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Alternating polyesteramides based on 1,4-butylene terephthalamide: 3. Alternating polyesteramides based on mixtures of linear diols (4NTm,p)

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Strictly alternating polyesteramides consisting of 1,4-butylene terephthalamide diester and mixtures of aliphatic diols have been synthesised in the melt in the presence of a titanium catalyst. To increase the molecular weight a solid state post condensation was applied. The composition was determined with ^{1}H NMR. The thermal properties were analysed with differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). With the mixture of diols the structural regularity of the diester part in polymers was disturbed. Although this disturbance caused the polymers to be fast crystallising ($\Delta T < 32°$), highly crystalline polymers. It was found that the melting temperature decreased linearly with increasing length of the diols in the mixture. The melting temperatures with the mixtures of diols were lower than with a single diol. The reason for this is probably thinner lamella. Mechanical tests on the melt processed polyesteramides showed high glass transition temperatures and a high modulus above the glass transition temperature. These polyesteramides have a T_g/T_m ratio of 0.70–0.72. This high ratio is probably due to the relatively low melting temperatures. The water absorption, is close to the values for polyesters (1.3–1.7 wt%). Disturbing the alternating structure of the polyesteramide by ester-amide interchange reactions resulted in a loss of the thermal and mechanical properties. © 1997 Elsevier Science Ltd.

(Keywords: bisesterdiamide; alternating polyesteramides; copolymers)

INTRODUCTION

Polyesteramides (PEA's) can be synthesised as random copolymers[1], alternating copolymers[2] or segmented copolymers[3]. Each type has its own characteristics. In random copolymers the structural order is lost and as the crystallinity is low the materials often possess poor thermal properties. Alternating copolyesteramides usually show intermediate properties between the polyesters and polyamides. If the diol takes part in the crystallisation it behaves as a homopolymer. In segmented copolymers phase separation can take place by crystallisation. A type of copolyesteramides which lies in between alternating copolymers and segmented copolymers are the spacered polyesteramides[4,5]. These copolymers consist of crystallisable diamide units and flexible ester spacers. In these systems the crystallisable unit is of uniform length. Uniform blocks in a segmented copolymer enhance the phase separation[6–9]. The crystallisable blocks order in lamellae and act as physical cross-links[10–12]. Polyesteramide-b-polyethers synthesized from T4T dimethyl (1,4-butylene terephthalamide dimethyl ester) and PTMO with different PTMO lengths have been studied[8,9]. The polymers with a short PTMO length ($M = 250$ g/mol) showed a glass transition temperature (T_g) of 43°C, whereas the longer PTMO blocks had a T_g of -65°C. These systems with diamide units crystallised very fast (undercooling of 11°C) and showed a decreasing melting temperature with increasing PTMO length.

Gaymans and De Haan[9] studied the copolyesteramide 4NT6,8 (T4T and a mixture of hexane and octane diols). These diols can be regarded as flexible spacers between the T4T units. The diols form the amorphous phase in the copolymer whereas the T4T units crystallise. The polymer exhibited a high T_g (103°C) and a high T_m (229°C).

In alternating copolyesteramides of the type 4NTm, the bisesterdiamide T4T dimethyl is polymerised with a single diol with a methylene length of m[4]. These polymers were fast crystallising and their melting temperatures exhibited an odd–even effect. Only one T_g was found. The T_g's of these polyesteramides were high and showed an odd–even effect which was opposite to the odd–even effect found for the T_m. The thermal and dynamic mechanical properties decreased with increasing loss of uniformity of the diamide segment.

In this study the results of the synthesis and the properties of alternating polyesteramides 4NTm,p, based on T4T dimethyl (1,4-butylene terephthalamide dimethylester) and a mixture of aliphatic diols are described. With this mixture of diols a disorder in the ester unit is created which probably prohibits the crystallisation of the diols. The effect of the disorder in the diol sequence on the order in the system and the thermal and mechanical properties is studied.

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EXPERIMENTAL

Materials

The α, ω-diols were purchased from Merck and used as received (purity > 95%). Tetraisopropyl orthotitanate (Ti(i-$OC_3H_7)_4$) was distilled prior to use and diluted in anhydrous m-xylene (0.100 M). The T4T dimethyl was synthesised and purified as described earlier[13].

Melt polycondensation.

The preparation of 4NT5,7 (mixture of 1,5-pentanediol and 1,7- heptanediol) is given as a typical example. The reaction was carried out in a 250 ml stainless steel vessel with nitrogen inlet and mechanical stirrer. The vessel, containing T4T dimethyl (30 g, 72.7 mmol), 1,5-pentanediol (9.09 g, 87.3 mmol) and 1,7-heptanediol (11.06 g, 83.7 mmol) was heated up to 180°C in an oil bath. After 15 min Ti(i-$OC_3H_7)_4$ (1.5 ml, 0.2 mol% Ti/mol T4T dimethyl) was added and the temperature was raised to 220°C. After 20 min at 220°C, the pressure was reduced (10–15 mmHg) while raising the temperature to 250°C (2°/min). After 10 min at 250°C a pressure of less than 1 mmHg was applied over an hour (polycondensation). After the reaction was stopped, the vessel was slowly cooled to room temperature, maintaining the low pressure. The obtained product was cooled with liquid nitrogen, grinded in a Fritsch Pulverisette and dried in a vacuum oven at 80°C for 24 h.

When synthesising the polymer in a 1.3 l stainless steel reactor (A31 type JUD25/1, Juchheim GmbH) equipped with mechanical stirrer, nitrogen inlet, vacuum supply and Pirani 503 gauge, the reaction time at 1 mmHg (polycondensation) was shortened to 30 min.

Solid state postcondensation

The grinded polymer was dried overnight in vacuo at 80°C. The postcondensation was carried out at reduced pressure (< 1 mmHg) in a glass tube which was placed in an oven at a temperature of 20–30° below the melting temperature with a maximum temperature of 250°C. The reaction time was 24 h.

Viscometry

The inherent viscosity (η_{inh}) of the polymers was determined using a 0.1 g/dl solution in p-chlorophenol and a capillary Ubbelohde 1B viscometer, placed in a water bath at 45.0 ± 0.05°C.

DSC

DSC spectra were recorded on a Perkin Elmer DSC7 apparatus equipped with a PE-7700 computer and TAS-7 software. The melting and crystallisation transitions were determined using samples of 5–8 mg with a heating and cooling rate of 20°C/min. The peak maxima of the second heating scan and the first cooling scan were taken as the transition temperatures T_m and T_c, and the area under the curve as ΔH_m. Tin was used as calibration standard.

NMR

Proton NMR and proton decoupled ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 and 62.9 MHz, respectively. Trifluoroacetic acid (TFA-d) was used as solvent without internal standard. ^{13}C NMR scans (3200) were recorded with an acquisition time of 2.097 s and a 45° pulse.

Injection moulding

Samples for the DMTA test (70 × 9 × 2 mm) were prepared on an Arburg-H manual injection moulding machine. The temperature setting of the barrel was 30–50° above T_m and the mould temperature was approximately 150°C.

Specimens of polymer 4NT5,7 for the tensile test (dumbbell shaped tensile specimens according to ISO R527-1) were prepared on an Arburg Allrounder 221-55-250 injection moulding machine. During injection moulding the polymer was kept under a nitrogen flow. Temperature setting of all zones was approximately 300°C whereas the mould temperature was kept at 85°C. The complete cycle time was 15.3 s. Before use, all polymers were dried in a vacuum oven at 80°C for 48 h.

DMTA

A Myrenne ATM 3 torsion pendulum was used at a frequency of approximately 1 Hz. Samples of 50 mm length (clamp length), 9 mm width and 2 mm thickness were monitored at a heating rate of 1.8°C/min. The glass transition temperature (T_g) was defined as the maximum of the loss modulus G″.

Tensile test

The tensile tests were performed at 20°C with a strain rate of 1 mm/min on a Zwick 1474, equipped with a 5 kN load cell and a strain gauge. All test bars were dried in vacuo at 80°C for 48 h.

Three point bending test

The deflection tests were performed on a Zwick 1474, equipped with a 5 kN load cell. Tensile bars were placed on two bars at a distance of 45 mm. A third bar was pushed downwards with a speed of 1 mm/min. All test bars were dried in vacuo at 80°C for 48 h.

Water absorption

The absorption of water was measured as weight gain after conditioning. Tensile bars were dried (80°C in vacuo for 48 h) and weighed (w_0). The samples were conditioned above water in a desiccator which was placed in an oven at 30°C for 30 days. After this treatment the samples were weighed again (w).

$$\text{absorbtion of water} = \frac{w - w_0}{w_0} \times 100\%(\text{wt}\%) \qquad (1)$$

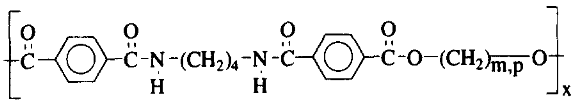
In a second test the tensile bars were immersed in water for 24 h at a temperature of 90°C. The water absorption was calculated according to equation (1).

RESULTS AND DISCUSSION

Introduction

The polyesteramides 4NTm,p (shown below) were synthesised by a melt polycondensation of T4T dimethyl and a mixture of diols. A small excess of the diols were added compared to T4T dimethyl. A solid state postcondensation was carried out to further increase the molecular weight of the polymers.

Thermal and dynamic mechanical properties were determined by means of DSC and DMTA. The results are compared with the results of the 4NTm polyesteramides. Tensile tests were performed on 4NT5,7.



4NTm,p

Melt synthesis

The polyesteramides 4NTm,p were synthesised in the same way as the 4NTm PEA's[4], according to the DMT route for PET/PBT[14,15]. An excess of diols was used to transesterify the T4T dimethyl at 180–220°C in the presence of a titanium catalyst. Once the formation of methanol had stopped, the temperature was raised to 250°C while at the same moment the pressure was reduced (< 1 mmHg). After removal of the excess of diols, the polycondensation started. The polymers were brittle and opaque at room temperature.

The diol with the lowest boiling temperature was added in a higher amount than the higher boiling diol. It was expected that the lower boiling diol would be stripped off more easily than the higher boiling diol. This was confirmed by ^1H NMR.

Polymer 4NT2,4,6 was synthesised through a solution polymerisation in 1,2-ethanediol. This diol was believed to be stripped off once a high vacuum was applied. But ^1H NMR analysis showed a large incorporation of the 1,2-ethanediol. The 1,2-ethanediol was present in the mixture in a large excess (ethanediol/butanediol/hexanediol = 10:1:1), despite the low boiling temperature compared to 1,4-butanediol and 1,6-hexanediol. The starting composition of the mixture of diols is, therefore, important for the final composition of the diols in the polyesteramide.

The obtained inherent viscosities range from 0.25 to 0.53 dl/g irrespective of the length of the diol (*Table 1*). The fact that the two 4NT5,7 polymers have a quite different inherent viscosity suggests that the reaction conditions are critical. A solid state postcondensation was applied to increase the molecular weight of the polyesteramides.

The extent of thermal degradation was investigated by endgroup analysis. Two batches of polymer 4NT5,7 were analysed, but no COOH and NH_2 endgroups were found (detection limit 0.01 meq/g). Thus, degradation reactions had hardly taken place during synthesis of these polymers.

Solid state postcondensation

The solid state postcondensations were carried out at 20–30°C below the melting temperature of the polymers (with a maximum of 250°C) in order to favour the diffusion rate of reactive endgroups and condensation products in the amorphous phase[9]. Reaction temperatures closer to the melting temperature lead to particle sticking and thus to surface reduction.

The partial pressure of the diols was lowered by applying a nitrogen flow or by reducing the pressure. For the polymers with longer diols the nitrogen flow was not effective anymore—the boiling temperature was too high. Applying a high vacuum, on the other hand, increased the inherent viscosity. For example, a batch of polymer 4NT10,12 with a starting viscosity of 0.37 dl/g did not show an increase in viscosity (0.38 dl/g) using a nitrogen flow during solid state postcondensation ($T = 210$°C), while the viscosity increased to 0.86 dl/g after reducing the pressure.

The influence of reaction time at two temperatures on the inherent viscosity of the polymers is given in *Figure 1*. The inherent viscosity of 4NT5,7 increases up to 24 h at 225°C while a constant value is reached after 12 h at 235°C. The higher reaction temperature leads to a higher mobility of reactive groups and thus to a higher reaction rate. The higher temperature, however, also increases the crystallinity due to an annealing effect, resulting in a reduction of the mobility of the endgroups. Furthermore, particle sticking may occur at higher temperatures. For these reasons the increase of the η_{inh} is limited at 235°C while η_{inh} still increases at 225°C, although to a lower extent. This increasing crystallinity was verified by DSC analysis.

After postcondensation, the polymers 4NT7,9 and 4NT8,10 were insoluble in trifluoroacetic acid (NMR) and p-chlorophenol (viscosity).

The molecular weight of the polyesteramides could be considerably increased by a solid state postcondensation. Thus, the solid state postcondensation is a very effective method for obtaining high molecular weight polymers without degradation.

Composition of diol mixture

The composition of the diol mixtures in the polyesteramides 4NTm,p was investigated through ^1H NMR. Only the composition of the postcondensated polymers (*Table 1*) was determined since after the melt polymerisation the polymers may contain some free diol, which could disturb the analyses.

Table 1 Results of solid state postcondensation for 4NT*m,p* polyesteramides

Code	Diols	Diol composition[a] (mol%)	T (°C)	p (mmhg)	η_{inh}^{b} (dl/g)	η_{inh}^{c} (dl/g)	X_{AA}/X_A (mol%)
4NT2,4	ethane/butane	47/53	250	0.1	0.24	0.37	29.2
4NT2,4,6	ethane/butane/hexane	44/32/24	245	0.2	0.30	0.97	11.6
4NT3,5	propane/pentane	43/57	235	0.2	0.41	1.40	13.7
4NT4,6	butane/hexane	54/46	235	0.2	0.30	0.43	< 2
4NT5,7	pentane/heptane	36/64	230	0.1	0.25	1.31	83
4NT6,8	hexane/octane	45/55	225	0.1	0.33	1.36	2.4
4NT7,9	heptane/nonane	—	215	0.1	0.44	ns	ns
4NT8,10	octane/decane	—	215	0.1	—	ns	ns
4NTI0,12	decane/dodecane	25/75	210	0.1	0.31	0.73	8.8
4NT5,7[d])	pentane/heptane	31/69	225	0.1	0.53	2.31	< 2

Postcondensation time = 24 hr; X_{AA}/X_A = relative amide block fraction[4]; (*a*) theoretical diol composition for all polymers: 50/50 mol%; (*b*) after polymerisation; (*c*) after solid state postcondensation; (*d*) 1.3 l stainless steel reactor (postcondensation time 18 h); ns not soluble in trifluoroacetic acid and in pchlorophenol.

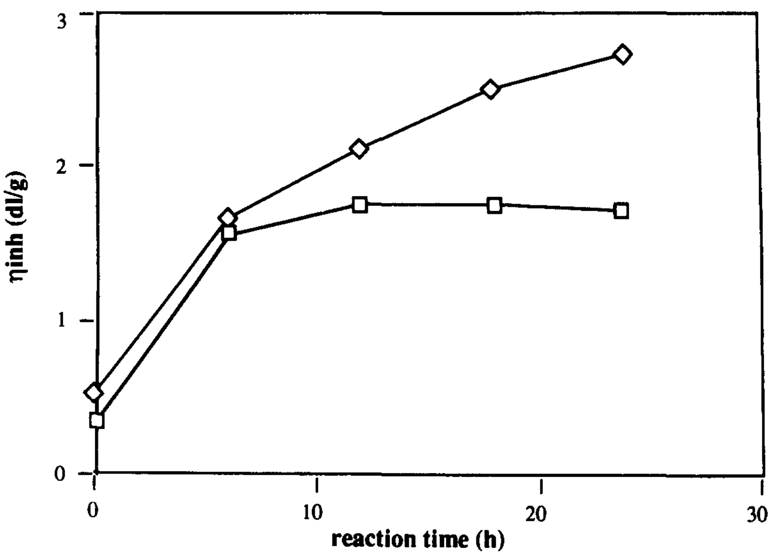


Figure 1 Viscosity increase during solid state postcondensation of polyesteramide 4NT5,7 as function of reaction time: (□) $T = 235°C$, (◇) $T = 225°C$.

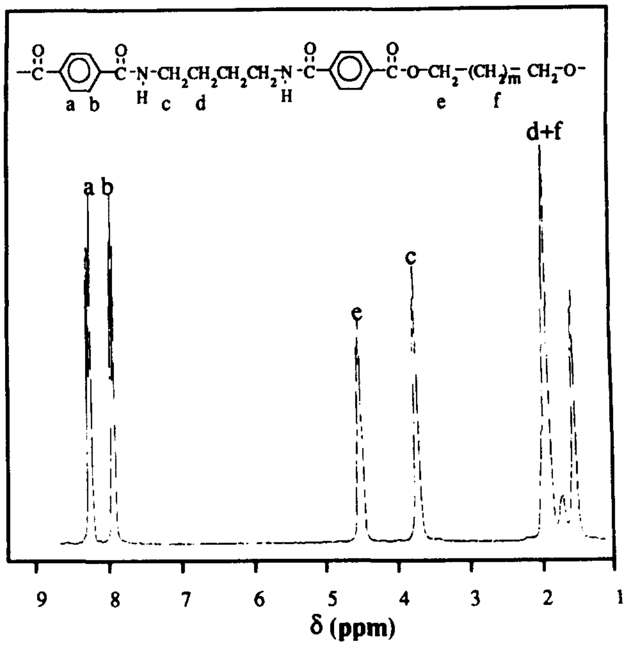


Figure 2 ^{1}H NMR spectrum of 4NT5,7 as a typical example for the determination of the diol composition.

In *Figure 2* a typical example of a proton NMR spectrum is given. The inner protons of the diols (f) are used for the calculation. The total of the integral (d) and (f) equals the number of inner protons of the T4T part (4) and the inner protons of the diols (2m). Subtracting 4 protons for the T4T part [(d) equals (c)] results in the number of inner protons of the diol. With the assumption that the sum of the fraction of both diols equals 1, the fraction of each diol can be calculated. For example, the composition of 4NT5,7 can be calculated with the next set of formulae:

$$I_p = \frac{(a)+(b)}{8} \tag{2a}$$

in which I_p is the average intensity of a proton. The average number of protons in the diol part (N_p) is given by equation (2):

$$N_p = \frac{(d)+(f)-(c)}{I_p} + 4 \tag{2b}$$

If only pentanediol is present in the polymer, the average number of protons in the diol part will equal 10. For heptanediol this will be 14. Defining f_p and f_h as the pentanediol en heptanediol fraction in the polymer respectively, the following equations are obtained:

$$f_p \mathrm{x} 10 + f_h \mathrm{x} 14 = N_p \tag{2c}$$

$$f_p + f_h = 1 \tag{2d}$$

From this the fraction of heptanediol can be calculated:

$$f_h = \frac{N_p - 10}{4} \tag{2e}$$

The composition of the diol mixtures of the 4NTm,p PEA's, calculated in the way described above is given in *Table 1*. A deviation of 4–5% is within the experimental error of ^{1}H NMR. The higher boiling diol is mostly present in a slightly higher amount, except in polymer 4NT4,6. A reason for this is not known.

Ester-amide interchange

In the alternating polyesteramide ideally only T4T amide groups are present. Due to impurities in the starting material and due to ester-amide interchange reactions T4T4T and T4T4T4T, segments can be formed and they disturb the regular alternating character of the polyesteramides, leading to some degree of randomness. The degree of ester-amide interchange is determined by triad analysis through ^{13}C NMR and is expressed in terms of the relative amide non uniformity:

$$\frac{X_{AA}}{X_A} = \frac{3AA}{3EAA + 3AA} \times 100\% \ (\mathrm{mol}\%) \tag{3}$$

in which X_{AA} is the mole fraction of amide triads, X_A the mole fraction of total amide groups, 3AA the integrated peak of the 3AA carbons and 3EAA the integrated peak of the 3EAA carbons.

This expression is a measure for the loss of uniformity of the amide segments. In *Table 1* this loss of uniformity of the polymers is given. All polymers show some ester-amide interchange during synthesis and postcondensation. The polymers with short diols exhibit a large X_{AA}/X_A because of the high postcondensation temperatures (250°C). The loss of uniformity of some polymers (4NT2,4 and 4NT3,5) is high because of the impurities in the T4T dimethyl used.

THERMAL ANALYSIS (DSC)

Melting temperature

Upon heating, the polyesteramides 4NTm,p show two endothermic transitions. This is attributed to the rearrangement of crystals[16,17]. This phenomenon of melting and recrystallisation of less perfect crystals into more stable lamellae could be influenced by changing the heating rate. The positional change of both melting peaks is not equal with increasing heating rate, whereas the beginning of the first melting peak is the same at all rates. This is an indication for a metastable phase[16]. At high heating rates the double peak disappears and only one peak is found. As with the 4NTm polyesteramides, the melting temperature decreases with increasing average length of the diols. Furthermore, the odd–even effect is absent, indicating that the diols do not crystallise together with the T4T segments or to a lesser extent. The melting temperatures (T_m) of the 4NTm,p PEA's are lower than the T_m's of the corresponding 4NTm polymers (*Figure 3* and *Table 2*).

The T_m of polyesteramide 4NT6,8 (246°C) is considerably higher than reported by Gaymans and De Haan[9] (229°C). The authors also reported a lower T_c, whereas a higher undercooling ($T_m - T_c$) was found. This might be due to the impurity of the T4T dimethyl or due to some residual diol.

Despite the diol mixture the melting enthalpy is high and comparable with the ΔH_m of the 4NTm polyesteramides. The undercooling of the 4NTm,p is still small, indicating fast crystallisation despite the irregular structure of the diols.

The crystallisation and the crystallinity does not seem to be hindered by irregularity in the diol. The observed gradual lowering melting point with increasing methylene length could be described by the theory of Flory[18,19]. Flory found that the melting point depression of a semicrystalline polymer by the addition of a solvent or plasticiser could be described by the following equations:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_m^0} \times \frac{V_p}{V_s} \times (V_1 - \chi^{v_1^2}) \qquad (4a)$$

and

$$\chi = \frac{\mathrm{BV_S}}{\mathrm{RT}} \qquad (4b)$$

in which T_m is the observed melting temperature of the copolymer, T_m^0 the theoretical melting temperature of the

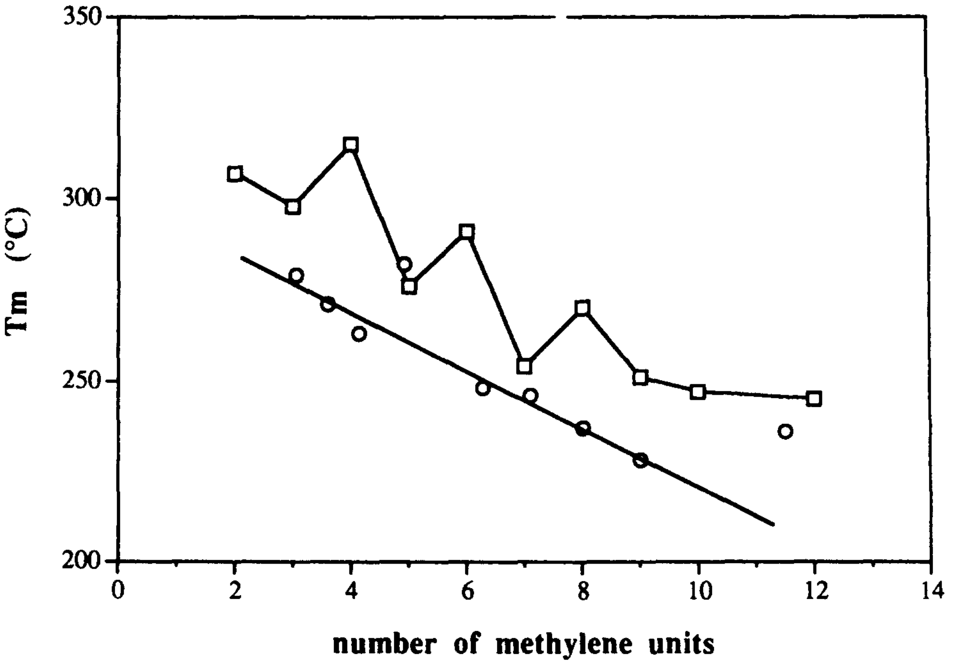


Figure 3 Melting temperature of 4NTm,p (○) and 4NTm (□)[4] polyesteramides *versus* average number of methylene groups in the diols.

Table 2 Thermal properties (DSC) of 4NT*m,p* polyesteramides

Code	Diol	T_m (°C)	T_c (°C)	($T_m - T_c$) (°C)	ΔH_m (J/g)
4NT2,4	ethane/butane	279	247	32	9.2
4NT2,4,6	ethane/butane/hexane	271	247	24	16.5
4NT3,5	propane/pentane	263	235	28	50.2
4NT4,6	butane/hexane	282	247	35	42.9
4NT5,7	pentane/heptane	248	218	30	39.3
4NT6,8	hexane/octane	246	218	28	34.6
4NT7,9	heptane/nonane	237	211	26	38.4
4NT8,10	octane/decane	228	—	—	30.3
4NTI0,12	decane/dodecane	236	207	29	40.1

Heating and cooling rate 20°C/min.

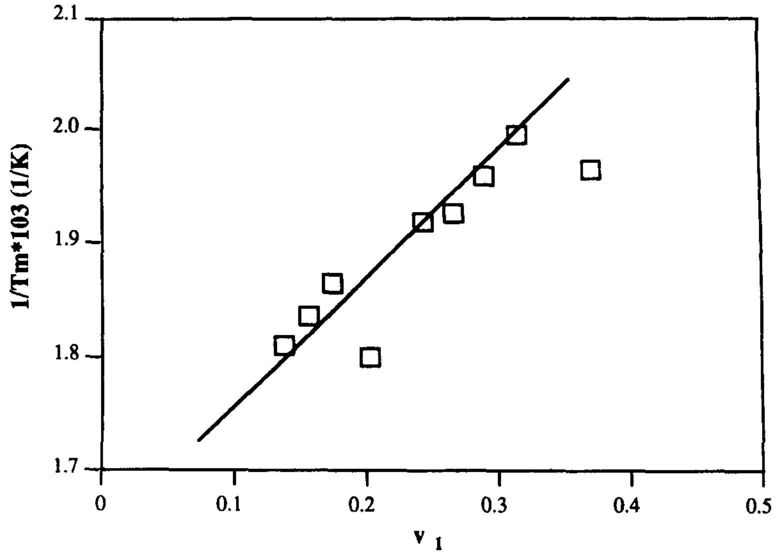


Figure 4 Plot of $1/T_m$ *versus* V_l for 4NT*m,p* polyesteramides.

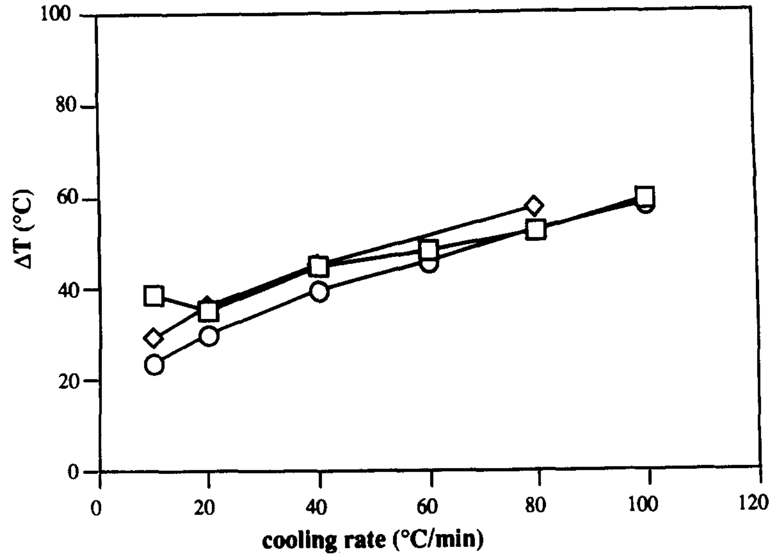


Figure 5 Undercooling DT *versus* cooling rate for PEA 4NT5,7 (○) and 4NT6 (□). For comparison also the values for PBT[29] (◇) are shown.

homopolymer, R the gas constant, ΔH_m^0 the theoretical heat of fusion, V_p the molar volume of a polymer repeating unit (T4T including the ester groups) (303.24 cm^3/mol), V_s the molar volume of the solvent (methylene group of the diol) (15.55 cm^3/mol), χ the Flory interaction parameter (1.960 at 25°C), B a constant and v_l the volume fraction of diluent. T_m^0 is obtained by plotting $1/T_m$ *versus* V_l (*Figure 4*)[20]. As a first approximation, the values of the molar volumes and the volume fraction of diluent were calculated with the group contribution method of HOY[21] (values at 25°C). The interaction parameter was obtained by plotting $(1/T_m - 1/T_m^0)/V_l$ *versus* V_l/T_m.

From *Figure 4* the T_m^0 was calculated to be 365°C. This is in good agreement with the values of T_m of the single even diol polymers (4NTm) when extrapolated to m = 0. The melting enthalpy was determined by plotting $1/T_m - 1/T_m^0/v_l$ *versus* V_l/T_m. The intercept of this figure gives the melting enthalpy (45 kJ/mol repeating unit T4T). The theoretical value, calculated with the group contribution method of Van Krevelen, is 59 kJ/mol[21]. Thus it seems that the system 4NTm,p can be described with this model. This suggests that the polyesteramides 4NTm,p can be regarded as consisting of crystalline T4T units and non-crystallisable spacers.

Rate of crystallisation

The rate of crystallisation is defined as the difference between the melting and crystallisation temperature (ΔT). A small undercooling implies a fast crystallisation rate. The ΔT of the 4NTm,p polymers (*Table 2*) is small. Surprisingly it is even smaller than the values of the 4NTm PEA'S. Increasing the disorder in the spacer groups thus lowers the undercooling. This small ΔT suggests a very fast crystallisation of the polymers. We think this is the result of some ordering in the melt of the uniform T4T segments caused by the hydrogen bonds[22,23].

The crystallisation temperature is dependent on the cooling rate[4]. We have measured the undercooling of 4NT5,7 with different cooling rates, while the heating rate was held constant (20°C/min)[24].

The results are given in *Figure 5* together with the results for 4NT6 and PBT[25]. As can be seen from this figure, the

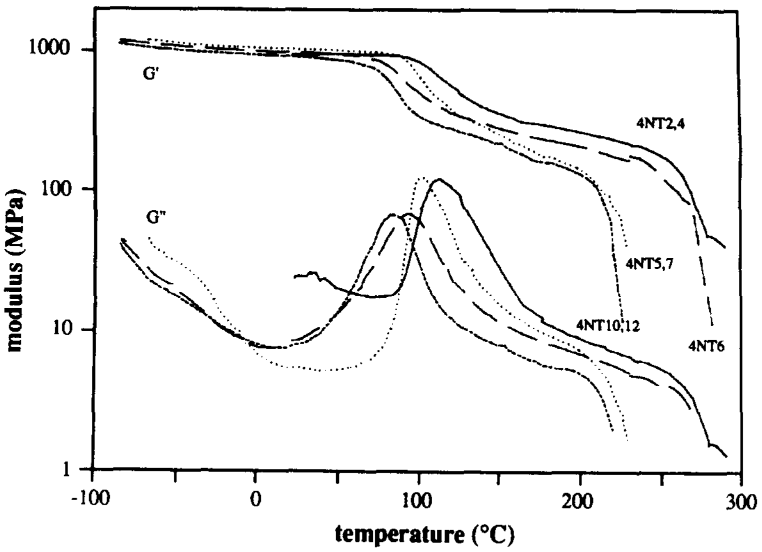


Figure 6 Typical DMTA curves of 4NTm,p PEA's (4NT2,4, 4NT5,7 and 4NT10,12). For comparison the curve of 4NT6 is also plotted.

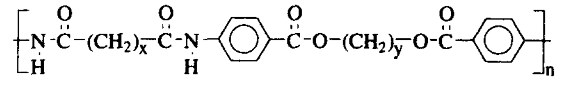
Table 3 DMTA results for 4NTm,p polyesteramides and PBT

Code	Diol	T_g (°C)	G' 150°C (MPa)	$\Delta G'$	T_g/T_m
4NT2,4	ethane/butane	114	241	2.4	0.70
4NT3,5	propane/pentane	115	176	2.0	0.72
4NT4,6	butane/hexane	—	—	—	—
4NT5,7	pentane/heptane	107	153	2.1	0.72
4NT6,8	hexane/octane	102	153	1.8	0.71
4NT7,9	heptane/nonane	103	99	2.0	0.74
4NT8,10	octane/decane	81	81	2.2	0.71
4NT10,12	decane/dodecane	83	124	2.2	0.70
PBT	butane	50	79	5.6	0.65

values of ΔT for 4NT5,7 are small and increase slightly with increasing cooling rate. It seems that the crystallisation rate of the polyesteramides 4NT6 and 4NT5,7 show, an almost equal dependency on the cooling rate. But the 4NT5,7 polymer crystallises faster at lower cooling rates.

The values of the undercooling of the 4NT5,7 polymer are lower than those of PBT. This means that 4NT5,7 can be considered to be a very fast crystallising copolymer. It is obvious that a fast crystallisation is an advantage in the melt processing of polymers.

With optical light microscopy[4] no liquid crystalline behaviour was observed. Aharoni[26] found LCP behaviour for PEA's from bis(aminobenzoyl) alkanes and aliphatic dicarboxylic acids with more than 4 methylene units in the diamine and three or more methylene groups in the diol:



$$\left[-\overset{\displaystyle H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{O}{\overset{\|}{C}}-\overset{\displaystyle H}{N}-C_6H_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_y-O-\overset{O}{\overset{\|}{C}}-C_6H_4- \right]_n$$

As with the 4NTm polymers, negative spherulites were also observed[4], which remained upon cooling the sample. This is also an indication of the existence of an order in the melt[23].

Dynamic mechanical thermal analysis

The DMTA tests were performed with injection moulded samples. The glass transition temperature was taken as the maximum of the curve of the loss modulus.

In *Figure 6* examples of DMTA curves are given. The α-transition (T_g) is clearly visible. Sometimes a β-transition at about – 50°C was seen, caused by the amide linkages in the amorphous phase which are not involved in hydrogen bonds [27]. This transition was clearly visible in our non-dried samples and has been observed by many authors[28].

The values of the glass transition temperature (*Table 3* and *Figure 7*) are high compared to the corresponding poly(alkylene terephthalates). This is because of the presence of amide linkages in the amorphous phase which form hydrogen bonds[4]. In this way the mobility of the amorphous chains is limited. As a result, T_g increases. Only one T_g is found for these systems, thus the ester and amide segments are compatible in the amorphous phase.

As expected, the T_g decreases with increasing diol length. Incorporating longer flexible chains will lower the T_g. However, there does not seem to be a linear relationship between the diol length and the T_g. There is also a difference between the T_g's of the 4NTm,p and the 4NTm systems. For very short diols, the T_g is lower than the corresponding 4NTm PEA's while the same is true for long diols. The 4NTm,p polymers with the pentane, hexane and heptanediol have a higher T_g than the corresponding 4NTm polymers.

In literature usually a monotonic decrease in T_g with decreasing amide content is reported for polyesteramides, while the glass transition temperature lies in between the two values of the constituent homopolymers[29,30].

The storage modulus of the 4NTm,p polyesteramides below T_g does not change much with temperature and

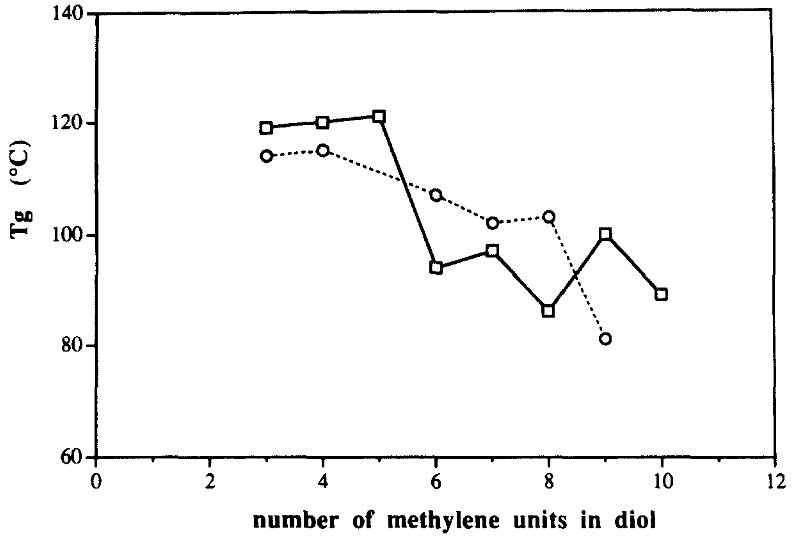


Figure 7 Glass transition temperature of 4NTm,p (○) and 4NTm (□) polyesteramides *versus* (average) number of methylene groups in the diol(s).

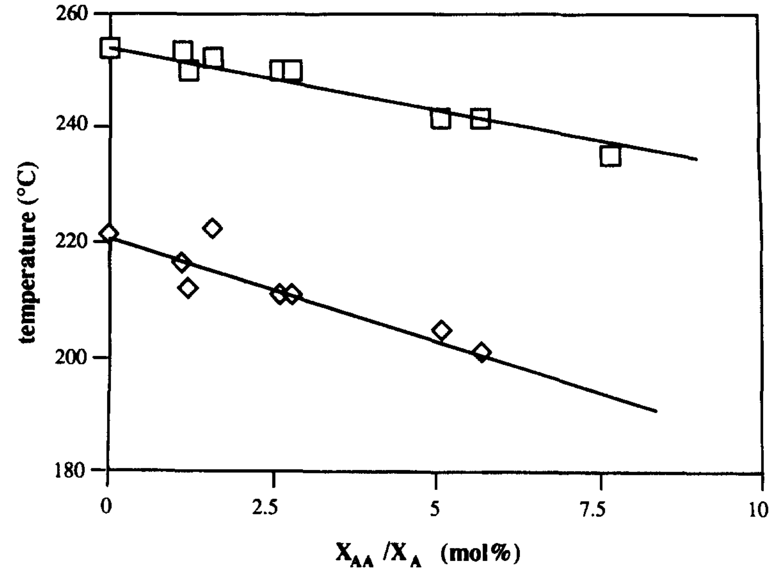


Figure 8 Melting (□) and crystallisation (◇) temperature of 4NT5,7 *versus* loss of diamide uniformity (X_{AA}/X_A).

reaches more or less the same value for all PEA'S. The values of the storage moduli at 150°C are all high and much higher than that of PBT (*Table 3*). Above the T_g the modulus slowly decreases with increasing temperature. This is caused by 'melting' of the crystallites, which form an interconnected network and act as a filler. The less perfect regions melt first, followed by the more perfect crystals. In this way a broad spectrum of melting temperatures is obtained. Since the modulus is dependent on the volume fraction of crystallinity above T_g, the G' also gradually decreases[31].

The decrease of the modulus above T_g is expressed as $\Delta G'$:

$$\Delta G' = \frac{G'(T_g + 40)}{G'(T_{fl} - 40)} \qquad (5)$$

This value is given in *Table 3*. From this table it is clear that the 4NTm,p polymers have a good mechanical behaviour above T_g. The values of $\Delta G'$ are lower than those of commercial polymers and are comparable with those of the 4NTm PEA'S.

The T_g/T_m ratios for the 4NTm,p PEA's are all above 2/3 [32–34]. This is mainly due to the lower melting temperature. The T_m might be lower due to a smaller thickness of the lamellae since the spacers do crystallise less or not at all. Solid state NMR analysis confirms these findings[33].

Although the PEA 4NT5,7 had a high melting enthalpy, the injection moulded tensile bars of this PEA were translucent. This could be a result of very small spherulites.

Uniformity of the amide segment

In the 4NT5,7 system the uniformity of the diamide T4T was changed with the formation of T4T4T and T4T4T4T. With increasing loss of uniformity of T4T the melting and crystallisation temperature decreased (*Figure 8*). The loss of uniformity of the diamide segments results in a lower T_m and T_c because of the formation of less perfect lamellae[4]. Moreover, the melting as well as the crystallisation peak broadens and the melting enthalpy decreases. A decreasing uniformity (higher X_{AA}/X_A) also increases the undercooling ($T_m - T_c$).

Table 4 Thermal (DSC) and mechanical (DMTA) properties of 4NT2,6 polyesteramides

Composition expected (%)	Composition[a] in polymer (%)	η_{inh} (dl/g)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	T_g (°C)	$\Delta G'$	T_g/T_m
100/0	100/0	0.41	307	282	38.3	—	—	
90/10	98/2	0.58	—	288	10.5[b]	123	1.5	—
75/25	86/14	0.51	270	240	31.8	119	2.1	0.72
50/50	79/21	0.33	261	229	16.2	114	2.8	0.72
10/90	75/25	0.32	—	—	—	111	2.8	—
25/75	64/36	0.72	264	234	39.4	114	2.0	0.72
0/100	0/100	0.60	291	258	55.1	94	2.5	0.65

[a] Composition (1,2-ethanediol/1,6-hexanediol) in mol% determined with ^{1}H NMR; [b] ΔH_c.

The influence of the uniformity of the crystallisable blocks on the mechanical properties was investigated with PEA 4NT5,7 by introducing impurities. For the synthesis of this polymer, T4T dimethyl was used with a relative amide block fraction of 15 mol%. As a result, the $\Delta G'$ increased from 2.1 to 2.4. The T_g decreased from 107° to 100°C and was less well defined (broader peak in G'' curve). The ΔH_m was much lower than the ΔH_m of the uniform 4NT5,7.

In a second experiment the polymer was kept for a prolonged time (20 min at 300°C). Thermal degradation of the polymer occurred under these conditions, resulting in a decrease in T_g to 98°C and an increase of $\Delta G'$ (up to 2.7). Thus, with non-uniform diamide segments the T_m, T_c, T_g and ΔH_m are all lower and the structure is expected to be less ordered.

Polyesteramides 4NT2,6

The polyesteramide 4NT2 has a high T_g, but also a high T_m. This high T_m requires high melt processing temperatures, leading to degradation of the polymer. The polymer 4NT6 has a lower T_m, but also a T_g considerably lower than that of 4NT2 (*Figure 7*). The polyesteramide 4NT2,6 is expected to have a strongly lowered T_m combined with high T_g.

The 4NT2,6 polymers were prepared with gradual increasing hexanediol content. The results of the synthesis together with the thermal (DSC) and mechanical (DMTA) properties of the 4NT2,6 polymers are listed in *Table 4*. As can be seen from this table, the compositions calculated from the ^{1}H NMR spectra show a large deviation from the expected composition. The amount of 1,6-hexanediol was added in the stoichiometrical amount wanted in the polymer whereas the 1,2-ethanediol was added in a large excess (up to 43 times). The 1,2-ethanediol (low boiling temperature) was believed to be stripped off easily by increasing the reaction temperature and reducing the pressure. However, the results show a large incorporation of the 1,2-ethanediol. This might be due to the fact that transesterification of the T4T dimethyl with 1,2-ethane and 1,6-hexanediol probably takes place in a statistical way. Thus, the diols are present in the transesterified T4T in the same molar ratio as they were present in the reaction mixture. After evaporation of the non-reacted diols (1,2-ethanediol and 1,6-hexanediol), the lower boiling 1,2-ethanediol is stripped off slightly easier than the 1,6-hexanediol. This can be seen in the results. The higher the starting molar ratio 1,2-ethane/1,6-hexanediol, the more 1,2-ethanediol is incorporated. This explains the differences found in the composition of the polymers.

Because the postcondensation temperature was far below the T_m (to suppress ester-amide interchange), the inherent viscosities are low compared to the other 4NTm,p polymers. Still the molecular weights of the polymers were high enough to perform dynamic mechanical tests.

The melting temperature decreases rapidly with increasing amount of 1,6-hexanediol. It seems that the hexanediol spacer disturbs the crystallisation of the ethanediol spacer in the 4NT2, leading to thinner lamellae and thus to a decreasing T_m. The melting enthalpy, on the other hand, is hardly affected. The melting temperatures of the 4NT2,6 polymers are below the T_m's of the 4NT2 and 4NT6 PEA'S, indicating that the mixed diol spacer crystallises less or not at all.

For the 4NT2,6 polymers a second, small crystallisation peak was found except for the 98/2 mol% composition. This is an indication that some phase separation occurred.

The glass transition temperature decreases proportionally with increasing 1,6-hexanediol content. The decrease of the modulus above T_g is small.

Thus, it seems that the 4NT2,6 polymers resemble the other 4NTm,p PEA's concerning their thermal properties. Small amounts of a second spacer disturb the crystallisation of the spacers. As T_m decreases faster than T_g, a polymer can be obtained with a lower T_m (compared to 4NT2), still having a high T_g.

The melting temperature of 4NT6 can thus be decreased while the glass transition temperature is increased by incorporating a short second spacer. This is attributed to the smaller lamellar thickness of the 4NT2,6 polymers compared to the polymers with a single diol, as discussed before.

Using the data of ^{1}H NMR for the chemical composition and applying the Fox[35] relation on these copolymers, the T_g of 4NT2 could be calculated. The value of 122–123°C corresponds very well with the T_g values of the other 4NTm polymers[4].

Tensile test

Tensile and bending tests were performed with polymer 4NT5,7 at room temperature. The Young's modulus is 2.6 GPa with a yield stress of 83 MPa. The strain at fracture was approximately 6%. The flexural modulus found with the bending tests is also 2.6 GPa. Usually the flexural modulus is somewhat higher than the Young's modulus.

The values are in good agreement with the DMTA tests when applying equation (6), using $G' = 850$ MPa (DMTA, 25°C) and the poisson constant of nylon-6,6 ($\nu = 0.42$). A value of 2.4 GPa is calculated.

$$E = 2(1 + v)G' \qquad (6)$$

The values of the Young's modulus and the yield stress are in between those of the polyesters and polyamides. The flex modulus of 4NT6 was 2.9 GPa.

Water absorption

The water absorption is an important property for polyamides[36]. With increasing water content the T_g

decreases due to the plasticising effect of the water[37]. In the polyamides the water absorption is only in the amorphous part of the polymer.

The water absorption of 4NT5,7 has been tested by immersing dumbbell shaped tensile bars in water at 90°C for 24 h, and by placing the bars in a 100% RH environment for 30 days at 30°C. The values found are 1.7 and 1.3 wt%, respectively. These values are close to the values of polyesters and are in the same range as the water absorption of 4NT6 (1.6 wt%). The slightly higher value in hot water may be due to the attack of crystalline domains by water molecules. Due to this low water absorption, the dimensional stability of the 4NT5,7 polymer is high.

CONCLUSIONS

Alternating polyesteramides can be regarded as crystallisable diamide segments with spacer groups of diols. Depending on the structure of the diols, the spacers may or may not take part in the crystallisation.

In this study it is shown that alternating polyesteramides can be synthesised by polycondensation of T4T dimethyl and a mixture of two aliphatic diols in the presence of a titanium catalyst. The diol with the lowest boiling temperature was slightly less built in. With solid state postcondensation a further increase of the molecular weight of the polyesteramides could be obtained. During synthesis and postcondensation ester-amide interchange reactions occurred, resulting in some randomisation of the alternating polyesteramides.

DSC analysis showed a decreasing melting temperature of the 4NTm,p polymers with an increasing number of methylene groups in the diol. With the mixtures of diols the irregularity was in all cases high and no odd–even effect as with the 4NTm polyesteramides was found. The melting point depression with the methylene length could be explained according to Flory's theory. From this theory a melting enthalpy of 133 J/g was calculated for the crystallisable T4T segment (Van Krevelen 155 J/g). The T_m of the 4NTm,p are lower than the 4NTm, this is probably due to thinner lamella.

The 4NTm,p polyesteramides were surprisingly fast crystallising (small values for the undercooling), showing a crystallisation rate comparable to or better than PBT.

No liquid crystalline behaviour of the polyesteramides was observed, although the fast crystallisation of the polyesteramides suggests some order of the diamide units in the melt.

The polyesteramides had a high glass transition temperature which decreased with increasing diol length. The odd–even effect found for the T_g of the 4NTm polymers was absent. The decrease of the modulus above T_g was in the same order as for the corresponding 4NTm polymers. The high T_g/T_m ratio (up to 0.72) is an indication that the lamella are thinner than usual

A decreasing uniformity of the diamide segment resulted in a decrease of the melting and crystallisation temperature. Furthermore, the decrease of the storage modulus between T_g and T_{flow} was stronger than for polymers with uniform segments.

The Young's modulus of 4NT5,7 was 2.6 GPa with a yield stress of 83 MPa. These values are in between those of polyesters and polyamides. The PEA 4NT5,7 exhibited a low water absorption (1.3–1.7 wt%, 100% RH) which is close to the values found for polyesters.

With the system 4NT2,6 it was shown that small amounts of a second diol already disturbs the crystallisation of the other spacer groups.

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