

Influence of Extenders on Thermal and Elastic Properties of Segmented Copolyetheresteraramides

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ABSTRACT: Copolyetheresteraramides with bisesterdiamide units of a uniform length were synthesized in the current study, and the dynamic mechanical and elastic properties of the copolymers produced were studied. Diols are used to extend the length of uniform bisesterdiamide hard segments. Extenders have a twofold effect: increasing the lamellar thickness of the bisesterdiamide crystals and having the ability to independently adjust the ratio between the hard and soft segment. It was found that polymers containing 1,12-dodecanediol as an extender possess a multiphase structure. Two glass-transition temperatures (T_g) were observed along with a very broad melting transition. The T_g at about -70°C was found to originate from the amorphous polyether phase, the T_g at about $140\text{--}175^\circ\text{C}$ was attributed to a glassy aramid-1,12-dodecanediol phase. The broad melting transition was caused by the presence of the wide variety of lamellar sizes. This multiphase morphology is probably results from the liquid-liquid demixing of an aramid-polyether and from the aramid-extender phase. Polymers containing 1,12-dodecanediol and 13 wt % aramid had an improved elasticity compared to similar polymers without an extender. It is thought this is the result of large isolated, spherically shaped domains become less plastically deformed than the crystalline network of thin lamellae. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1605–1613, 2001

Key words: segmented copolymers; copolyetheresteraramides; extenders; uniform

INTRODUCTION

Segmented copolymers with a low glass-transition temperature are elastic materials. Their elasticity is a direct result of their phase-separated morphology. The hard segments form crystalline or glassy domains, which act as physical crosslinks for the amorphous soft segments.¹ The lower the plastic deformation of the physical crosslinks, the better is the elasticity of the material. Phase separation between the hard and soft segments can occur in two ways: through liquid-liquid demixing² or through crystalliza-

tion³ of the hard segments. Segmented polyurethanes are known to phase-separate through liquid-liquid demixing⁴; the hard polyurethane segments first cluster into domains, and it is often the case that part of the already phase-separated hard segments crystallize upon cooling. If fast-crystallizing hard segments such as polyester (PET, PBT) or polyamide segments are used, phase separation occurs through crystallization.⁵ The two types of phase separation result in different morphologies. Segmented polyurethanes possess a multiphase structure with several glass and melting transitions, and they contain isolated spherical glassy domains.⁶ Segmented copolyetheresters, on the other hand, contain an interconnecting network of hard segments crystallized into lamellae.^{3,5} Isolated glassy domains are gen-

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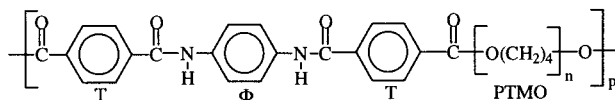


Figure 1 Structure of segmented copolymer TΦT-PTMO.

erally larger and are expected to deform harder than a network of crystalline lamellae. The question is: does a liquid-liquid demixing copolymer have a better elasticity than a two-phase copolymer containing a crystalline network?

Alternating segmented copolyetheresteramides with uniform thin crystallizable aramid (TΦT) units and PTMO-based soft segments (Fig. 1) are very fast-crystallizing materials with a well-defined two-phase structure. The TΦT units phase-separate easily into a crystalline network, and if the aramid content is small, there is low crystallinity and a highly elastic copolymer.⁷ However, at a TΦT concentration below 13 wt %, the melting temperature drops below 170°C. The melting temperature of a segmented copolymer decreases with increasing soft-segment content because of the solvent effect.⁸ In alternating TΦT-PTMO copolymers with uniform TΦT units, decreasing the TΦT content automatically results in an increase of the soft-segment content (length) and consequently a larger solvent effect. The low melting temperature might be overcome by using extenders, as the melting temperature of the polymers is influenced by the lamellar thickness.⁹ Extenders are short diols that couple two TΦT units. Using extenders, the hard- and soft-segment content in the polymers can be independently adjusted. A schematic representation of copolymers containing extenders is shown in Figure 2. The transesterification reaction of a diol being incorporated between two TΦT units is random; consequently, the formation of a distribution of extended block lengths is likely. A side effect of using extenders is the possibility of melt phasing occurring during polymerization.

Eisenbach¹⁰ investigated the influence of different types of extenders in segmented polyurethanes with hard segments of uniform length. The short extender 1,4-butanediol resulted in ex-

tended crystallization. Longer extenders such as 1,6-hexanediol or 1,8-octanediol tended to produce extended crystallization upon crystallization from solution, while on crystallization from the melt, they primarily produced chain-folded crystals. By using the folded extender 2,2'-(1,2-phenylenedioxy)diethanol, only chain folded crystals were formed. Hirt and Herlinger¹¹ studied alternating copolyetheresteramides with aromatic uniform amide as the hard segments and either alkanediol or PTMO as the soft segments. The diols that were shorter than the hard segments (<2 nm) were able to crystallize with the hard segments. These researchers concluded that PTMO with a minimum length of 650 g/mol is needed to form a continuous soft phase that does not extend the hard segments.

In copolyetheresteramides with T6T (1,6-hexanediamine-based) as the crystalline segment, PTMO as the amorphous segment, and 1,6-hexanediol as the extender, an increase in the hexanediol content resulted in an increase of the melting temperature.¹²⁻¹⁵

Bouma¹⁶ studied the T2T-PTMO system (1,2-ethanediamine-based), in which 1,2-ethanediol is used as the extender. In this way alternating amide-ester-amide segments were introduced, which formed a separate crystalline lamellar phase with a much higher melting temperature ($T_m > 300^\circ\text{C}$) than the nonextended T2T segments ($T_m = 110-160^\circ\text{C}$).

Guang and Gaymans¹⁷ investigated the T4T-PTMO₁₀₀₀ system (1,4-butanediol-based), using 1,5-pentanediol as an extender. T4T-(PTMO₁₀₀₀/pentanediol) copolymers have two glass-transition temperatures (T_g) and two melting temperatures. The positions of the two glass-transition temperatures are independent of the composition, and therefore two fully phase-separated amorphous phases are present. The melting temperatures were found to change with composition, the amount of pentanediol affecting both melting temperatures and thus the lamellar structures. One T_g , which originated from the PTMO amorphous phase, was -65°C . The other T_g was 120°C and represented the glass transition of the T4T-pentanediol phase. There was a crystalline T4T



Figure 2 Schematic representation of TΦT-PTMO copolymers containing an extender: (□) TΦT unit; (—) extender; and (~~~~) PTMO.

phase that consisted of very thin crystalline lamellae, and finally there was a crystalline T4T-pentanediol phase that melted at a higher temperature than the T4T lamellae because the T4T-pentanediol lamellae were thicker. Because of the presence of the glassy T4T-pentanediol phase, some liquid-liquid demixing occurred, resulting in a multiphase structure similar to that of segmented polyurethanes.

The current study attempted to increase the melting temperature of the polymers by incorporating diols as extenders of the T Φ T units. Extenders might result in polymers with a multiphase structure similar to polyurethanes. The question the study asked was: Can such a multiphase structure influence the elasticity of the polymers? Thus, the study investigated the influence of diols as extenders of the T Φ T units on the thermal and elastic properties of T Φ T-PTMO_{2000m} copolymers.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), 2,5-hexanediol, 1,8-octanediol, 1,12-dodecanediol, and *N*-methyl-2-pyrrolidone (NMP) were purchased from Merck (Darmstadt, Germany). 2,2'-(1,2-phenylenedioxy)-diethanol was purchased from Aldrich (Bornem, Belgium). Tetraisopropyl orthotitanate [Ti(i-OC₃H₇)₄], obtained from Merck, was diluted in anhydrous *m*-xylene (0.05*M*), obtained from Fluka (Steinheim, Germany). T Φ T-dimethyl was synthesized as described in a previous article.¹⁸ Poly(tetramethylene oxide) (PTMO, *M* = 250–2000 g/mol) was provided by DuPont (Wilmington, DE) and modified PTMO (PTMO_m, *M* = 1000–2000 g/mol) by Mitsui (Japan). Irganox 1330 was obtained from CIBA. All chemicals were used as received.

Polymerization

The procedure for the preparation of T Φ T-(PTMO₂₀₀₀/1,12-dodecanediol), which follows, is indicative of the preparation done for all the materials. The reaction was carried out in a 250-mL stainless-steel vessel with a nitrogen inlet and a mechanical stirrer. The vessel, containing T Φ T-dimethyl (4.41 g, 0.0102 mol), PTMO₂₀₀₀ (12 g, 0.06 mol), 1,12-dodecanediol (0.85 g, 0.0042 mol), Irganox 1330 (0.2 g), and 100 mL of NMP, was

heated in an oil bath to 180°C. Then the catalyst solution was added [1 mL of 0.05*M* Ti(i-OC₃H₇)₄ in *m*-xylene]. After a reaction time of 30 min, the temperature was raised to 250°C, which was maintained for 2 h. The pressure was then carefully reduced (*P* < 20 mbar) to distill off then NMP and then was further reduced (*P* < 1 mbar) for 60 min. Finally, the vessel was allowed to cool slowly to room temperature while maintaining the low pressure.

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.

Dynamic Mechanical Analysis

Samples for the dynamic mechanical analysis (DMA) test (70 × 9 × 2 mm) 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 functions 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 taken as the glass-transition temperature. The flow temperature was defined as the temperature at which the storage modulus reached 1 MPa.

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, with strain measured as clamp displacement with a starting clamp distance of 40 mm. The samples were strained to 100% within 5 s at room temperature. The decay of the stress was measured for 30 min. The absolute value of the slope of the line, was used as the measure of stress relaxation (*SR*_{*x*%}). It was obtained from the stress plotted versus the logarithm of time .

$$SR_{x\%} = \frac{|\Delta\sigma_{x\%}|}{\Delta \log t} \quad (1)$$

Table I Composition and DMA Properties of T Φ T-(PTMO_{2000m}/PTMO)

M_{PTMO_m} [g/mol]	Extender	T Φ T Content [wt %]	η_{inh} [dl/g]	T_g (°C)	T_f (°C)	G' (25°C) (MPa)
1000	None	22	1.10	-76	250	49
2000	None	13	2.38	-75	193	10
2000	PTMO ₁₀₀₀	16	1.05	-75	198	20
2000	PTMO ₆₅₀	18	0.81	-75	214	27
2000	PTMO ₂₅₀	20	0.95	-75	270	36

Tensile Set

Samples for the tensile set determination were prepared by extruding the polymers into unoriented threads on an Arburg H manual injection-molding machine. The barrel temperature of the injection molding machine was set at 50°C above the flow temperature of the polymer. The thread was directly extruded from the barrel, with the mold removed from the injection molding machine.

The tensile set was determined by applying a 300% cyclic strain at a strain rate of 200 mm/min, with a starting clamp distance of 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:

$$TS_{300\%} = \frac{\text{residual strain}}{300} \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

Introduction

Different diols were incorporated into T Φ T-PTMO copolymers to extend the T Φ T units. First, a series of polymers containing 1:1 wt % (molar) mixtures of PTMO and modified PTMO (containing 15 wt % of various methyl side groups, PTMO_m) were synthesized. The length of the PTMO segments was reduced from 1000, from 650 to 250 g/mol, while the PTMO_m length was kept constant at 2000 g/mol. From this series the PTMO length at which PTMO acts as an extender (crystallizes with T Φ T) was determined. Furthermore, these polymers were used to study the effect of broadening the PTMO molecular weight distribution on the modulus of the materials. In the next series of polymers, different diols [2,5-hexanediol, 1,8-octanediol, 1,12-dodecanediol, and 2,2'-(1,2-phenylenedioxy)diethanol] were incorporated into

T Φ T-PTMO_{2000m} as extenders in order to study the effect of the different extenders on the melting temperature of the polymer. Modified PTMO was chosen for its low T_g in order to obtain a polymer with a large rubbery plateau. Finally, using 1,12-dodecanediol as the extender, several polymers with a T Φ T content varying from 13 wt % to 22 wt % were synthesized to relate the structure of the polymers to their elasticity.

PTMO as Extender

Table I shows the composition and dynamic mechanical properties of T Φ T-(PTMO_{2000m}/PTMO) copolymers. The molar ratio of PTMO_{2000m} and PTMO is 1:1, leading to an increase in the T Φ T content from 13 wt % (no PTMO) to 20 wt % (PTMO₂₅₀). As a comparison, data for T Φ T-PTMO_{1000m} (22 wt %) are also shown.

The polymers have one glass-transition temperature, at -75°C, originating from the mixed PTMO phase (PTMO + PTMO_m). In Figure 3 the flow temperature (T_f , the temperature where G' reaches 1 MPa, the onset of melting) is plotted

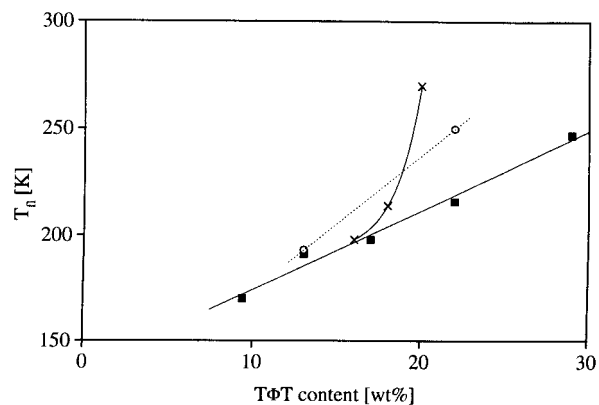


Figure 3 Flow temperature versus T Φ T content for (■) T Φ T-PTMO, (○) T Φ T-PTMO_m; and (×) T Φ T-(PTMO_{2000m}/PTMO).

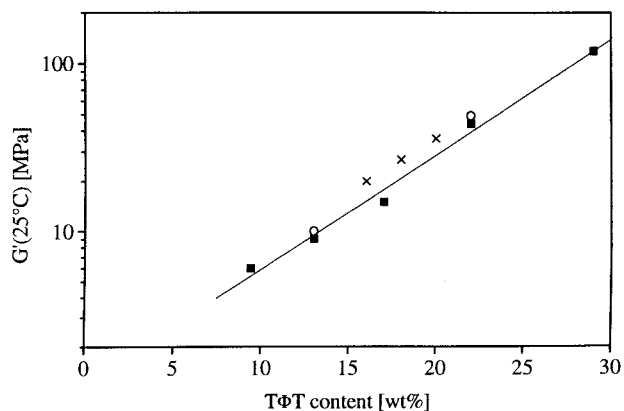


Figure 4 Shear rubbery modulus versus TΦT content for (■) TΦT-PTMO (values reported in chapter 2), (○) TΦT-PTMO_m, and (×) TΦT-(PTMO_{2000m}/PTMO).

versus the TΦT content for TΦT-PTMO,¹⁸ TΦT-PTMO_m, and TΦT-PTMO_{2000m}/PTMO).

The flow temperature, which decreases with decreasing TΦT content, depends on the lamellar thickness and on the solvent effect.^{8,9} In the TΦT-PTMO and in TΦT-PTMO_m copolymers, the lamellar thickness is constant; hence, the decrease in the melting temperature with decreasing TΦT content can be fully ascribed to an increase of the solvent effect. The flow temperature of TΦT-(PTMO_{2000m}/PTMO₁₀₀₀) lies on the line of TΦT-PTMO; thus, it can be concluded that TΦT lamellae are formed, while PTMO₁₀₀₀ and PTMO_{2000m} together form one amorphous phase. As expected,¹¹ only PTMO₂₅₀ is short enough to lead to extended crystallization of the TΦT units, producing a high flow temperature, of 270°C, even higher than the flow temperature of TΦT-PTMO_{1000m}, which has a comparable TΦT content. This suggests that in this polymer extended TΦT-PTMO₂₅₀ crystalline lamellae are formed that melt at a higher temperature than do the TΦT lamellae. The polymer containing PTMO₆₅₀ has a somewhat higher flow temperature than would be expected if only TΦT lamellae were present. It is possible that some of the PTMO₆₅₀ has formed extended lamellae. PTMO segments longer than PTMO₂₅₀ mainly mix with PTMO_{2000m}, forming one amorphous matrix.

An effect of using mixtures of PTMO is an increase in the PTMO molecular weight distribution. In Figure 4 the shear rubbery modulus is plotted versus the TΦT content for TΦT-PTMO, TΦT-PTMO_m, and TΦT-(PTMO_{2000m}/DMT) copolymers. The rubbery modulus increases with increasing TΦT content because of an increase in

crystallinity and hence an increase in the physical crosslink density. The rubbery moduli of TΦT-(PTMO_{2000m}/PTMO) lie on the line of TΦT-PTMO, and therefore it is clear that the molecular weight distribution of the PTMO phase does not influence the rubbery modulus.

Types of Extenders

Several diols were incorporated as extenders in the TΦT-PTMO_{2000m}. Half the PTMO_{2000m} segments were replaced by diols. The following diols were used: 2,5-hexanediol, 1,8-octanediol, 1,12-dodecanediol, and 2,2'-(1,2-phenylenedioxy)diethanol (Fig. 5). The composition and DMA properties of these polymers are shown in Table II.

In Figure 6 the storage modulus of the polymers is plotted versus the temperature. TΦT-PTMO_{1000m} and TΦT-PTMO_{2000m} are included as references. For all polymers the drop of the modulus at the T_g is sharp, suggesting that the phase separation between the TΦT units and the PTMO segments is very good. The shoulder in the temperature range from -50°C to 0°C is caused by PTMO crystallization. The rubbery plateau is temperature independent over a wide temperature range. The flow transitions of TΦT-PTMO_{2000m} (curve a) and TΦT-PTMO_{1000m} (curve b) are very sharp because of the uniform TΦT units, which form crystalline lamellae with a constant thickness and melt in a narrow temperature range. Polymers containing 2,5-hexanediol or 1,12-octanediol (curves c and e) possess a gradually decreasing rubbery plateau above the flow temperature of TΦT-PTMO_{2000m}, suggesting that a range of lamellar sizes is present. Apparently extended crystals, such as TΦT-diol-TΦT and TΦT-diol-TΦT-TΦT-diol-TΦT, are formed. The polymers with 1,8-octanediol (curve d) and 2,2'-(1,2-phenylenedioxy)diethanol (curve f) seem to have two flow transitions and a second rubbery plateau after the first flow transition. It is probable that two crystalline phases are present: one consisting of TΦT lamellae, the other of TΦT-octanediol or TΦT-2,2'-(1,2-phenylenedioxy)di-

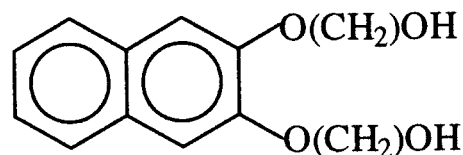


Figure 5 Structure of 2,2'-(1,2-phenylenedioxy)diethanol.

Table II Composition and DMA Properties of T Φ T-(PTMO_{2000m}/diol)

M_{PTMO_m} [g/mol]	Extender		T Φ T-Content (wt %)	η_{inh} (dl/g)	T_g (°C)	T_f (°C)	G' (25°C) (MPa)
1000	None	a	22	1.10	-76	250	49
2000	None	b	13	2.38	-75	193	10
2000	2,5-Hexanediol	c	20	1.05	-73	259	19
2000	1,8-Octanediol	d	19	1.10	-72	273	19
2000	1,12-Dodecanediol	e	19	0.68	-75	> 290	18
2000	2,2'-(1,2-phenylenedioxy)diethanol	f	19	0.75	-72	277	16

ethanol lamellae. Eisenbach¹⁰ also observed that these two diols prefer to give folded polyurethane crystalline lamellae. As 2,2'-(1,2-phenylenedioxy)diethanol itself forms a fold, the fraction of folded lamellae will be higher than for 1,8-octanediol, which explains the more pronounced second rubbery plateau of polymer (curve f) as compared to polymer (curve d). From Figure 6 it is clear that the T Φ T-2,2'-(1,2-phenylenedioxy)diethanol lamellae melt at a higher temperature than do T Φ T lamellae, probably because the diol is very rigid. It is expected that a shorter diol crystallizes better into extended T Φ T-diols lamellae than does a long diol, resulting in a higher melting temperature. However, the melting temperature of the polymer with 1,8-octanediol is lower than of the polymer with 1,12-dodecanediol, which can be explained by assuming that part of the 1,8-octanediol forms lamellar folds instead of extending the T Φ T lamellae.

Influence of Extender 1,12-Dodecanediol on Phase Structure

1,12-Dodecanediol was chosen as the extender for a more detailed study of the effect of extenders on

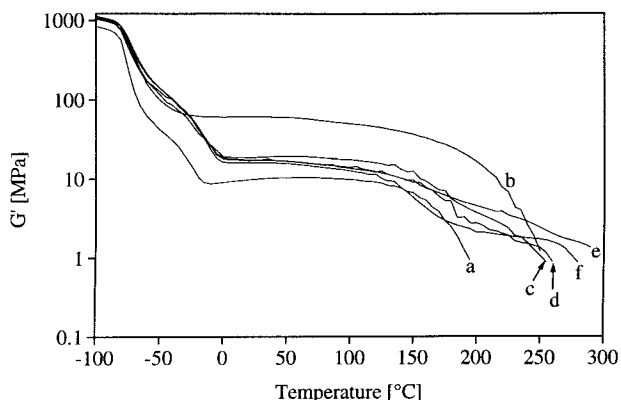


Figure 6 Storage modulus versus temperature for (a) T Φ T-PTMO_{2000m}, (b) T Φ T-PTMO_{1000m}, (c) T Φ T-(PTMO_{2000m}/hexanediol), (d) T Φ T-PTMO_{2000m}/octanediol, (e) T Φ T-(PTMO_{2000m}/dodecanediol), and (f) T Φ T-(PTMO_{2000m}/(phenylenedioxy)diethanol).

the phase structure. It was incorporated in T Φ T-PTMO_{2000m} and T Φ T-PTMO₂₀₀₀, with a T Φ T content of 20 wt %. In Figure 7 loss modulus is plotted versus temperature for these two polymers. Both curves show two peaks, indicating two glass transitions. The large peaks, at -75°C and at -70°C, originate from the amorphous PTMO_{2000m} and PTMO₂₀₀₀ phases, respectively. The small peaks, at approximately 140°C and 175°C, respectively, suggest that there is also a glassy T Φ T-dodecanediol phase present. Since there is a glass transition above room temperature, some liquid-liquid demixing must have occurred. PBT-PTMO copolymers are known to melt-phase during polymerization at certain compositions. For PBT-PTMO copolymers melt phasing depends on the PTMO length and concentration.¹⁹ T Φ T-PTMO copolymers have been found to form a homogeneous melt during polymerization up to a PTMO₁₀₀₀/DMT molecular weight of 9000 g/mol. Apparently, if at a constant PTMO length the T Φ T content is increased by using an extender, melt phasing already occurs. This is shown schematically in Figure 8.

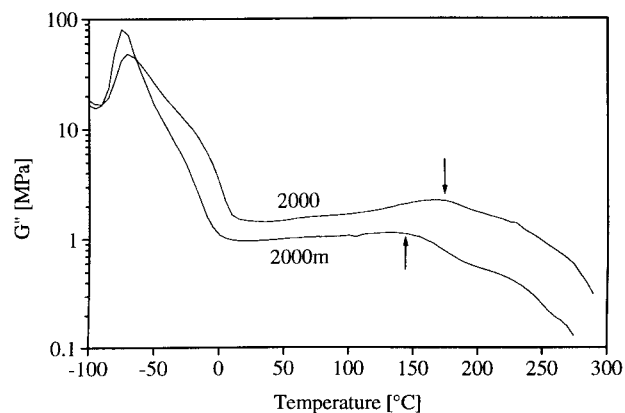


Figure 7 Loss modulus versus temperature for T Φ T-(PTMO_{2000m}/dodecanediol) and T Φ T-(PTMO₂₀₀₀/dodecanediol).

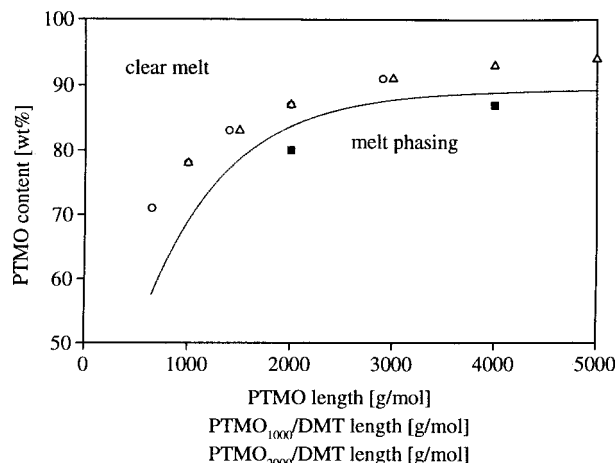


Figure 8 Melt phasing during polycondensation as a function of PTMO or PTMO-DMT length and content for (○) TΦT-PTMO, (△) TΦT-(PTMO₁₀₀₀/DMT), and (■) TΦT-(PTMO₂₀₀₀/DMT/1,12-dodecanediol).

Unfortunately, melt phasing could not be observed visually because the extended TΦT-1,12-dodecanediol-TΦT lamellae crystallized at 250°C. In accordance with the observations of Guang and Gaymans¹⁷ on the T4T-(PTMO/pentanediol) system, the following morphology is proposed, as can be seen in Figure 9: A represents the PTMO amorphous phase and B the TΦT crystalline phase; together they form part I. C is the TΦT-dodecanediol amorphous phase and D the extended TΦT crystalline phase; together they form part II. E is the adjacent reentry group and is present in parts I and II. Parts I and II phase-

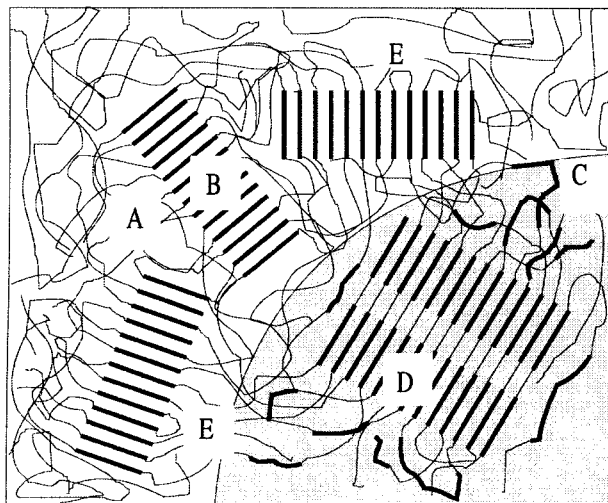


Figure 9 Proposed morphology of TΦT-(PTMO/1,12-dodecanediol).

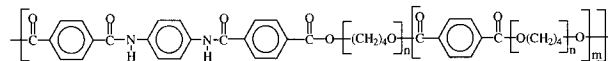


Figure 10 Structure of TΦT-(PTMO₂₀₀₀/DMT).

separate through melt phasing, followed by crystallization and vitrification of the TΦT and TΦT-dodecanediol phases, respectively. This morphology has some similarity with the morphology of polyurethanes.

Influence of the Extender 1,12-Dodecanediol on Elasticity and Melting Temperature

The multiphase structure of TΦT-(PTMO_{2000m}/1,12-dodecanediol), described above, might result in a different elasticity than that of the TΦT-PTMO copolymers. In the latter, only a crystalline TΦT and an amorphous PTMO phase are present. In a previous study²⁰ it was shown that the elasticity of TΦT-PTMO copolymers increases with decreasing TΦT content because of a decrease in crystallinity. Especially elastic are polymers with TΦT contents below 13 wt %. The TΦT content in TΦT-(PTMO_{2000m}/1,12-dodecanediol) can be reduced by adding dimethyl terephthalate (DMT). This is a method of making long PTMO blocks from short PTMO segments (Fig. 10). In a previous study²⁰ it was shown that DMT mixes with the PTMO amorphous phase without affecting the T_g .

A side effect of incorporating DMT into this system is the presence of some 1,12-dodecanediol in the amorphous PTMO because of reacting with DMT molecules. Unfortunately, this reduces the effectiveness of 1,12-dodecanediol as the extender. Table III gives an overview of the composition and dynamic mechanical and elastic properties of the polymers. The incorporation of 1,12-dodecanediol has almost no effect on the T_g of the PTMO phase. The storage moduli of the 1,12-dodecanediol-containing polymers with different TΦT contents (indicated between brackets) are plotted versus the temperature in Figure 11. At high temperatures all the polymers possess a gradually decreasing rubbery plateau because of the presence of extended TΦT crystalline lamellae melting in a broad temperature range. In Figure 11 curves a and b (20 wt %) show a more gradually decreasing modulus above 150°C than do curves c and d (13 wt %). The polymers with 20 wt % TΦT do not contain DMT. The effect of 1,12-dodecanediol is reduced if DMT is incorporated, as is the case for the polymers containing

Table III Composition and DMA Properties of TΦT-(PTMO_{2000(m)})/(DMT)/1,12-dodecanediol

Polymer	TΦT-Content [wt %]	η_{inh} [dl/g]	T_g [°C]	T_{fl} [°C]	G' (25°C) [MPa]	$SR_{100\%}$	$TS_{300\%}$
TΦT-PTMO _{1000m}	22	1.10	-76	250	49	0.79	—
TΦT-PTMO _{2000m}	13	2.38	-75	193	10	0.43	21
TΦT-ddd-PTMO _{2000m}	b	20	0.68	-75	> 290	—	—
TΦT-ddd-(PTMO _{2000m} /DMT) ₄₀₀₀	13	1.00	-75	229	13	0.41	—
TΦT-ddd-(PTMO _{2000m} /DMT) ₄₀₀₀	13	1.00	-75	240	11	0.35	24
TΦT-ddd-(PTMO _{2000m} /DMT) ₄₀₀₀	d	13	1.18	-70	205	5	0.29
TΦT-PTMO ₁₀₀₀	22	1.81	-69	216	44	0.82	46
TΦT-PTMO ₂₀₀₀	13	2.04	-65	191	10	0.48	27
TΦT-ddd-PTMO ₂₀₀₀	a	20	0.80	-70	> 290	—	—
TΦT-ddd-(PTMO ₂₀₀₀ /DMT) ₄₀₀₀	c	13	1.20	-70	230	12	0.39

SR , stress relaxation; TS , tensile set.

13 wt % TΦT. In addition to being an extender of the TΦT units, 1,12-dodecanediol also will then be partly present in the amorphous PTMO-DMT phase by reacting with DMT.

The surprising difference in the rubbery modulus for polymers with the same composition might be attributed to the multiphase structure of these polymers, a result of melt phasing, which is temperature dependent. Thus, small variations in the reaction temperature might result in a different phase structure.

The stress relaxation and tensile set were determined as a measure of elasticity. In an ideal elastomer no stress relaxation occurs, and the tensile set is zero. The stress relaxation was measured at 100% strain, and the tensile set after

300% strain. The polymers containing 20 wt % TΦT were too brittle to determine stress relaxation and tensile set. In a previous study²¹ it was shown that the stress relaxation and tensile set of TΦT-(PTMO₁₀₀₀-DMT) copolymers decrease with decreasing TΦT content and thus with decreasing crystallinity. The rubbery modulus increased with the TΦT content, and an almost linear relationship between the tensile set and rubbery modulus was found. In Figure 12 the stress relaxation and tensile set of the 1,12-dodecanediol-containing polymers are compared to the TΦT-(PTMO₁₀₀₀/DMT) series by plotting stress relaxation and tensile set versus the logarithm of the shear rubbery modulus.

Stress relaxation and tensile set decrease with decreasing rubbery modulus because of a decrease in TΦT content and thus in crystallinity. The 1,12-dodecanediol-containing polymers with 13 wt % TΦT [G' (25°C); 10–12 MPa] have a lower stress relaxation and tensile set than similar polymers without 1,12-dodecanediol. This improved elasticity might be a result of the multiphase structure of these polymers. Apparently, liquid-liquid demixing yields some isolated domains, which are expected to plastically deform less than a crystalline network of extremely thin TΦT lamellae.

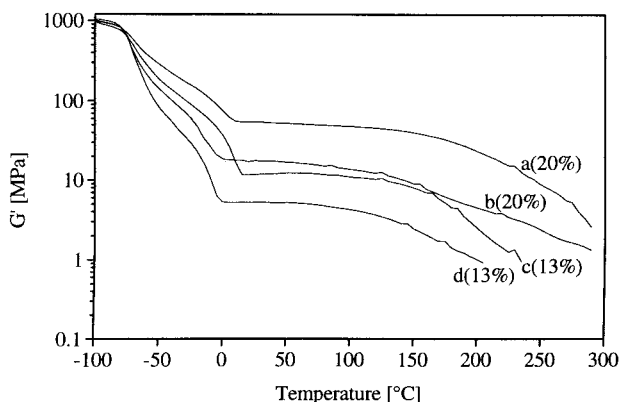


Figure 11 Storage modulus versus temperature for (a) TΦT-(PTMO₂₀₀₀/1,12-dodecanediol), 20 wt % TΦT; (b) TΦT-(PTMO_{2000m}/1,12-dodecanediol), 20 wt % TΦT; (c) TΦT-[(PTMO₂₀₀₀/DMT)₄₀₀₀/1,12-dodecanediol], 13 wt % TΦT; and (d) TΦT-[(PTMO_{2000m}/DMT)₄₀₀₀/1,12-dodecanediol], 13 wt % TΦT.

CONCLUSIONS

The melting temperature of TΦT-PTMO copolymers can be increased considerably by building in extenders such as 2,5-hexanediol, 1,8-octanediol, 1,12-dodecanediol, 2,2'-(1,2'-phenylenedioxy)diethanol, and PTMO₂₅₀. The folded extender 2,2'-

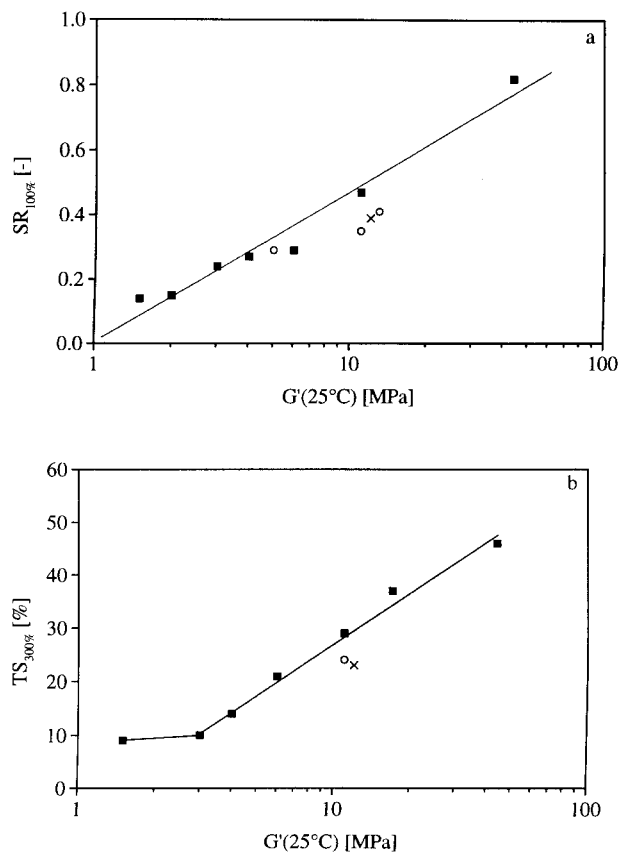


Figure 12 (a) Stress relaxation at 100% strain and (b) tensile set after 300% strain versus shear rubbery modulus for (■) T Φ T-(PTMO₁₀₀₀/DMT); (○) T Φ T-[(PTMO₂₀₀₀ml/DMT)₄₀₀₀/1,12-dodecanediol], 13 wt % T Φ T; (×) T Φ T-[(PTMO₂₀₀₀/DMT)₄₀₀₀/1,12-dodecanediol], 13 wt % T Φ T.

(1,2'-phenylenedioxy)diethanol results in crystalline lamellae that have an increased melting temperature compared to the "pure" T Φ T lamellae, and the melting temperature is still sharp. PTMO segments longer than 650 g/mol do not act as an extender but mix with the amorphous phase. Extenders couple two T Φ T units, leading to an increase of the lamellar thickness and thus an increase and broadening of the melting temperature. Polymers containing 1,12-dodecanediol as an extender possess a multiphase structure. Two glass transitions were observed along with a very broad melting transition. The T_g at about -70°C originates from the amorphous PTMO phase, the T_g at about 140 – 175°C is attributed to a glassy T Φ T-1,12-dodecanediol phase. The broad melting

transition is caused by the presence of a wide variety of lamellar sizes, such as T Φ T, T Φ T-diol-T Φ T, and T Φ T-diol-T Φ T-diol-T Φ T. This four-phase morphology is probably caused by liquid-liquid demixing of a T Φ T-PTMO and a T Φ T-dodecanediol phase. Polymers containing 1,12-dodecanediol and 13 wt % T Φ T have an improved elasticity as compared to similar polymers without an extender. This can be understood by the idea that large, isolated spherically shaped domains plastically deform less than a crystalline network of thin lamellae.

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