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Alternating copolyesteramides based on mixtures of 1,4-butyleneterephthalamide and -isophthalamide and ethanediol (4NT/I2)

M. C. E. J. Niesten*, K. Bouma and R. J. Gaymans
University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
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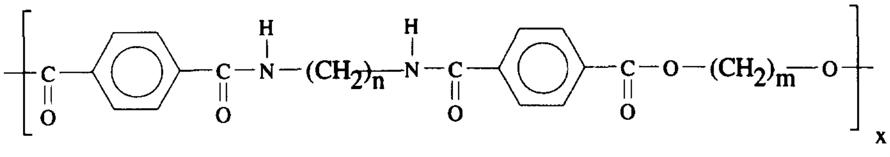
Alternating copolyesteramides (APEA's) consisting of mixtures of 1,4-butyleneterephthalamide ester (N,N'-bis(p-carbomethoxybenzoyl) diaminobutane) and 1,4-butyleneisophthalamide ester (N,N'-bis(m-carbomethoxybenzoyl) diaminobutane) polymerized with ethanediol were synthesised in an ethanediol solution. The bisesterdiamides were prepared from 1,4-butanediamine and dimethyl terephthalate or dimethylisophthalate respectively. They were analyzed by ^{1}H n.m.r., differential scanning calorimetry (d.s.c.) and high pressure liquid chromatography (h.p.l.c.). The melting behaviour of the copolyesteramides was studied by d.s.c. The dynamic mechanical properties were investigated on injection moulded bars using dynamic mechanical thermal analysis (DMTA). The melting temperature decreased with increasing 1,4-butyleneisophthalamide ester content. The crystallisation rate, the modulus above the glass transition temperature and the glass transition temperature hardly changed. The APEA of 1,4-butyleneisophthalamide ester and ethanediol was amorphous. The lowering of the melting temperature of the copolymers was probably caused by a decrease in lamellar size. The high crystallisation rate and the high physical crosslink density of the copolymers must be ascribed to the presence of 1,4-butyleneterephthalamide ester units which are able to crystallise fast and to form strong crystallites. © 1997 Elsevier Science Ltd.

(Keywords: bisesterdiamide; alternating polyesteramides; copolymers)

INTRODUCTION

Alternating Polyesteramides (APEA's) are regular copolymers which behave like homopolymers. They crystallise well, they have one T_g and one T_m with values in between the T_g and T_m of polyesters and polyamides and their T_g/T_m ratio is 0.65. A class of APEA's that has interesting engineering properties are made from terephthalic acid bisesterdiamides and diols, abbreviated to *n*NT*m* (1)



(1)

nNTm

In *n*NT*m* *n* refers to the number of methylene units in the diamide, *m* to the number of methylene units in the diester and T to terephthalic[1]. In the most studied *n*NT*m* systems the *n* and *m* are even and *n* is 4 or 6[1–3]. Serrano *et al.*[4] studied the system 4NT*m*. In these polymers the bisesterdiamide unit 1,4-diaminobutane terephthalate (N,N'-bis (p-carbomethoxybenzoyl)butanediamine) is named T4T. 4NT*m* polyesteramides with even diols are highly crystalline, they crystallise fast and when short diols are used they have a melting, temperature above 250°C.

If the structural regularity in copolymers is lost, the crystallinity is usually low and the materials possess poor thermal properties. In the 4NTm series with uneven diols or mixtures of diols the structural regularity is disturbed but surprisingly these polymers were still found to be fast crystallising, highly crystalline and they have a high modulus in the rubbery region[4]. Since their melting temperatures are considerable lower than the 4NT*m* APEA's with even diols and the decrease of the T_g is very small, the T_g/T_m ratio increases to 0.70–0.74. A high T_g/T_m ratio is interesting because for a given melting temperature the glass transition temperature is appreciable higher than usual for a semi-crystalline polymer and thus an improved dimensional stability is obtained.

The thermally most stable polyesters are made from

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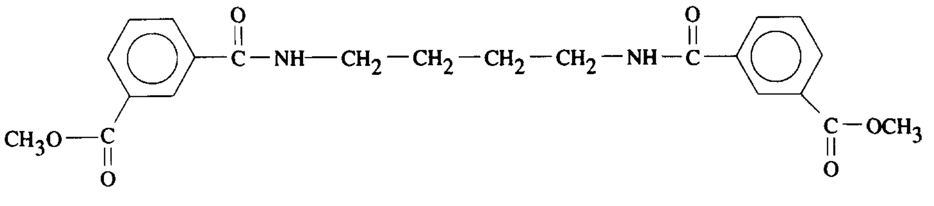
* To whom correspondence should be addressed

ethylene glycol[5]. The 4NT*m* polymers made with ethylene glycol have a high melting temperature of about 310°C[4], which is too high for melt polymerization and melt processing. The melting temperature can be drastically lowered while keeping the crystallisation rate and the crystallinity high by using a second diol e.g. hexanediol[6]. Unfortunately, with increasing second diol content the T_g also decreases.

In this study, an attempt is made to decrease the melting temperature of 4NT2 without changing the T_g, by copolymerization with a bisesterdiamide unit based on isophthalic acid named I4I-dimethyl (2). These polymers will be abbreviated as 4NT/I2.



(2)

I4I-dimethyl

The effect of using a mixture of two different uniform bisesterdiamides in 4NT/I2 APEA's on the crystallisation behaviour, the glass transition temperature and the shear modulus is studied.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI), 1,4-butanediamine (BDA), anhydrous toluene and anhydrous methanol, m-xylene, N-methyl-2-pyrrolidone (NMP), butylacetate and ethanediol were obtained from Merck. BDA was distilled prior to use. Lithium was purchased from Aldrich. $LiOCH_3$ was prepared by adding lithium to anhydrous methanol (1.25 M). Tetraisopropyl orthotitanate ($Ti(i\text{-}OC_3H_7)_4$) was distilled prior to use and diluted in anhydrous m-xylene (0.100 M).

Synthesis of T4T-dimethyl

Dimethyl terephthalate (275 g, 1.42 mole) was dissolved at 65°C in a mixture of 1100 ml anhydrous toluene and 85 ml anhydrous methanol in a 2 litre flask equipped with stirrer, condenser, calcium chloride tube and nitrogen inlet. When all the DMT was dissolved, 15 ml lithiummethanolate (1.25 M) was added. BDA (34 ml, 0.34 mole), dissolved in 150 ml anhydrous toluene and 10 ml anhydrous methanol, was added dropwise in 4–6 h while the nitrogen flow was stopped. 3 h after the start of the BDA addition,the temperature was gradually increased up to 90°C (5°C h^{-1}) while the methanol was stripped off. After a total reaction time of 24 h the reaction was stopped. The white precipitate was filtered through soxhlet extraction thimbles and washed twice with hot m-xylene to remove DMT. The product was subsequently dried overnight in a vacuum oven at 70°C.

Recrystallisation of T4T-dimethyl

T4T-dimethyl was recrystallised from hot 1-methyl-2-pyrrolidon (50 g/l at 160°C) and washed with hot acetone twice. The purified T4T-dimethyl was dried overnight in a vacuum oven at 70°C.

Synthesis of I4I-dimethyl

Dimethyl isophthalate (275 g, 1.42 mole) was dissolved at 50°C in 200 ml anhydrous toluene in a 2 l flask equipped with stirrer, condenser, calcium chloride tube and nitrogen inlet. When all the DMI was dissolved 15 ml lithiummethanolate (1.25 M) was added. BDA (34 ml, 0.34 mole), dissolved in 100 ml anhydrous toluene was added dropwise in 1–3 h while the nitrogen flow was stopped. When all the BDA was added the temperature was increased to 70°C, 400 ml anhydrous toluene was added gradually and methanol was stripped off. After a total reaction time of 5–8 h the reaction was stopped. The white precipitate was filtered through soxhlet extraction thimbles and washed twice in hot m-xylene to remove the DMI. The product was dried overnight in a vacuum oven at 70°C.

Recrystallisation of I4I-dimethyl

I4I-dimethyl was recrystallised from hot butylacetate (25 g l^{-1} at 120°C) and washed with hot acetone twice. The purified I4I-dimethyl was dried overnight in a vacuum oven at 70°C.

Solution polymerization

The preparation of 4NT2 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, 72.8 mmole) and ethanediol (30 g, 0.48 mole) was heated up in an oil bath of 200°C. After 15 min $Ti(i\text{-}OC_3H_7)_4$ (1.5 ml 0.1 M) was added and subsequently the temperature was gradually raised to 260°C (1°C min^{-1}). After 10 min at 260°C the pressure was reduced (10–15 mmHg) for 5 min. Then the pressure was reduced further ($<$ 2 mmHg) for 45 min. The vessel was cooled down slowly to room temperature, maintaining the low pressure. The polymer was grinded in a Fritsch pulverisette (particle size $<$ 1 mm) and subsequently dried in a vacuum oven at 80°C.

Solid state postcondensation

The grinded polymer (particle size $<$ 1 mm) 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°C below the melting temperature, with a maximum temperature of 260°C. The reaction time was 24 h.

Viscosimetry

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

D.s.c.

D.s.c. spectra were recorded on a Perkin-Elmer d.s.c.7 apparatus equipped with a PE-7700 computer and TAS-7 software. The melting and crystallisation transitions were determined using samples of 4–7 mg with a heating and cooling rate of 20°C min^{-1}. The peak onset was taken as the melting temperature of the bisesterdiamides and the area under the curve as ΔH_m. The polymers were first heated to 340°C at a rate of 100°C min^{-1} and then cooled and heated again at a rate of 20°C min^{-1}. 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 a calibration standard.

Proton n.m.r.

^{1}H n.m.r. spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz. Deuterated trifluoroacetic acid (TFA-d) was used as solvent without internal standard. The purity of T4T-dimethyl[7], I4I-dimethyl and the composition of the 4NT/I2 copolymers was checked with n.m.r.

H.p.l.c.

Reverse phase h.p.l.c. measurements were carried out using an apolar column. A Varian 2500 apparatus, a Varian pump 2510, a variable detector 2550, a Valco injector 10 μl loop and an integrator of the type Merck Hitachi D2500 were used. The material was dissolved in NMP (3–7 mg ml^{-1}). A Lichrospher 100 RP-8 125 × 4 mm column was used. The eluent was a mixture of 35% acetonitrile and 65% water. The eluent speed was 1 ml min^{-1}. After 3 min the eluent was changed in such a way that a mixture of 60% acetonitrile and 40% water would be reached in 55 min. Detection was at UV 288 nm.

Injection moulding

Samples for the DMTA test (70 × 8.8 × 2.2 mm) were injection moulded on a manual operated Arburg H machine. The temperature of the barrel was 350–380°C, the temperature of the mould was approximately 150°C.

DMTA

A Myrenne ATM3 torsion pendulum was used at a frequency of approximately 1 Hz. The samples of 12 mm or 50 mm length (clamp length), 9 mm width and 2 mm thickness were monitored at a heating rate of 1.8°C min^{-1}. The glass transition temperature (T_g) was defined as the maximum of the loss modulus.

RESULTS AND DISCUSSION

Introduction

The APEA 4NT2 is a highly crystalline, fast crystallising polyesteramide with a very high melting temperature (316°C) and a high glass transition temperature (124°C). Copolymerizing 4NT2 with 4NI2 is replacing terephthalic groups with isophthalic groups. Despite this copolymerization, T4T units remain in the chain and these units are known to be easily crystallisable in an otherwise amorphous chain[8].

Copolymerization will certainly disturb the chain order and consequently the lamellar structure. The question is too what extend the crystallisation rate, the crystallinity and the dimensional stability are disturbed by this copolymerization.

First the synthesis of the bisesterdiamides will be discussed. They were analyzed by d.s.c., ^{1}H n.m.r. and h.p.l.c. Second, the polymerization will be discussed. The thermal properties of the polymers were investigated by d.s.c. The dynamic properties were studied by DMTA.

Bisesterdiamides synthesis

T4T-dimethyl was synthesised from dimethyl terephthalate (DMT) and 1,4-butanediamine (BDA) according to the method reported in the literature. The melting temperature was 264–268°C, the heat of fusion ΔH_m was 160–165 J g^{-1} and the purity according to ^{1}H n.m.r. was 96%–98%[7]. The overall yield after recrystallisation was 50%–60%. H.p.l.c. diagrams of T4T-dimethyl before and after recrystallisation are given in *Figure 1a*. Before purification two small peaks on the right to the main peak were visible, indicating the presence of two impurities. These peaks belong to components which are less polar than the main component T4T-dimethyl and were supposed to originate from higher oligomers such as T4T4 and T4T4T-dimethyl. After purification these impurities had disappeared. I4I-dimethyl was synthesised from dimethylisophthalate (DMI) and 1,4-butanediamine (BDA). As DMI dissolves better in toluene than DMT, the reaction time and temperature of the 141-dimethyl synthesis could be lower compared with the T4T-dimethyl synthesis. Also the amount of solvent (toluene) could be reduced. Purification of the final product was, however more difficult. In *Figure 1b* the h.p.l.c. diagrams of I4I-dimethyl before and after recrystallisation are shown. Recrystallised I4I-dimethyl gave one peak, indicating that the final product was pure. Several small extra peaks, resulting from impurities, were present in non recrystallised I4I-dimethyl. These extra peaks belong to components which are less polar than the main component I4I-dimethyl and were therefore supposed to originate from higher oligomers such as I4I4, I4I4I-, and I4I4I4I-dimethyl or cyclic products such as cyclic 14 and cyclic I4I4. Cyclic products could have been formed during the synthesis of I4I-dimethyl because of the meta substitution of the

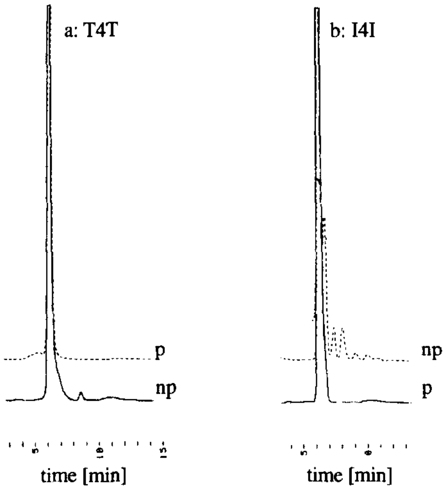
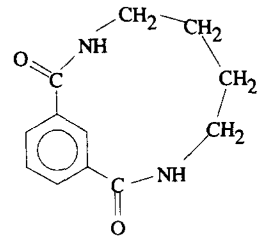


Figure 1 H.p.l.c. diagrams of T4T-dimethyl (a) and I4I-dimethyl (b) (p: purified, np: non purified)

aromatic ring, as an example the structure of cyclic I4 is given (3).



(3)

Cyclic I4

With the shorter ethylenediamine a cyclic product is unlikely to be formed and was not observed during the synthesis of I2I-dimethyl. It is assumed that the cyclic products were more difficult to separate from I4I-dimethyl than higher oligomers. Therefore a much weaker solvent than NMP, which was used for recrystallising T4T-dimethyl, had to be used to recrystallise I4I-dimethyl. Butylacetate was chosen as recrystallisation solvent in a trial and error procedure. After recrystallisation of I4I-dimethyl the side peaks, were absent and the product was 'pure'. The final yield was low (15%). In *Figure 2* the ^{1}H n.m.r. spectrum of I4I-dimethyl is given. The melting temperature of I4I-dimethyl was 215–217°C and the melting enthalpy ΔH_m was 150–170 J g^{-1}. The melting peak was not sharp, a left shoulder was clearly visible. This indicates that the impuritie(s) were not removed completely.

Polymerizations

The polymers were synthesised from mixtures of T4T- and I4I-dimethyl and ethanediol. First the bisesterdiamine mixtures were transesterified with an excess of ethanediol at 200–260°C for 1 h in the presence of a titanium catalyst. Ethanediol also acts as a solvent for T4T-dimethyl since T4T-dimethyl melts at a much higher temperature. During the transesterification methanol is formed and stripped off. When no more methanol was stripped off , the pressure was reduced ($<$ 2 mmHg) and the polycondensation started. The excess of ethanediol was distilled off first. The polymers crystallised a few minutes after vacuum was applied. The reaction was stopped 45 min later. The polymers were brittle and had a white-brown colour, except for 4NI2 which was transparent. A solid state postcondensation was necessary to increase the molecular weight. During solid state postcondensation ester exchange can occur, increasing the molecular weight. Also carboxylic acid endgroups can react with alcohol or amino endgroups. The postcondensation temperature was 20°C below the melting temperature with a maximum of 260°C. Serrano[9] found that above 260°C degradation increases strongly. The viscosities of the postcondensated polymers are above 0.61 dl g^{-1}. The inherent viscosity increases with decreasing melting temperature of the copolymers. 4NI2 is amorphous and could therefore not undergo a solid state postcondensation at a high temperature. The inherent viscosity of 4NI2 directly after synthesis was high enough (η_{inh} = 0.54 dl g^{-1}) for injection moulding. A typical ^{1}H n.m.r. spectrum of a 4NT/I2 copolymer is given in *Figure 3*. From these spectra the composition of the copolymers was checked.

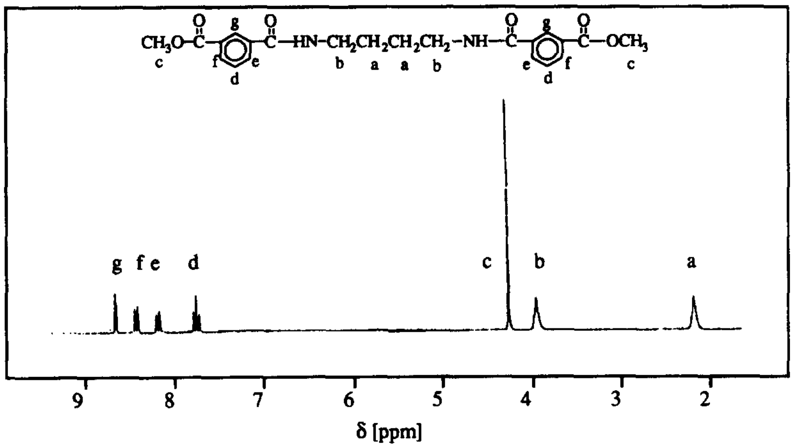


Figure 2 ^{1}H n.m.r. spectrum of I4I-dimethyl

Table 1 Composition, postcondensation temperature, thermal and dynamic properties and inherent viscosities of 4NT/I2 polyesteramides.

Polymer	%I4I(–)	$T_{postcond.}$ (°C)	η (dl g^{-1})	T_m(°C)	ΔH_m(J g^{-1})	T_c (°C)	$T_m - T_c$(°C)	T_g(°C)	T_g/T_m (–)	$\Delta G'(T_g)^a$(–)
4NT2	0	250	0.61	316	20	290	26	124	0.67	0.18
4NT/I2	5	260	0.77	299	51	261	35	122	0.69	0.18
4NT/I2	10	250	0.74	279	29	249	30	121	0.71	0.16
4NT/I2	20	235	0.86	274	37	236	38	120	0.72	0.14
4NT/I2	40	220	0.89	250	21	222	28	119	0.75	0.12
4NI2	100	–	0.54	–	–	–	–	107^B	–	∞
PBT	–		1.36	222	42	186	36	47	0.65	0.12

[a] according to equation 4.
[b] also measured with d.s.c.

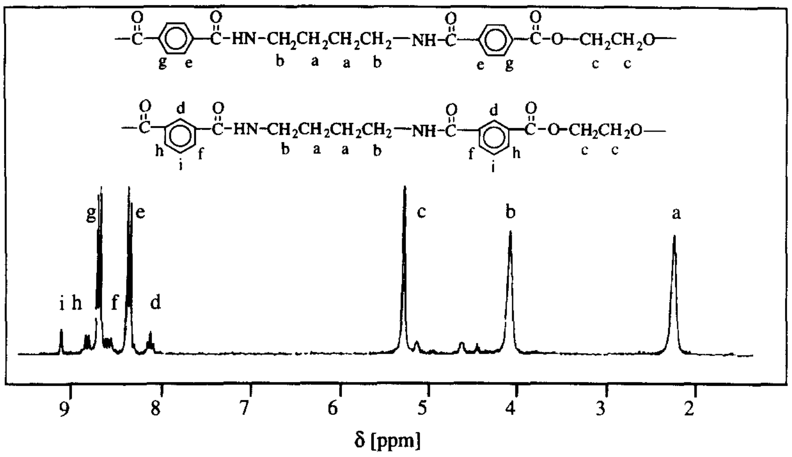


Figure 3 ^{1}H n.m.r. spectrum of 4NT/I2 with 20% I4I

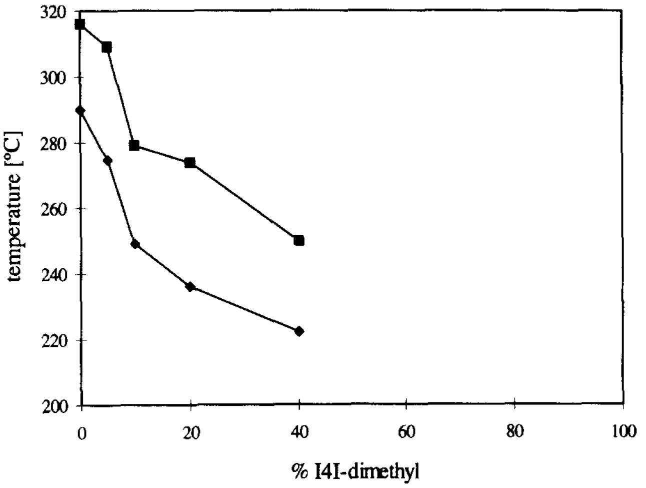


Figure 4 Melting (■) and crystallisation (◆) temperature of 4NT/I2 polyesteramides as function of I4I content

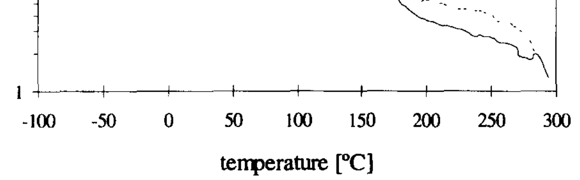


Figure 5 Storage (G') and loss (G") modulus versus temperature for 4NT2 (straight line) and 4NT/I2 with 20% I4I (dotted line)

Polymer properties

The composition, postcondensation temperature, thermal properties determined with d.s.c., the dynamic properties determined with DMTA and the inherent viscosities of the polymers are given in *Table 1*. The d.s.c. melting and crystallisation peaks were very broad. Integration of these peaks was rather inaccurate and as a consequence the enthalpy and undercooling values are not very exact.

Thermal analysis (d.s.c.)

The APEA 4NT2 has a melting temperature of 316°C and a low undercooling ($T_m - T_c$). T_m and T_c have a somewhat higher value than reported earlier[4]. This is probably because of somewhat milder reaction conditions. The APEA 4NI2 is transparent and no melting endotherm was observed in the d.s.c. The storage modulus dropped strongly by passing the glass transition temperature. It can therefore be concluded that 4NI2 is amorphous. The 4NT2 melting temperature and crystallisation temperature decreases with copolymerization (*Table 1* and *Figure 4*).The decrease in melting temperature with copolymerization is caused by loss in order resulting in smaller lamellae. 4NI2 which does not cocrystallise with 4NT2, is placed at random in the chain, preventing the formation of thick lamellae.

The ΔH_m values are not changing consistently. The value for 4NT2 is very low, lower than was expected from the torsion data and the n.m.r. data[10] and 4NI2 is amorphous. For the copolymers the trend of decreasing ΔH_m values with increasing 4NI2 content is not very consistent.

The undercooling $\Delta T = T_m - T_c$ is a measure of the rate of crystallisation. The lower the undercooling, the faster the crystallisation. For PBT,which is regarded as a fast crystallising polymer the undercooling is 36°C[11]. The undercooling of 4NT/I2 polyesteramides was always lower than 40°C, indicating that these copolymers crystallise surprisingly fast. In 4NT/I2 copolymers the long order is gradually lost, but the T4T units are still present in the chain. It is known that even isolated T4T units can crystallise fast[8]. This phenomena is possibly also the reason for the fast crystallisation of these polymers. It seems that replacing T4T with I4I does not slow down the crystallisation rate very much.

Dynamic mechanical thermal analysis

The DMTA tests were carried out on a pendulum apparatus. The storage modulus (resistance against applied torque) and the loss modulus (dissipated energy) were determined. The glass transition temperature (T_g) was defined as the maximum of the loss modulus curve. The samples were shorter than the apparatus standard sample length and therefore not too much importance should be attached to the values of the moduli, the course of the curves did however not change.

The moduli as function of the temperature of 4NT2 and 4NT/12(20%) are shown in *Figure 5*. The storage modulus below T_g is almost independent of temperature. The drop of the storage modulus at the T_g and the decrease of the storage modulus above the T_g are of the same order for 4NT2 and 4NT/I2(20%). The modulus in the rubbery region remains high up to the melting temperature. This high modulus above the T_g suggest the presence of a well formed crystalline network. For a copolymer this is unusual but we have seen this behaviour before in other T4T copolymers[6].

The drop of the storage modulus at the T_g was expressed as (4) and given in *Table 1* for the polymers:

$$\Delta G'(T_g) = \frac{G'(150°\mathrm{C})}{G'(25°\mathrm{C})}\ [-] \qquad (4)$$

The higher this value, the lower the drop of the storage modulus and the higher the physical crosslink density. The physical crosslink density is usually directly related to the crystallinity and the log modulus forms a linear relationship with the crystallinity[12]. In our copolymers the $\Delta G'(T_g)$ remains high though the crystallinity is reduced.This suggests that in 4NT/I2 as well as in other T4T copolymers the physical crosslink density remains high though the crystallinity is lowered. This is only possible if the size of the crystalites (lamellae) is reduced while being a strong physical crosslink. $\Delta G'(T_g)$ decreased gradually from 0.18 to 0.12 up to a 40% I4I content. For PBT, this value was 0.12[11]. The observed decrease of $\Delta G'(T_g)$ for 4NT/I2 polyesteramides with increasing I4I content is extremely small, indicating the I4I does not disturb the T4T crystallisation. The crystallinity compared to PBT was high.

The values of the glass transition temperatures (T_g) of the polymers are given in *Table 1*. The T_g of 4NT2 is 124°C and the T_g of 4NI2 is still high, 107°C. The T_g of 4NT/I2 polyesteramides remains practically constant at 120°C up to 40% I4I. 4NT2 behaves like a homopolymer, having a T_g/T_m ratio of 2/3. The T_g/T_m ratio of 4NT/I2 can be varied between 0.67 and 0.75 with increasing I4I content because the melting temperature decreases strongly while the glass transition temperature remains constant.

CONCLUSION

The APEA 4NT2 is a highly crystalline material with a high melting temperature and a high modulus in the rubbery region. 4NI2 is a glassy material. Copolymerizing 4NT2 with 4NI2 decreases the melting temperature strongly without lowering the crystallisation rate much, the T_g and the modulus above the T_g. The lower melting temperature is probably caused by a thinning of the lamellae. The high crystallisation rates and the high physical crossink density of these copolymers must be ascribed to the presence of the T4T units which even if they are not connected with a regular group (even diols) are still able to crystallise fast and to form strong lamellae. By copolymerization of 4NT2 with 4NI2 the melting temperature can be varied from 316°C to 250°C and the glass transition temperature can be varied between 124°C and 119°C. Copolymers with the uniform T4T units and possibly also other structural regular diamides have the unique set of properties of a low melting temperature combined with fast crystallisation and a high dimensional stability.

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