Polyether-amide Segmented Copolymers Based on Ethylene Terephthalamide Units of Uniform Length

KRISTA BOUMA,* GEERTJE A. WESTER,† REINOUD J. GAYMANS

University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

ABSTRACT: Segmented copolymers were synthesized using the crystallizable bisester-diamide segment (N,N'-bis(p-carbomethoxybenzoyl)ethanediamine) T2T-dimethyl (a one-and-a-half repeating unit of nylon 2,T) and poly(tetramethyleneoxide) segments. Poly(tetramethyleneoxide) (PTMO) is amorphous and has a low T_g. The segment length was varied from 650 to 2800 g/mol by extending $PTMO_{650}$ using dimethyl isophthalate. The polymers were synthesized in the melt, and test samples were prepared by injection molding. The melting behavior, as well as the torsion modulus spectrum as a function of temperature, were studied using DSC and DMA, respectively. The T2T-PTMO polymers were found to have sharp glass (T_g) and flow transitions (T_{fl}), and the modulus at the rubbery plateau appeared to be virtually temperature independent. The T_g value was found to be independent of the diamide concentration, thus indicating that the T2T segments were fully crystallized. The T_{fl} was found to decrease with increasing soft segment length; this was ascribed to a "solvent" effect of the amorphous phase of the crystalline T2T units. The difference between the melting and crystallization temperatures was found to be low, thus suggesting that on cooling, there is a high rate of crystallization. When ethanediol was added as a T2T segment extender, amide-ester-amide segments were introduced. These amide-ester-amide segments form a separate lamellar phase with a much higher melting temperature ($>300°C$). It was found that the crystallization rate of the T2T units was enhanced by the presence of the amide-ester-amide segments, indicating that upon cooling, the crystallized amide-ester-amide segments form the nucleation sites for the nonextended T2T segments. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1173–1180, 2001

Key words: diamide segment; ethylenediamine; poly(tetramethyleneoxide); segmented copolymers

INTRODUCTION

In segmented copolymers with crystallizable units, the chemical composition of the crystalline phase is different from that of the amorphous phase. As a result, these copolymers exhibit a low glass transition temperature of the amorphous phase and a high melting temperature of the crystalline phase. Typical examples include the polyurethanes,[1] as well as the poly(ester-ether)[2] and the poly(ether-amide)[3] segmented copolymers; all of these polymers exhibit interesting thermoplastic elastomer (TPE) properties. The segments that are able to crystallize are usually only partially crystallized, with the noncrystallized units being mixed with the amorphous segments or forming a

separate amorphous phase. Due to this partial crystallization, the low-temperature flexibility of the copolymer is reduced. The degree of crystallization of the crystalline units is decreased if the segment length is short or the segment length distribution broad. In poly(butyleneterephthalate-polytetramethyleneoxide) (PBT-PTMO) segmented copolymers, the PBT segments that crystallize with a preferred length of at least four repeat units (6 nm).[2]

For TPEs, a high elasticity is desirable, this can be obtained by having a low crystalline segment content. A material with a low crystalline segment content, which crystallizes fast, is a difficult combination and cannot be obtained by reducing the segment length too much (e.g., PBT). A good phase separation by crystallization can be obtained in crystallizable segments having a uniform length.[4–6] Surprisingly, units of uniform length not only improve low temperature elasticity but also improve the fracture strain. A good phase separation can be obtained with a segment length of 2 nm. Polyurethanes containing uniform urethane units can be synthesized at low temperatures; however, these units randomize at high temperatures.[8,9] Uniform ester segments are not obtainable in polyester–polyether systems that are synthesized in, and processed from, the melt. Amide units randomize much slower than urethanes or esters, and uniform amide units can withstand randomization at much higher temperatures.[10] The amide unit that has been found to be resistant to randomization is the diamide based on butylene terephthalamide (T4T).[4,5]

Hard segments:

T2T

T4T

TφT

Soft segments:
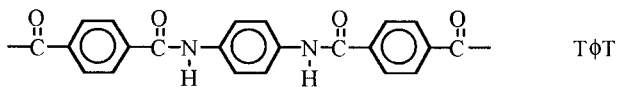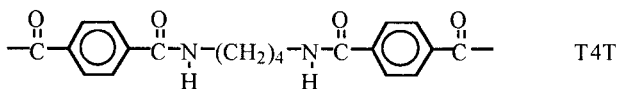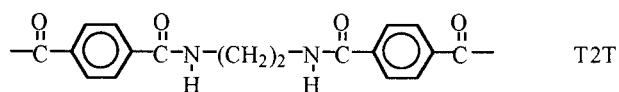
PTMO

PTMO extended with DMI
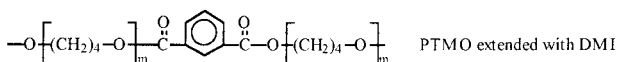
Structure of hard segments based on uniform diamide units and polyether segments of PTMO and PTMO extended with DMT

In these studies the dimethyl ester of the diamide (bisesterdiamide) (T4T-dimethyl) and PTMO were used to synthesize T4T–PTMO segmented copolymers. These copolymers crystallized extremely rapidly, having a low T_g in the PTMO phase, a rubber modulus plateau, which was little temperature dependent, and a had very high elongation at break (>1000%).

The melting temperature of T4T–PTMO polymers is not very high; for instance, the monomer, bisesterdiamide T4T-dimethyl, has a T_m of 265°C,[4] and a copolymer containing PTMO segments with a molecular weight 650 g/mol (PTMO$_{650}$) has a T_m of only 163°C. It is possible that the melting temperature of the polymer could be increased by using the higher melting bisesterdiamide based on 1,2 ethylene diamine (T2T-dimethyl), this has a T_m of 313°C.[7] Both T4T and T2T have been used to improve the thermal properties of PBT[11] and PET,[12] respectively; in addition, T4T has also been used in the synthesis of rapidly crystallizing alternating polyesteramides.[13]

An other bisesterdiamide unit that has been studied, is based on paraphenylene diamine (TφT–dimethyl).[6] This bisesterdiamide has a very high melting temperature (375°C), and is difficult to dissolve. TφT–PTMO polymers exhibit an interesting combination of properties in that TφT–PTMO$_{650}$ has a T_m of 266°C. The melting temperatures of the T×T–PTMO polymer is considerably lower than that of the bisesterdiamide (T×T–dimethyl) starting material, due to the solvent effect pf the PTMO soft phase.

In TPE polymers, PTMO is often chosen as a low T_g segment, as this segment has a low water absorption, and it can strain harden easily, resulting in high strength materials. The crystallization of PTMO increases strongly with increasing PTMO molecular weight, from a molecular weight 1000 to 2900. For a TPE having low modulus and a high elasticity, the molecular weight of the PTMO should be high; however, the PTMO crystallinity should remain low.[2] For example PTMO$_{2900}$ crystallize well, and thus, the low-temperature elasticity of the polymers containing PTMO$_{2900}$ is poor.[1] The crystallization of high molecular weight PTMO can be suppressed by reducing the structural regularity. A way to achieve this is by introducing terephthalic or

isophthalic groups in the PTMO chain.[6] This is accomplished by reacting a low molecular weight PTMO with either dimethyl terephthalate or dimethyl isophthalate. In this way polymers were obtained that have a low modulus, low temperature flexibility, and high elasticity. Surprisingly, using DMI to extend PMTO, does not increase the T_g of the polyether phase.[6]

The melting temperature of the diamide–PTMO polymers is not very high, and therefore, it was studied whether this melting temperature could be increased by extending the diamide unit using a diol. In T6T–PTMO copolymers the melting temperature was indeed increased by the incorporation of 1,6-hexanediol as the extender of the T6T units[14]; this effect can be explained by an increase in the lamellar thickness.[14,15] The melting temperature of the T4T–PTMO$_{1000}$ system can also be increased by using 1,5-pentanediol as an extender.[16] T4T–(PTMO$_{1000}$/pentanediol) copolymers have two glass transition temperatures and two melting temperatures. The positions of the two glass transition temperatures are independent of the copolymer composition, and therefore, two, fully phase separated, amorphous phases are able to exist. These are comprised of PTMO (T_g of $-65°C$) and T4T–pentanediol (T_g of $120°C$). The T_g of T4T–pentanediol is only visible when the pentanediol concentration is greater than 50 mol %. The two crystalline phases are comprised of the T4T segments and T4T segments extended with pentanediol. The melting temperature changes according to the amount of pentanediol present in the copolymer. This change in the melting temperature is a consequence of the lamellar thickening. In short, the diamides can be extended, containing longer crystallizing units, but these units then have a separate, high melting temperature.

The aim of the work described in this article was to study segmented copolymers based on bisesterdiamide T2T–dimethyl and PTMO. To date, these T2T–PTMO polymers have not yet been described. The effect of varying the PTMO length was studied by extending PTMO$_{650}$ using DMI. A PTMO having a very short length was taken to suppress possible crystallization of unstrained PTMO. We also studied the effect of extending the T2T unit with 1,2-ethanediol. This is expected to increases the thickness of the lamellae and with that the melting temperature.

EXPERIMENTAL

Materials

Dimethyl isophthalate (DMI), 1,2-ethanediol, tetraisopropyl orthotitanate (Ti(i-OC$_3$H$_7$)$_4$), and N-methyl-pyrrolidone (NMP) were purchased from Merck. Ti(i-OC$_3$H$_7$)$_4$ was diluted in anhydrous m-xylene (0.1M). All chemicals were used as received. PTMO$_{650}$ was obtained from BASF, and Irganox 1330 was provided by CIBA Geigy. The bisesterdiamide T2T–dimethyl was synthesized and purified as described previously.[7]

Melt Polycondensation of T2T–(PTMO$_{650}$/DMI)

The preparation of T2T–(PTMO$_{650}$/DMI)$_{1290}$ 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 T2T–dimethyl (5.76 g, 0.015 mol), PTMO$_{650}$ (19.50 g, 0.030 mol), DMI (2.91 g, 0.015 mol), Irganox 1330 (0.28 g), and 125 ml NMP was heated in an oil bath to 180°C, after which the catalyst solution (1.4 mL) was added. After 45 min reaction time, the temperature was increased to 250°C (15°C/10 min) 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 cool slowly to room temperature while maintaining the low pressure.

Viscometry

The inherent viscosity of the T2T–PTMO polymers at a concentration of 0.1 g/dL in a 50/50 mixture (molar fraction) of phenol/1,1,2,2-tetrachloroethane at 25°C was determined using a capillary Ubbelohde 1B.

NMR

Proton NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz using deuterated trifluoroacetic acid (TFA-d) as a solvent, without an internal standard.

Differential Scanning Calorimetry (DSC)

DSC spectra were recorded on a Perkin-Elmer DSC7 apparatus equipped with a PE7700 computer and TAS-7 software. Dried samples (2–5 mg) were measured at a cooling and heating rate of 20°C/min. First, the samples were heated to 250°C. This temperature was maintained for 2

Table I DSC and DMA Results of T2T-(PTMO$_{650}$/DMI)$_x$ Copolymers with Varying Amorphous Segment Length

(PTMO$_{650}$/DMI)$_x$ (g/mol)	T2T (wt %)	η_{inh} (dl/g)	T_m (°C)	T_c (°C)	ΔT (°C)	T_g (°C)	T_{fl} (°C)	G' (25°C) (MPa)
650	33	1.34	163	137	26	−51	158	77
940	25	1.76	145	122	23	−60	135	25
1290	20	1.53	133	107	26	−60	117	14
1930	14	1.09	—	—	—	−60	87	7
2770	10	1.52	—	—	—	−60	80	4

min, followed by cooling to 20°C, the maximum of the cooling scan being taken as the crystallization temperature. After 2 min at 20°C, the sample was heated for the second time to 250°C; the maximum of the second heating scan being taken as the melting temperature.

Dynamic Mechanical Analysis (DMA)

Samples for the 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, with the mold temperature being 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 then measured. Dried samples were first cooled to −100°C and then 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 (T_{fl}) was defined as the temperature where the storage modulus reached 1 MPa.

RESULTS AND DISCUSSION

Introduction

Segmented copolymers containing crystallizable T2T segments and amorphous PTMO segments were synthesized and the crystallization behavior of the diamide segments in these copolymers then studied. A polyether PTMO of a molecular weight of 650 (PTMO$_{650}$) having a low T_g was used as amorphous segment, as this short PTMO does not readily crystallize. The PTMO$_{650}$ was extended up to a molecular weight of 2770 g/mol, and DMI was used as extender in an attemp to suppress the PTMO crystallization. This would allow us to

study the way that the T2T concentration influences the properties, without having the side effect of crystallizing PTMO segments. The length of the T2T segment is only 1.7 nm; therefore, the expected lamellar thickness of this unit in the polymer is very small. However, extending the T2T segments with 1,2-ethanediol to amide-ester-amide segments, is believed to result in longer crystallizable units having a higher melting point.

T2T-(PTMO$_{650}$-DMT) Copolymers

A series of polyetheresteramides with varying amorphous segment lengths from 650 to 2770 g/mol were synthesized (Table I), the amorphous segment length being determined by ^{1}H-NMR. The inherent viscosity of the polyetheresteramides was found to be high—over 1.0 g/dL—and the melting and crystallization temperatures were found to decrease with decreasing diamide content. The melting endotherm and crystallization exotherms were difficult to determine due to the low T2T concentrations used. In the DSC-spectra of the T2T–(PTMO$_{650}$-DMI)$_{1930}$ and T2T–(PTMO$_{650}$-DMI)$_{2770}$ copolymers, we were unable to observe the melting and crystallization temperatures. The DMA flow temperatures (T_{fl}) are sensitive to the presence of a crystalline phase and the T_{fl} decreases with decreasing diamide content in a similar way to the T_m. Although the diamide concentrations were very low, the material crystallized easily on cooling. To obtain a measure of the ease of crystallization, the $T_m - T_c$ (ΔT) was calculated. The ΔT values were found to be low (<30°C), indicating that although there was a low T2T content and the length of the T2T unit was small, the crystallization was very rapid.

DMA analysis of the polymers was carried out on the injection moulded bars, the results of which are given in Figure 1. The T2T–PTMO$_{650}$,

T2T–(PTMO$_{650}$-DMI)$_{940}$, and the T2T–(PTMO$_{650}$-DMI)$_{1290}$ copolymers exhibited two transitions—a T_g at a low temperature ($-60°C$), and a T_m at a high temperature ($80–160°C$). In addition, the T2T–(PTMO$_{650}$-DMI)$_{1930}$ and T2T–(PTMO$_{650}$-DMI)$_{2770}$ copolymers exhibited a small shoulder at $-25°C$, as shown in Figure 1(a). This shoulder is very small, occurring at a low temperature, and is due to the melting of the PTMO crystalline phase. The T_g (the maximum in G'') of T2T–PTMO$_{650}$ copolymer occurs at $-51°C$, whereas in the DMI extended copolymers it occurs at $-60°C$. Suprisingly, extending PTMO$_{650}$ using DMI was found to shift the T_g to a lower temperature. Apparently, the effect of the lower chain flexibility due to the presence of the isophthalic ester group must be smaller than that of the increasing chain length between entanglements. As in T2T–PTMO$_{650}$ copolymers, the T_g of the polyether phase is also less dependent than the T2T con-
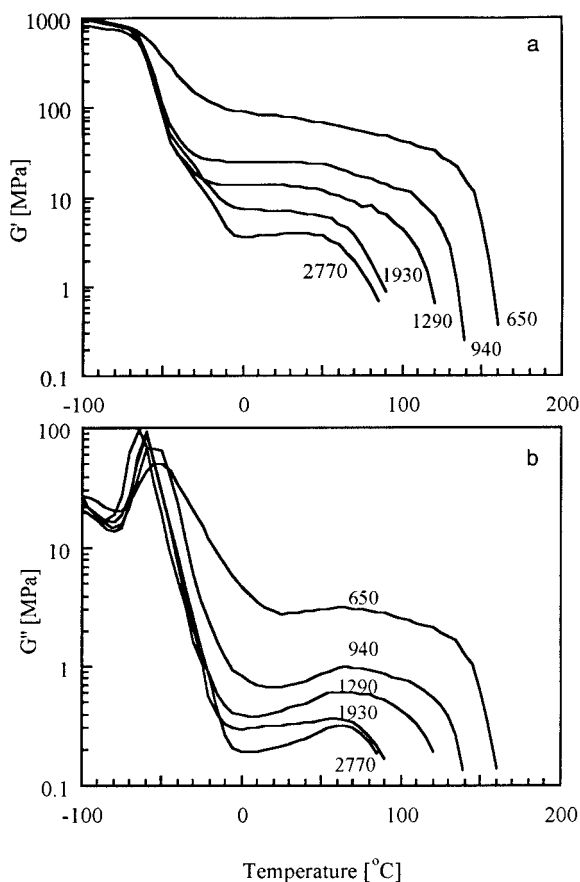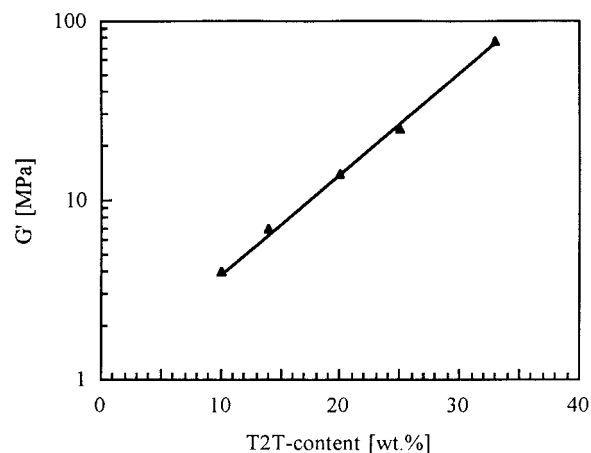

Figure 2 Log G' (25°C) versus the T2T content for T2T-(PTMO$_{650}$/DMI) copolymers.

tent, indicating that none, or only a small amount of T2T, is present in the polyether phase. The rubbery plateau starts at a low temperature, and is fairly independent of the temperature. The low temperature achieved for the T2T–(PTMO-DMI) is good due to the low T2T segment content and the low level of diamide segments in the polyether phase.

The modulus of the rubbery plateau decreases with decreasing T2T content, and when compared to PBT–PTMO copolymers, the T2T–PTMO copolymers have low moduli. The storage modulus in the rubbery plateau is dependent on the chain interaction of the rubbery phase, i.e., the crystallinity and the lamellar packing of the crystalline phase.[17] The T2T segments form the physical crosslinks for the amorphous PTMO segments, but the lamellar thickness of the T2T crystalline phase can be expected to remain unchanged. The log shear modulus at 25°C was found to decrease linearly with decreasing T2T content (Fig. 2). Similar relationships have been found for other segmented copolymers.[5,18]

The flow transition (T_{fl}) was found to be very sharp, probably due to the uniform thickness of the melting lamellae, and was somewhat lower than the melt temperature (T_m) (Table I). The T_{fl} was more accurately measured than T_m, as the melting endotherms in the DSC spectra were broad and low. The flow temperature was also found to decrease with decreasing T2T content. However, given that the T2T segments are of a uniform length, this decrease in flow temperature cannot be due to a decrease in lamellar thickness. It is possible that the effect was due to the in-
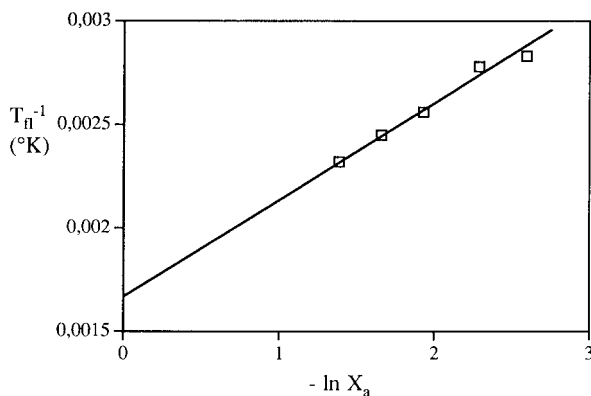

Figure 1 Storage modulus (G') and Loss modulus (G'') versus the temperature of T2T-(PTMO$_{650}$/DMI) copolymers with varying amorphous segment length (g/mol).

Figure 3   Reciprocal of the flow temperature versus $-\ln X_a$ for T2T-(PTMO$_{650}$/DMI) copolymers.

crease in PTMO content. A similar decrease has also been observed in T4T–PTMO[4,5] and TϕT–PTMO polymers.[6] This PTMO effect has been suggested to be due to a "solvent" effect of the amorphous segments, as described by Flory.[19] According to Flory, the melting temperature of a copolymer, comprised of crystallizable units A and noncrystallizing units B, can be described by the following equation[2]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{R}{\Delta H_f}\right)\ln X_A \qquad (2)$$

where T_m is the melting temperature of the copolymer, T_m^0 is the melting temperature of the homopolymer, X_A is the molar fraction of the A-units (crystallized) in the copolymer, ΔH_f is the latent heat of fusion of the homopolymer A, and R is the gas constant. This equation is based on the assumption that the solution is ideal and that the enthalpy and entropy of melting are both temperature independent. The equation neglects a possible influence of an interaction between the crystalline and amorphous phases.

For the T2T–(PTMO$_{650}$/DMI) copolymers, relationship (3) was evaluated, X_A was calculated by taking equal molar volume segments. In Figure 3,

$1/T_{fl}$ is plotted vs. $-\ln X_A$, and a straight line can be drawn through these points, having an intercept at 320°C. This intercept corresponds well to the melting temperature of the bisesterdiamide unit (315°C) and, therefore, the reduced melting temperature with increasing PTMO content can be described by the "solvent" effect as described by the Flory relationship.

TPE polymers based on PTMO$_{650}$ have also been synthesized using other amide segments, such as T4T and TϕT, and a comparison has been made between these copolymers in Table II. The melting temperature of T2T–dimethyl (312°C) is in between that of T4T–dimethyl (265°C) and TϕT-dimethyl (375°C). Therefore, it was expected that the melting temperature of the T2T copolymers would exhibit a similar pattern. However, the copolymer containing T2T–PTMO$_{650}$ was found to have the lowest T_m, and also the modulus was lower. Possible reasons for these effects are the smaller lamellar thickness, with this diamide and the not being fully crystallized of the T2T segments.

T2T-PTMO$_{650}$ Copolymers with 1,2-Ethanediol as an Extender

The T2T–PTMO polymers have a relatively low melting temperature; this is partly due to the short length of the T2T units (1.7 nm). The length of the crystallizable unit was be increased by using a diol (1,2-ethanediol, ED) forming amide–ester–amide segments. However, extending T2T results in a loss of the uniformity of the crystallizable T2T segments. In this article, the (T2T/ED)–PTMO$_{650}$ copolymers were made with increasing ED concentrations (0–20 mol %) (Table III). The 1,2-ethanediol content was determined by ^{1}H-NMR.

During synthesis at 250°C, the amide–ester–amide units were found to crystallize, this was most pronounced in the polymer containing 20 mol % ED. Phase separation during synthesis limits the reaction of the end groups, and thus reduces the molecular weight of the polymer. In

Table II   Properties of Alternating Copolymers of PTMO$_{650}$ and Different Diamide Segments

Amide Segment	Diamide (T_m)	η_{inh} (dL/g)	T_m (°C)	T_c (°C)	ΔT (°C)	T_g (°C)	T_{fl} (°C)	G' (25°C) (MPa)	Reference
T2T	315	1.34	163	137	26	−51	158	77	
T4T	265	1.40	179	160	19	−51	170	116	4
TϕT	375	1.40	266	238	28	−58	247	118	6

Table III   DSC and DMA Results of (T2T/ED)-PTMO$_{650}$ Copolymers

ED (mol %)	η_{inh} [dl/g]	T_m (°C)	T_c (°C)	ΔT (°C)	T_g (°C)	T_{fl} (°C)		G' (25°C) (MPa)
0	1.34	163	137	26	−51	158		77
5	0.75		139		−60	145		66
10	0.80	143	128	15	−62	138		72
20	0.49	127	123	4	−65	(138)	> 300	85

DSC analysis of the copolymers, only one melting and one crystallization temperature of the (T2T/ED)–PTMO copolymers was observed, and these were found to decrease with increasing ED content. This was surprising, as it had been expected that incorporation of amide–ester–amide segments would increase the T_m or at least leave it unaffected. It is possible that the alternating amide–ester–amide segments form a separate crystalline phase, which is not observed in the DSC spectrum. In contrast, the undercooling (ΔT) is substantially lowered by the incorporation of ED as an extender of the T2T segments, thus suggesting an extremely rapid crystallizing system.

Figure 4 shows the storage modulus and the loss modulus of (T2T/ED)–PTMO$_{650}$ copolymers as a function of temperature with increasing ED content. The T2T–PTMO copolymer show two transitions, a low temperature T_g of the PTMO phase and the melting of the T2T segments. Extending T2T with ED (20%) has some effect on the T_g of the PTMO phase and the T_m of T2T units; however, the main effect is the appearance of a second rubbery plateau and a flow temperature greater than 300°C. This suggests that two types of lamellar structures are present, one melting at about 150°C and another melting at a higher temperature (>300°C). A mixed lamellar phase is apparently not formed. Clearly, the lamellae of the amide–ester–amide segments have a much higher melting temperature than the nonextended T2T segments, but no second glass transition was detected.

The low temperature T_g of the PTMO phase was shifted to a somewhat lower temperature; this effect is as yet unexplained. The T_m of the T2T units decreased in temperature, which must have been due to the lowering in concentration of the T2T units. As we have already seen, the T_m is a function of the T2T concentration, and the T2T concentration is reduced when the amide–ester–amide units are formed. Thus, it is surprising, that up to 120°C, there is little change in modulus

on extending with ED. What is lost in concentration of the unextended T2T part is formed with amide–ester–amide units. The very low ΔT values of the ED extended copolymers suggest that the crystalline amide–ester–amide phase must have a strong nucleating effect on the T2T crystallization.

CONCLUSIONS

Rapidly crystallizing T2T–PTMO polymers can be made, and in the T2T–(PTMO$_{650}$/DMI) polymers,
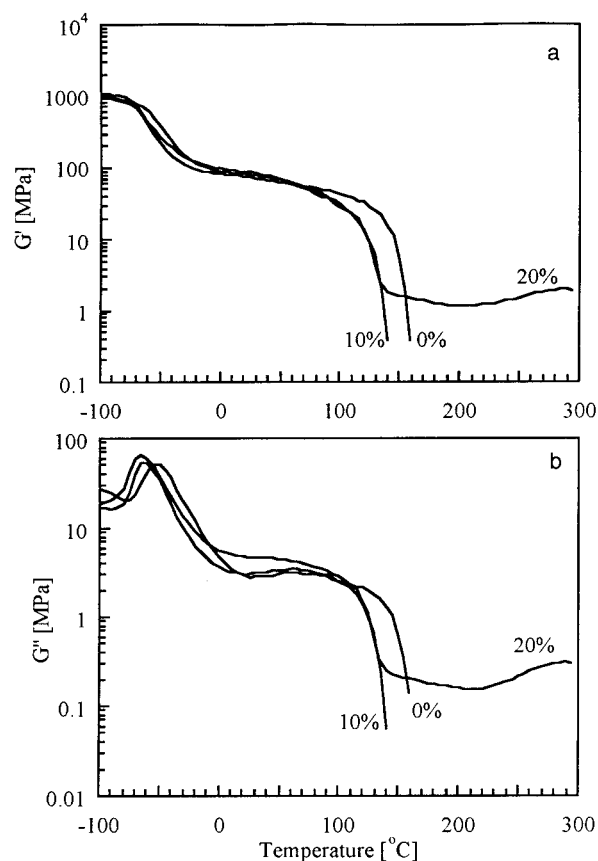

Figure 4   Storage modulus (G') and loss modulus (G'') versus the temperature of (T2T/ED)-PTMO$_{650}$ copolymers with 1,2-ethanediol as extender in mol %.

two transitions can be observed; a low temperature T_g of the PTMO phase and a T_m of the T2T phase; crystallization of PTMO in the PTMO_{650}–DMI system was almost completely suppressed. The DMI extension of the PTMO has no negative effect on the T_g of the PTMO phase, and therefore, materials having excellent low temperature properties can be made in this way. The T_g of the PTMO phase is not affected by the T2T concentration, indicating that probably little or no T2T is dissolved in the PTMO phase. The log modulus in the rubbery region was found to increase linearly with the T2T content, as has been observed for other segmented copolymers. The melting temperature was found to decrease with increasing amorphous segment length. This can be explained by the "solvent" effect of the amorphous phase. The $T_m - T_c$ (undercooling) values of the polymers were low, despite the small length of T2T unit. The melting temperatures of the T2T–PTMO polymers were lower than expected compared to the melting temperature of the starting bisesterdiamide and T4T–PTMO polymers. The reason for the lower melting temperatures are the smaller T2T length and possibly a lower crystallinity.

Extending T2T segments with 1,2-ethanediol, introduces alternating amide–ester–amide segments. These segments form a separate crystalline phase with a much higher melting temperature ($T_m > 300°C$) than nonextended T2T segments (T_m 163°C). However, if some extended T2T segments are present, then the crystallization of the nonextended T2T segments is extremely rapid with the crystallized amide–ester–amide segments acting as nucleation sites for the nonextended T2T segments. The melting temperature of the 1,2-ethanediol extended polymer is very high—too high for melt synthesis and melt processing without degradation. The melting temperature is expected to be lowered if a longer diol is used.

REFERENCES

1. Meckel, W.; Goyert, W.; Wieder, W. In Thermoplastic Elastomers; Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E., Eds.; Hanser: Munich, 1996, p. 15, 2nd ed.
2. Adams, R. K.; Hoeschele, G. K.; Wispie, W. K. In Thermoplastic Elastomers; Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E., Eds.; Hanser: Munich, 1996, p. 15, 2nd ed.
3. Nelb, R. G.; Chen, A. T. In Thermoplastic Elastomers; Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E., Eds.; Hanser: Munich, 1996, p. 15.
4. Gaymans, R. J.; de Haan, J. L. Polymer 1993, 34, 4360.
5. Van Hutten, P. F.; Mangnus, R. M.; Gaymans, R. J. Polymer 1993, 34, 4193.
6. Niesten, M. C. E. J.; ten Brinke, A.; Gaymans, R. J. Polym Prepints 1999, 40, 1012.
7. Bouma, K.; Lohmeijer, J. H. G. M.; Gaymans, R. J. Polymer 2000, 41, 2719.
8. Harrell, L. L. Macromolecules 1969, 2, 607.
9. Miller, J. A.; Shaow, B. L.; Hwang, K. K. S.; Gibson, P. E.; Cooper, L. S. Macromolecules 1985, 18, 32.
10. Eisenbach, C. D.; Baumgartner, M.; Guther, G. In Advances in Elastomer and Rubber Elasticity, Proc. Symposium; Lai, J.; Marj, J. E., Eds.; Plenium Press: New York, 1985, p. 51.
11. Van Bennekom, A. C. M.; Gaymans, R. J. Polymer 1997, 38, 657.
12. Bouma, K.; de Wit, G.; Lohmeijer, J. H. G. M.; Gaymans, R. J. Polymer 2000, 41, 3965.
13. Serrano, P. J. M.; Thüss, E.; Gaymans, R. J. Polymer 1997, 38, 3893.
14. Sorta, E.; della Fortuna, G. Polymer 1980, 21, 728.
15. Perego, G.; Cesart, M.; della Fortuna, G. J Appl Polym Sci 1984, 29, 1141.
16. Guang, L.; Gaymans, R. J. Polymer 1997, 38, 4891.
17. Young, R. J. Mater Forum 1988, 11, 210.
18. Wegner, G. In Thermoplastic Elastomers; Legge, N. R.; Holden, G.; Schroeder, H. E., Eds.; Hanser: Munich, 1987.
19. Flory, P. J. Trans Faraday Soc 1955, 51, 848.