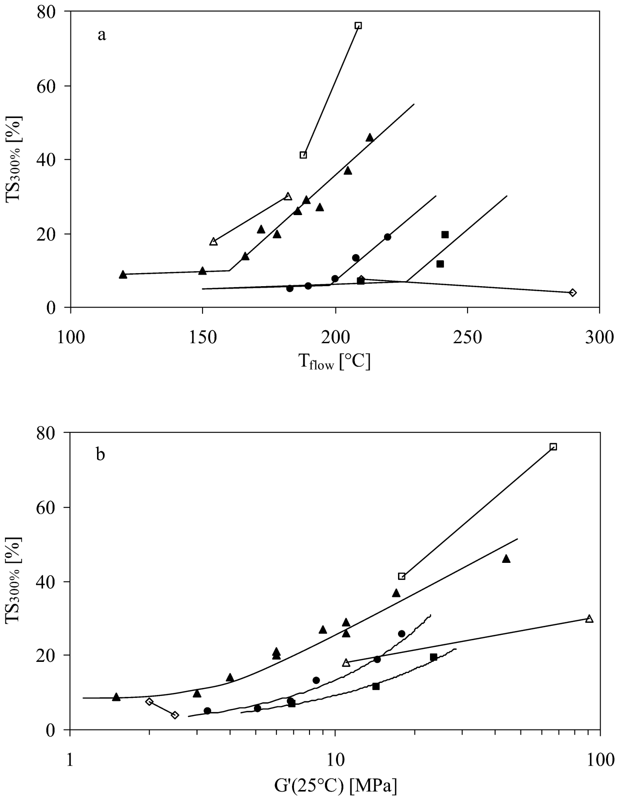

Fig. 12. Tensile set after 300% strain as a function of (a) the flow temperature and (b) the rubber modulus for different copolymers with T6T6T or TΦT as crystallisable segment compared to commercial materials: (●), T6T6T-(PTMO$_{1000}$/DMT), series 1; (■), T6T6T-(PTMO$_{1000}$/DMT), series 2, non-uniform; (▲), TΦT-(PTMO$_{1000}$/DMT) [13]; (□), Arnitel® [25]; (△), Desmopan® [25]; (◇), Lycra® [25].

Table 4
Comparison of T6T6T-($PTMO_{1000}$/DMT) segmented copolymers with other systems [12,13,25] (Desm. = Desmopan)

	Hard segment (wt%)	G' (25 °C) (MPa)	T_{flow} (°C)	T_g (°C)	σ_b (MPa)	ε_b[a] (%)	$TS_{300\%}$ (0%) (%)	$TS_{300\%}$ (500%) (%)	$CS_{55\%}$ (20 °C) (%)	$CS_{55\%}$ (70 °C) (%)
T6T6T-($PTMO_{1000}$/DMT) with PTMO/DMT length										
6000	8.6	6.8	200	−61	25	1450	7.5	5	9	29
10,000	5.4	3.3	183	−63	31	1400	5.1	4	6	33
TΦT-($PTMO_{1000}$/DMT) [12,13] with PTMO/DMT length										
4000	7	4	155	−65	21	1250	14	–	24	55
9000	3	1.5	102	−65	15	1600	9	7	23	67
Commercial polymers [25]										
Arnitel® EM400	–	18	182	−7	61	860	41	–	15	36
Arnitel® EL550	–	67	205	−50	106	470	76	–	30	58
Desm.® KU-8672	–	11	150	−45	79	950	18	–	13	41
Desm.® 955u	–	91	176	−31	86	830	30	–	23	60
Lycra® 269B	–	2.5	290	–	–	–	–	4[b]	–	–
Lycra® 136C	–	2	210	–	–	–	–	7.5[b]	–	–

Explanation of symbols: G' (25 °C), T_{flow} and T_g = rubber modulus at 25 °C, flow temperature and glass transition temperature of injection moulded test bar; σ_b and ϵ_b = stress and strain at break of melt spun threads; $TS_{300\%}$ = tensile set of melt spun threads after 300% strain; $CS_{55\%}$ = compression set after 55% compression.

[a] After correction for necking in the clamps above 500% strain; (b), oriented fibre used as received.

[b] Commercial, pre-oriented fibre.

copolyether-esteramides, a special type of the thermoplastic copolyether-amides (TPE-A). These materials are new compared to the commercial materials that are described here, as they contain crystallisable segments that are uniform in length. The commercial material Arnitel® is a segmented copolyether-ester (TPE-E) based on a PBT-PTMO copolymer. Desmopan® is a commercial thermoplastic polyurethane (TPE-U), based on polyether soft segments. In both materials the hard segment are not of uniform length. Lycra® is a segmented polyurethane fibre that was spun by solution spinning. The properties of a hard and a soft grade of these commercial materials were evaluated [25].

The fracture stress and strain of extruded threads of T6T6T-($PTMO_{1000}$/DMT) copolymers are comparable with that of similar materials, in particular TΦT-($PTMO_{1000}$/DMT). The flow temperature of polymers with T6T6T is higher compared to TΦT, while the compression and tensile set are lower. Another advantage of copolymerisation with T6T6T instead of TΦT is that the products are less coloured. Therefore the use of T6T6T is preferred over the use TΦT in segmented copolymers.

T6T6T-($PTMO_{1000}$/DMT)$_{6000}$ has a tensile set of only 5% after straining to 500%, in combination with a flow temperature of 200 °C and a rubber modulus of 6.8 MPa. A high flow temperature is important for dying of the fibre, a high rubber modulus is important for processing of pellets. Another advantage of the T6T6T-($PTMO_{1000}$/DMT) copolymers is that they can be recycled. Lycra®-269B shows a tensile set of 4% at a flow temperature of 290 °C. Lycra®, however, does not really melt and cannot be melt spun or recycled. Furthermore Lycra® has a very low modulus, which makes the material sticky. The new T6T6T-($PTMO_{1000}$/DMT) materials are very interesting as elastic fibres.

Arnitel and Desmopan are not well suitable for application as elastic fibre due to the high tensile set values and low flow temperatures. These commercial materials are mainly used for other applications for thermoplastic elastomers where a high modulus in combination with a good compression set and good processability are most important. The T6T6T-($PTMO_{1000}$/DMT) copolymers are very interesting for such applications as well [8].

It is expected that the properties of T6T6T-($PTMO_{1000}$/DMT) copolymers can probably be changed and optimised in several ways: the choice of the soft segment type and length, the melt polymerisation conditions, the processing conditions and by using additives. The elastic properties of the material can, for example, be improved further by using DMI instead of DMT as PTMO extender [15]. The synthesis would become more economically feasible when it can be performed in the melt, so when the T6T6T segment is formed in situ, for example, by starting from 6T6-diamine or even by starting from 1,6-hexamethylenediamine. Of course this is at the cost of uniformity of the T6T6T in the copolymer, but it was shown that a uniformity of at least 76% is sufficient for good properties. Another interesting modification would be to use other tetra-amides as crystallisable segment instead of T6T6T, for example, T4T4T. The melting temperature of nylon-4,T is 60 °C higher than that of nylon-6,T [26] and therefore, the melting temperature of a copolymer with T4T4T instead of T6T6T is expected to be about 60 °C higher. It is expected that the elasticity will be the same with T4T4T. Furthermore fibres that are processed by a commercial meltspinning process, where processing conditions are optimised will have better properties.

4. Conclusions

The tensile and elastic properties of segmented copolymers based on T6T6T-dimethyl (uniform and 76% uniform) and ($PTMO_{1000}$/DMT) of different lengths (3000–10,000 g/mol) are good. Stress–strain measurements show that extruded threads of these polymers have high fracture strains ($>1000\%$) and little strain hardening. The modulus and yield stress increase with increasing T6T6T content. The modulus decreases with increasing drawing-strain as a result of the breaking up of the crystalline network (strain softening). The influence of the uniformity of T6T6T is as yet not fully understood.

The compression and tensile set decrease with decreasing T6T6T content and are very low. The tensile set correlates well with other systems when it is given as function of soft segment length. The lower the hard segment content and the longer the length between the cross-link points, the higher is the elasticity. The tensile set ($TS_{300\%}$) decreases after pre-drawing of the extruded threads.

With T6T6T-($PTMO_{1000}$/DMT) with soft segment lengths of 6000–10,000 g/mol a tensile set lower than 5% is feasible. At a soft segment length of 6000 g/mol such a fibre has a flow temperature of 200 °C and the rubber modulus is 6.8 MPa, which means that the granulate will not be sticky. This type of thermoplastic elastomers is very interesting for application as elastic fibres. The segmented copolymers show a good combination of properties as they have a very good elasticity, are melt-processable (and can be recycled), have a high modulus (non-sticky), are transparent and are dimensionally stable up to high temperatures.

References

[1] Holden G, Legge NR, Quirk R, Schroeder HE, editors. Thermoplastic elastomers, 2nd ed. Munich: Hanser Publishers; 1996.
[2] Grady BP, Cooper SL. In: Mark JE, Erman B, Eirich FR, editors. Science and technology of rubber. San Diego: Academic Press; 1978. Chapter 13.
[3] Harrell LL. Macromolecules 1969;2:607.
[4] Ng HN, Allegrazza AE, Seymour RW, Cooper SL. Polymer 1973;14: 255.
[5] Eisenbach CD, Baumgartner M, Gunter G. In: Lal J, Mark JE, editors. Advances in elastomer and rubber elasticity. Proceedings Symposium, vol. 51. New York: Plenum Press; 1985.
[6] Miller JA, Shaow BL, Hwang KKS, Wu KS, Gibson PE, Cooper SL. Macromolecules 1985;18(1):32.
[7] Krijgsman J, Husken D, Gaymans RJ. Polymer 2003;44(23):7043.
[8] Krijgsman J, Husken D, Gaymans RJ. Polymer 2003;44(25):7573.
[9] Cella RJ. J Polym Sci: Symp 1973;42:727.
[10] Zhu L, Wegner G. Makromol Chem 1981;182:3625.
[11] Sauer BB, McLean RS, Thomas RR. Polym Int 2000;49:449.
[12] Niesten MCEJ, Gaymans RJ. Polymer 2001;42:6199.
[13] Niesten MCEJ, Krijgsman J, Gaymans RJ. J Appl Polym Sci 2001;82: 2194.
[14] Niesten MCEJ, Feijen J, Gaymans RJ. Polymer 2000;41:8487.
[15] Niesten MCEJ, Ten Brinke JW, Gaymans RJ. Polymer 2001;42:1461.
[16] Hoffman JD, Weeks JJ. J Res Nat Bur Stand, Sect A 1962;66:13.
[17] McCrum NG, Buckley CP, Bucknall CB, editors. Principles of polymer engineering, 1st ed. Oxford: Oxford University Press; 1988. Chapter 5.
[18] Sperling LH, editor. Introduction to physical polymer science, 2nd ed. New York: Wiley; 1992. Chapter 8.
[19] BASF, Lupolen series, Datasheet; 1979.
[20] Brown N. In: Browstow W, Corneliussen RD, editors. Failure of plastics. Munich: Hanser Publishers; 1979. Chapter 6.
[21] Young RJ. Mater. Forum 1988;11:210.
[22] Niesten MCEJ, Harkema S, Van der Heide E, Gaymans RJ. Polymer 2001;42:1131.
[23] McLean RS, Sauer BB. J Polym Sci: Part B: Polym Phys 1999;37:859.
[24] Krijgsman J. Thesis. Engineering polymers with uniform crystallisable units, University of Twente; 2002.
[25] Niesten MCEJ, Gaymans RJ. J Appl Polym Sci 2001;81:1372.
[26] Morgan PW, Kwolek SL. Macromolecules 1975;8:104.