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Alternating polyesteramides based on 1,4-butylene terephthalamide: 2. Alternating polyesteramides based on a single, linear diol (4NTm)

P. J. M. Serrano*, E. Thüss† and R. J. Gaymans‡
University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

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Strictly alternating polyesteramides consisting of 1,4-butylene terephthalamide and aliphatic diols have been synthesized in the melt in the presence of a titanium catalyst. The influence of diol length on the thermal and mechanical properties was studied. Depending on its structure, the diol took part in the crystallization. All polymers crystallized very fast ($T_m - T_c < 33°$) and had a lamellar structure. The melting and glass transition temperatures decreased with increasing diol length, and both showed an odd–even effect. The polyesteramides were melt processed and their mechanical properties were determined using torsional (d.m.t.a.) and tensile tests. The polymers have a high glass transition temperature. The polyesteramides have a flexural modulus close to those of polyamides (2.9 GPa), whereas the water absorption is close to the values of polyesters (1.6 wt%). Loss of the alternating structure of the polymers, caused by ester–amide interchange reactions, was studied through ^{13}C n.m.r. It was found that the melting and glass transition temperatures decreased with increasing loss of uniformity. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Harrell[1] and Allegrezza *et al.*[2] showed, in the early 1970s, that segmented block copolymers with uniform blocks have interesting mechanical properties. These thermoplastic urethanes had a constant rubber plateau above the glass transition temperature (T_g) over a large temperature range. Furthermore, the elongation at break above their T_g was much higher than that of polymers with non-uniform blocks.

Eisenbach *et al.* synthesized polyurethane-b-polyether copolymers with similar mechanical properties[3,4]. These polymers also showed interesting thermal properties. The melting and crystallization peaks were very sharp, which was explained by the formation of lamellae with a uniform thickness.

Lenz *et al.*[5,6] synthesized main-chain thermotropic liquid crystalline polyesters. These polyesters were based on aromatic esters of uniform length and flexible spacers (diols). The melting temperature (T_m) of these polyesters showed an odd–even effect with the spacer length. Polymers with an even spacer (diol) had a higher melting temperature than the polymers with the neighbouring odd-numbered spacers. The flexible spacers reduced the melting temperature and the length of the spacers determined whether a nematic or a smectic phase was formed. This difference in melting temperature might have been caused by differences in lamellar thickness of the odd and even polymers.

Kricheldorf *et al.*[7] found similar results with polyesteramides. The polymers with even spacers showed a higher T_m than the polymers with odd spacers. Moreover, the odd-spacer polymers crystallized much more slowly. WAXS experiments on fibres showed, for the polymers with odd spacers, a smaller tilt angle of the mesogens. This resulted in a less stable crystal lattice and thus in a lower melting temperature. So the odd–even effect of T_m is explained by different tilt angles of the mesogens.

Williams *et al.*[8] synthesized alternating polyesteramides nNTm (*Scheme 1*), which can be regarded as polymers with uniform amide units and ester spacers. These polyesteramides (PEAs) were made from preformed bisesterdiamides and diols. The melting temperature of the polyesteramides decreased with increasing number of methylene groups in the diamine and in the diol, and showed an odd–even effect. De Chirico[9] studied the polyesteramide 6NT6 in more detail. He observed a decrease in the melting temperature (from 265 to 253°C) with loss of the alternating character of the polymer.

These alternating polyesteramides showed a behaviour resembling that of homopolymers. The melting temperatures were in between those of the constituent polyesters and polyamides. Borri *et al.*[10] studied similar polyesteramides and found the glass transition

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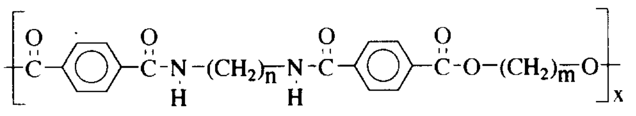
*Currently at General Electric Plastics bv, PO Box 117, 4600 AC Bergen op Zoom, The Netherlands

†Currently at Hevea bv, Kanaalstraat OZ 21, 8102 GG, Raalte, The Netherlands

‡To whom correspondence should be addressed



nNTm

Scheme 1

temperature also to lie between the values for the homopolymers.

Gaymans[11] and Van Hutten[12] and their colleagues reported on the synthesis of copolymers with polyesteramide units of uniform length. These polymers were synthesized from T4T dimethyl (1,4-butylene terephthalamide) and aliphatic diols or poly(tetramethylene oxide). The undercooling ($T_m - T_c$) of those polymers appeared to be very small (11–15°), indicating an extremely fast crystallization. PBT, for example, which is considered to be a fast crystallizing polymer, has an undercooling of about 30°. These copolymers can be regarded as consisting of crystallizable diamides and non-crystalline polyether segments, while the diols can be regarded as segments or as spacer groups.

The glass transition temperature of the polymers could be varied between −70°C and 100°C depending on the length of the amorphous segment. The length of the amorphous segment also strongly influenced the melting temperature of the system, but not the crystallization rate. The decreasing melting temperature was explained by the melting point depression theory according to Flory[13]. In this series of polymers, the T_g/T_m ratio changed from 0.49 (T4T–PTMO) to 0.75 (T4T–hexanediol/octanediol). The influence of the purity of the T4T segments on the properties has not yet been studied.

In semi-crystalline homopolymers the chemical composition of the crystalline and amorphous phase is the same. These homopolymers show a T_g/T_m ratio of about 2/3[14,15]. Only highly symmetrical polymers with short repeating units have lower values, mostly $T_g/T_m \approx 1/2$ (e.g. POM and PE)[16]. In segmented block copolymers, on the other hand, the chemical composition of the amorphous and crystalline phase is different. Usually only one of the blocks crystallizes whereas the second block remains in the amorphous phase. The block copolymers, therefore, have T_g/T_m ratios deviating from 2/3. In polymers with spacer groups, the spacer group can or cannot take part in the crystallization. This depends on the structural regularity of the spacer group. Thus, polymers with spacer groups may show a T_g/T_m ratio different from 2/3.

Alternating polyesteramides 4NTm are copolymers based on T4T dimethyl[17] (1,4-butylene terephthalamide, nylon-4,T) and a single aliphatic diol. The diol can be regarded as a spacer group between the diamide segments. In this study the conditions under which the spacer group takes part in crystallization is studied. Furthermore, the influence of crystallization on the thermal and mechanical properties is reported.

First, the results of the synthesis, including a solid-state postcondensation, are discussed. Ester–amide interchange reactions can disturb the alternating character of the PEAs. This is investigated by ^{13}C n.m.r. The influence of the diol length on the mechanical and thermal properties is studied.

EXPERIMENTAL

Materials

The α,ω-diols were purchased from Merck and used as received (purity >95%). Tetraisopropyl orthotitanate ($Ti(i\text{-}OC_3H_7)_4$) was distilled prior to use and diluted in anhydrous *m*-xylene (0.100 M). The T4T dimethyl was synthesized and purified as described earlier[17].

Melt polycondensation

The preparation of 4NT6 (1,6-hexanediol) 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 (40 g, 97.0 mmol) and 1,6-hexandediol (25.22 g, 213.4 mmol) was heated to 180°C in an oil bath. After 15 min $Ti(i\text{-}OC_3H_7)_4$ (2 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 mm Hg) while the temperature was raised to 250°C (2° min^{-1}). After 10 min at 250°C a pressure of less than 1 mm Hg was applied for 1 h. After the reaction was stopped, the vessel was slowly cooled down to room temperature, maintaining the low pressure. The polymer was cryogened, ground in a Fritsch pulverisette and subsequently dried in a vacuum oven at 80°C.

During synthesis of the polymer in a 1.3 litre stainless steel reactor (A31 type JUD25/1, Juchheim GmbH) equipped with mechanical stirrer, nitrogen inlet, vacuum supply and Pirani 503 gauge, the diol/T4T dimethyl molar ratio was increased from 2.2 to 7.7. Furthermore, the reaction time during the low pressure stage (at 10–15 mm Hg) was increased to 1.5 h in order to distil off the excess diol.

Solid state postcondensation

The ground polymer (particle size <1 mm) was dried overnight *in vacuo* at 80°C. The postcondensation was carried out at reduced pressure (<1 mm Hg) in a glass or stainless steel tube which was placed in an oven at a temperature of 20–30° below the melting temperature, with a maximum temperature of 260°C. The reaction time was usually 24 h.

Viscometry

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 viscometer, placed in a water bath at 45.0 ± 0.05°C.

D.s.c.

D.s.c. spectra were recorded on a Perkin Elmer DSC7 apparatus equipped with a PE-7700 computer and TAS-7 software. The melting and crystallization transitions were determined using samples of 5–8 mg with a heating and cooling 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 calibration standard.

N.m.r.

Proton n.m.r. and proton decoupled ^{13}C n.m.r. 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 n.m.r. scans (3200) were recorded with an acquisition time of 2.097 s and a 45° pulse.

Optical microscopy

The polymer was placed between two glass slides and heated rapidly. After the formation of a thin melt layer, the sample was cooled down and analysed using a Leitz Ortholux II pol-BK optical microscope equipped with a camera. The samples were heated using a Mettler hot stage FP82 equipped with a Mettler FP80 central processor. The applied heating rate was 20°C min^{-1}.

Endgroup analysis

The NH_2 and COOH endgroup concentration of the polymers was determined using a Metrohm titroprocessor type 636 with Ross glass electrodes. For NH_2 endgroup detection, trifluoromethane sulfonic acid (TFMS) in isopropanol was used as titrant (0.1 M). The polymer was dissolved in phenol/water (85/15 vol%). The COOH concentration was determined according to a new procedure described by Van Bennekom and Gaymans[18]. The PEA (100 mg) was dissolved in a mixture of 1 ml hexafluoroisopropanol (HFIP) and 9 ml trifluoroethanol (TFE). First, a certain amount of tetrabutylammonium hydroxide was added, followed by a back titration with TFMS. Comparison of the equivalency points with a reference of pure HFIP/TFE enabled calculation of the COOH endgroup concentration.

Injection moulding

Samples for the d.m.t.a. 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 4NT6 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 settings were 310–305–305–315°C whereas the mould temperature was 120°C. The complete cycle time was 14.2 s. Before use, all polymers were dried in a vacuum oven at 80°C for 48 h.

D.m.t.a.

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^{-1}. The glass transition temperature (T_g) was defined as the maximum of the loss modulus G''.

Three-point bending test

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 at a rate of 1mm min^{-1}. 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 25°C for 64 days. After this treatment the samples were weighed again (w).

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

Table 1 Results of solid-state postcondensation for 4NTm polyesteramides

Code	Diol	T (°C)	P (mm Hg)	η_{inh}[a] ($dl\,g^{-1}$)	η_{inh}[b] ($dl\,g^{-1}$)	X_{AA}/X_A (mol%)
4NT2	ethane	260	0.1	0.14	0.41	9.0
4NT3	propane	260	0.1	0.22	1.26	6.3
4NT4	butane	260	0.2	0.16	0.66	9.0
4NT5	pentane	250	0.1	0.17	1.05	7.5
4NT6	hexane	230	0.6	0.32	0.96	<2
4NT7	heptane	230	0.1	0.34	2.55	11.9
4NT8	octane	245	0.1	0.41	1.15	3.8
4NT9	nonane	220	0.1	0.25	2.40	7.4
4NT10	decane	230	0.1	0.34	1.13	11.6
4NT12	dodecane	220	0.1	0.23	1.38	9.9
4NT6[c]	hexane	240	0.1	0.32	1.34	2.2

T = postcondensation temperature, X_{AA}/X_A = relative amide block fraction

[a] After polymerization

[b] After solid-state postcondensation

[c] 1.3 litre stainless steel reactor

RESULTS AND DISCUSSION

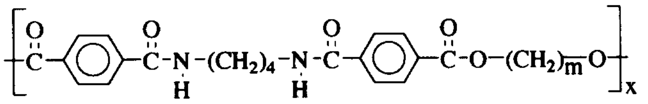
Introduction

The synthesis of the polyesteramides 4NTm (*Scheme 2*) is discussed first, together with the solid-state postcondensation which was necessary to enhance the molecular weight. The thermal properties of the polymers were investigated by d.s.c. Furthermore, the dynamic behaviour was determined (d.m.t.a.) for all polymers and tensile tests were performed with the PEA 4NT6.

The diol in the alternating polyesteramide 4NTm can be regarded as a spacer unit for easily crystallizable diamide units. This spacer might take part in the crystallization or might remain in the amorphous phase.

Melt synthesis

The polyesteramides (PEAs) were synthesized according to the DMT route for PET/PBT[19,20]. First, the T4T dimethyl was transesterified at 180–220°C with an excess of diol for 20–30 min in the presence of a titanium catalyst. Because the T4T dimethyl melted at much higher temperatures, it had to be dissolved in the diol. After transesterification of the T4T dimethyl, the mixture was a homogeneous melt. The transesterification temperature was allowed to be higher than with PBT since the T4T dimethyl did not sublimate as easily as DMT. When this reaction was complete (no more methanol was distilled off), the temperature was raised and the pressure was reduced (<1 mm Hg). First, the excess of diol was distilled off. Then the equilibrium was shifted



4NTm

Scheme 2

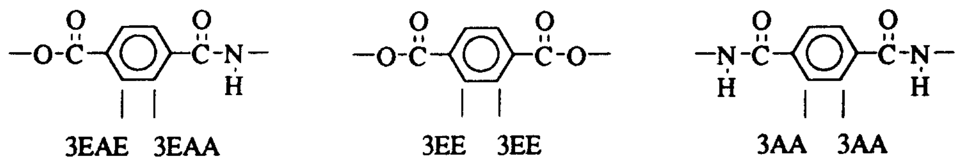


Figure 1 Codes for the different triads used in the n.m.r. analyses

by removing the condensation product, the diol. The maximum temperature used was 260°C. Higher temperatures were avoided as they would have led to an unacceptable degree of ester–amide interchange[21] and thermal degradation. The reaction was stopped after 1 h. The polymers obtained were brittle and opaque.

Only for the polymers with longer diols was the reaction mixture a melt during the entire process. For the polymers with shorter diols the reaction mixture quickly solidified once oligomers were formed, because of the high melting temperatures of the polymers. Further reaction was then limited. For the polymers with shorter diols this solidification resulted in products with low inherent viscosities, as can be seen in *Table 1*. Thus, a postcondensation in the solid state was necessary to obtain polymers with a high molecular weight.

According to Della Fortuna *et al.*[22], the molecular weight obtained by melt polymerization depends on the configuration of the reactor. We have synthesized some of the PEAs in two small reactor types, viz. a round-bottomed glass flask and a cylindrical stainless steel reactor. We found, however, no differences in the inherent viscosities of the same polymers synthesized in either of these reactors. Van Bennekom and Gaymans[18], on the other hand, found the round-bottom glass flask to be the better reactor because of the absence of cold spots.

Thermal degradation occurred only to a small extent during the synthesis. Polymer 4NT6, for example, synthesized in a 1.3 litre reactor, contained no carboxylic acid endgroups. These endgroups are usually formed during ester degradation. However, the NH_2 endgroup content was 0.067 meq g^{-1}. It is unlikely that these amino endgroups originate from the thermal degradation of the amide bond since the amide bond is more stable than the ester bond due to its partial double-bond character[23,24]. Probably the T4T dimethyl contained some NH_2 endgroups. Van Bennekom[18] also reported on the presence of NH_2 endgroups in T4T dimethyl.

Solid-state postcondensation

Since the inherent viscosity of most polymers after melt polymerization was not high enough for meaningful mechanical testing, a solid-state postcondensation was necessary to enhance the molecular weight of the PEAs. During solid-state postcondensation ester exchange can occur, increasing the molecular weight. Also, carboxylic acid endgroups can react with alcohol or amino endgroups.

The reaction temperature was 20–30°C below the melting temperature of the polymer in order to favour the diffusion rate of reactive endgroups and condensation products in the amorphous phase[25]. Temperatures closer to the melting temperature would lead to particle sticking and, as a consequence, to surface reduction. The use of a vacuum lowered the partial pressure of the diols, shifting the equilibrium to the right. In the course of the reaction the mobility of the endgroups might have been reduced because of higher crystallinity. This is caused by an annealing effect which changes the crystallite size and thus the crystallinity.

It is known from literature that the increase of the molecular weight of the polymer during solid-state postcondensation is logarithmically related to the postcondensation time[26–28]. The largest increase in molecular weight is attained within the first few hours. We found similar results. The inherent viscosity increases with increasing reaction time up to about 24 h, depending on the initial inherent viscosity[29]. Longer times lead to more degradation and a decrease in the inherent viscosity. With increasing post-condensation temperature from 210° to 250°C the η_{inh} of 4NT6, with a starting viscosity of 0.39 dl g^{-1} and a reaction time of 24 h, increased from 0.96 to 1.33 dl g^{-1}. However, there will be a maximum in the reaction temperature above which the molecular weight will not increase further because degradation of the polymer outweighs the effects of further polymerization. Above 250°C ester–amide interchange also becomes more important.

As the postcondensation temperature for the PEAs with longer diols was closer to the melting temperature than for the polymers with shorter diols, the diffusion of reactive endgroups and condensation products was enhanced, resulting in higher inherent viscosities than those of the PEAs with shorter diols. Furthermore, the increase in viscosity is higher for the polymers with an odd number of carbon atoms in the diol than for the polymers with an even number of carbon atoms in the diol. This odd–even effect is probably caused by differences in crystallinity and T_m of the polymers.

Ester–amide interchange

The regular structure of the alternating PEAs can be disturbed by degradation reactions. Thermal degradation will lower the molecular weight, whereas interchange reactions can lead to random segments in the polymer. Della Fortuna *et al.*[22] investigated ester–amide interchange in the polyesteramide 6NT6 by ^{13}C n.m.r. The analysis was based on three types of ester–amide triads.

We determined the degree of ester–amide interchange reactions by integration of the peaks of the three carbon atoms (*Figure 1*). The assignment of the chemical shifts is similar to the one for T4T dimethyl as described before[17].

The mole fractions of the different triads, X_{EE}, X_{EA} and X_{AA}, are calculated assuming that the probabilities of the triads EAE and EAA are equal. This is verified by comparison of the two integrated peaks 3EAE and 3EAA. In general, the mole fraction of X_{EE} has to be equal to the mole fraction of X_{AA} if only ester–amide interchange occurs. However, the value of X_{EE} is usually lower due to degradation of the ester bonds. Because of this degradation, the 3AA peak has been used to

Table 2 Ester–amide interchange (X_{AA}/X_A) (mol%) for PEAs at different stages in the synthetic procedure

Code	Diol	T (°C)	X_{AA}/X_A T4T dimethyl	X_{AA}/X_A polymerization	X_{AA}/X_A postcondensation
4NT2	ethane	250	6.5	7.1	8.0
4NT5	pentane	240	3.8	5.7	5.3
4NT8	octane	245	3.8	4.2	4.0
4NT10	decane	230	8.3	9.9	11.5
4NT12	dodecane	230	8.3	9.1	15.3

T = postcondensation temperature

Table 3 Thermal properties (d.s.c.) of 4NTm polyesteramides

Code	Diol	T_m (°C)	T_c (°C)	$(T_m - T_c)$ (°C)	ΔH_m (J g^{-1})
4NT2	ethane	307	282	25	38.3
4NT3	propane	298	251	47	39.8
4NT4	butane	315	284	31	34.7
4NT5	pentane	276	262	14	40.4
4NT6	hexane	291	258	33	55.1
4NT7	heptane	254	229	25	22.3
4NT8	octane	270	237	33	43.8
4NT9	nonane	251	228	23	35.4
4NT10	decane	247	230	17	29.6
4NT12	dodecane	245	220	25	47.7

Heating and cooling rate 20°C min^{-1}

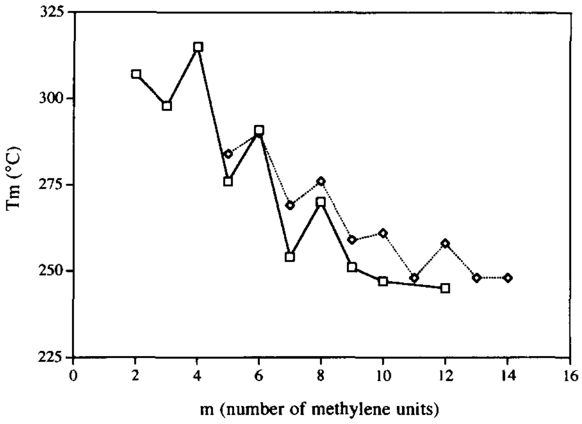


Figure 2 Melting temperature of 4NTm polyesteramides vs number of methylene groups in the diol (m): □, this study (d.s.c.); ◇, Williams *et al.* (optical light microscopy)[8]

determine the non-uniformity of the PEAs caused by ester–amide interchange.

$$X_{EE} = \frac{3EE}{3total} \times 100\% \qquad (mol\%) \qquad (2)$$

$$X_{EA} = \frac{3EAE + 3EAA}{3total} \times 100\% \qquad (mol\%) \qquad (3)$$

$$X_{AA} = \frac{3AA}{3total} \times 100\% \qquad (mol\%) \qquad (4)$$

The mole fractions of the ester and amide groups, X_E and X_A, with respect to the total number of ester and amide groups, are defined in the following equations:

$$X_E = \frac{3EAE + 3EE}{3total} \times 100\% \qquad (mol\%) \qquad (5)$$

$$X_A = \frac{3EAA + 3AA}{3total} \times 100\% \qquad (mol\%) \qquad (6)$$

These values should be 0.5 in a strictly alternating PEA. The relative amide non-uniformity fraction is now defined as X_{AA}/X_A:

$$\frac{X_{AA}}{X_A} = \frac{3AA}{3EAA + 3AA} \times 100\% \qquad (mol\%) \qquad (7)$$

This value is given in *Table 1* for the polyesteramides. The X_{AA}/X_A value of the starting T4T dimethyl used for the synthesis of the polymers given in *Table 1* was maximal, 4%. So it is obvious that during the melt synthesis and solid-state postcondensation ester–amide interchange occurred to some extent.

In *Table 2* the loss of uniformity is given for different polymers synthesized from non-purified T4T dimethyl. The X_{AA}/X_A value after each synthesis step is given. For all polymers some ester–amide interchange took place during melt polycondensation. Because most polymers were in the melt only for a short time, the interchange was limited. During postcondensation in the solid state, the interchange hardly took place for the polymers with shorter diols. The temperature was far below the melting temperature, at maximum 250°C. Below this temperature no ester–amide interchange was reported to take place[21]. However, as can be seen in *Table 2*, ester–amide interchange occurred in the polymers 4NT10 and 4NT12 although the temperature was below 250°C. The postcondensation temperature was close to the melting temperature, resulting in a higher mobility of the polymer chains and thus in an increasing diffusion rate of the ester and amide linkages.

The polyesteramides 4NT2, 4NT5 and 4NT12 showed a higher loss of uniformity after postcondensation at higher temperatures (compare the data in *Table 1* with those in *Table 2*). Van Bennekom[18] also found an increase of the ester–amide interchange with increasing reaction time in the melt.

Thermal analysis (d.s.c.)

Melting temperature. Thermodynamically, the melting temperature is defined as the ratio of the heat of melting ΔH_m to the entropy of melting ΔS_m. ΔH_m is usually determined by cohesion or intermolecular forces whereas ΔS_m depends on parameters such as regularity of arrangements and flexibility of polymer chains. In general, polyamides owe their high melting temperatures to a high ΔH_m because of hydrogen bonds and to a low ΔS_m because of associations which still exist in the melt. Introducing stiff phenyl groups, as with terephthalamides, will usually increase T_m even more[30]. Poly(alkylene terephthalate)s owe their relatively high melting temperature to this fact.

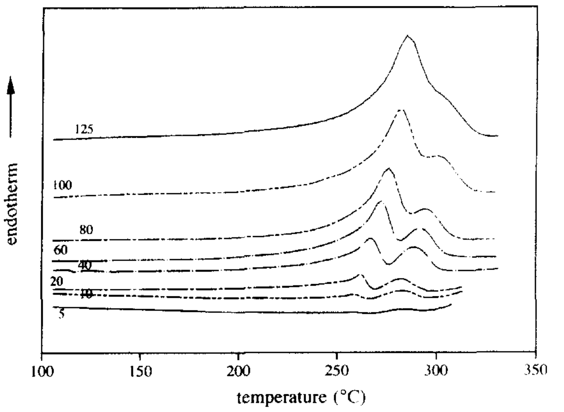


Figure 3 Melting curves (d.s.c.) of PEA 4NT6 at different heating rates (°C min^{-1})

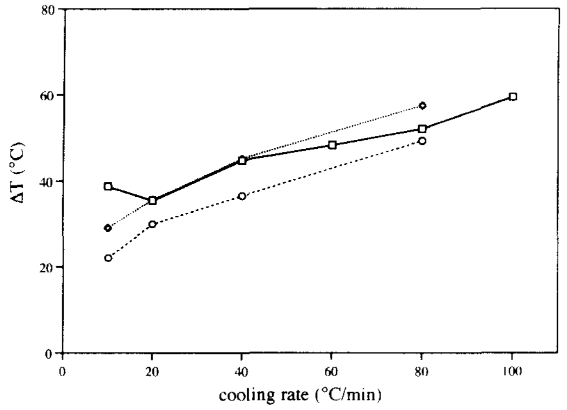


Figure 4 Undercooling ΔT ($T_m - T_c$) vs cooling rate: □, 4NT6; ◇, PBT[18]; ○, amide modified PBT[18]

The melting temperature of an alternating copolymer is expected to be between the two melting temperatures of the constituent homopolymers. With random copolymers, however, the melting point is depressed because of loss of structural order.

In *Table 3* and *Figure 2* the melting temperatures of the different PEAs are given. The melting temperature decreases with increasing number of methylene groups in the diol. This is caused by a faster increase of ΔS_m compared to the increase of ΔH_m with increasing diol length. Finally, the melting temperature will go (theoretically) to the value of polyethylene.

The melting temperatures of the PEAs 4NTm display an odd–even effect. This is also true for the crystallization temperatures (*Table 3*). This odd–even effect is a phenomenon well known for polyamides[31] and polyesters[32]. It is attributed to the (planar) zig-zag packing of the polymers. This is even more pronounced with polyamides since they form hydrogen bonds. The oxygen and nitrogen atoms of the amide bonds have to be opposite each other. With an even–even number of methylene groups, each amide linkage has the possibility to be positioned next to another amide linkage in the zig-zag structure. In this case the 'ideal' situation is obtained, resulting in a fully extended, planar zig-zag structure and thus in a good packing of the chains. This leads to a high melting temperature.

With an odd–even or odd–odd numbered polyamide this is not the case. It is known that the hydrogen bonds in odd–even or odd–odd polyamides are still formed to the same extent as in even–even polyamides[33,34]. However, because of the odd number of methylene groups, this leads to a zig-zag structure of the methylene chain being slightly out of the plane and not fully extended, or to a non-zig-zag structure. This non-planar zig-zag structure leads to a less good packing of the chains[35]. The unit cell differs and the long range packing is less, resulting in a lower melting temperature. For this reason, the melting temperature and crystallinity of nylon-6 are lower than those of nylon-6,6, although the 'concentration' of amide bonds is equal.

This odd–even effect also indicates differences in the alternating polyesteramides 4NTm. With the even-numbered PEAs the diol, acting as a crystallizable spacer, takes more part in the crystallization, probably leading to thicker lamellae and thus to higher melting temperatures. For the PEAs with odd diols the flexible spacer is, according to solid-state n.m.r. data, more in the amorphous phase than in the polymers with even diols[36]. Thus, the lamellae are smaller than the lamellae in the even polymers. As a consequence, the T_m of the odd spacered polymers is somewhat lower and closer to the 4NTm,p polyesteramides[29]. This idea of the ease of crystallization of the diol spacers is supported by the results of d.m.t.a. and solid-state n.m.r.[29].

The melting temperature of 4NT2 is lower than that of 4NT4. The melting enthalpy of 4NT2, on the other hand, is comparable with those of the other PEAs. The same holds for the undercooling. An explanation might be the formation of smaller lamellae for the 4NT2 PEA. PET is known to form smaller lamellae than PBT. This is believed to be due to the diol conformation. The diol is not fully stretched (not in the *trans* conformation). This implies that fewer diol spacers crystallize with the T4T units to form longer lamellae. Thus the lamellae are smaller, resulting in a lower T_m of the 4NT2 polyesteramide.

The melting temperatures of the alternating PEAs are close to the values found by Williams *et al.*[8]. Our values are somewhat lower because we defined T_m as the maximum of the transition peak in the d.s.c. measurements, whereas Williams *et al.* used an optical light microscope and defined T_m as the temperature at which the polarization colours had completely disappeared. This results in a somewhat higher value for T_m.

Most PEAs show two endothermic transitions upon heating. This is often found for nylons and polyesters. Some authors have explained this by the existence of a distribution of lamellar thicknesses[37,38], resulting in multiple melting peaks. However, with increasing heating rate the second melting peak disappears (*Figure 3*). Thus the two transitions are related to each other[39]. With increasing heating rate the starting temperature of the melting process remains the same while the area under the melting peak increases. This is an indication of a metastable crystal[40]. Therefore, a rearrangement of crystals is more likely; the lamellae melt and immediately recrystallize into more stable lamellae. This was also observed for PBT and nylon-6,6[41–43].

Rate of crystallization. The kinetics of crystallization usually follow an S-shaped curve in time. The first step is the nucleation stage in which nuclei are formed which then grow to a critical size in the melt. This is followed by folding of polymer chains in lamellae on the surface of the spherulites, which grow in radial directions on these

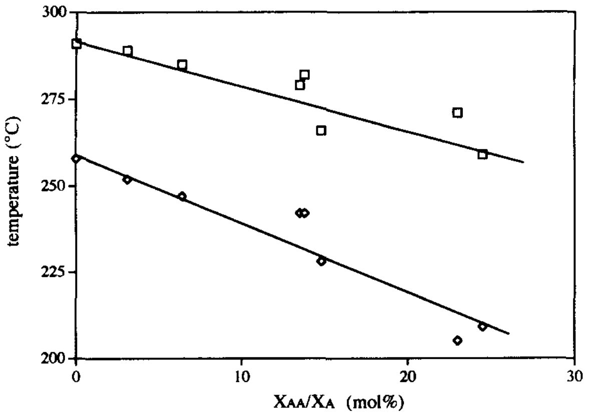


Figure 5 Influence of loss of uniformity in 4NT6: □, melting temperature; ◇, crystallization temperature

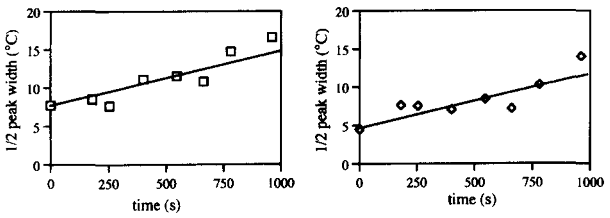


Figure 6 Peak width at 1/2 height of d.s.c. trace of 4NT12; □, melting temperature; ◇, crystallization temperature

nuclei. The rate of crystal growth remains constant until the spherulites meet. The non-crystallizing material is released and becomes entrapped in the interlamellar regions. A second crystallization process consists of a steady ordering inside this structure and leads to a further rise in density[44].

The temperature dependence of the crystallization rate is a combination of nucleation and crystal growth. Decreasing the temperature will increase the rate of nucleation. The rate of crystal growth is determined mainly by the mobility of the polymer chains in the melt. This means that there exists an optimum for the resulting crystallization rate at a certain temperature. Increasing the cooling rate during a non-isothermal experiment will lower the crystallization temperature. This was actually found for the polymer 4NT6 (*Figure 4*).

In accordance with earlier experiments by Bier *et al.*[45], we plotted the undercooling (ΔT) vs the cooling rate. ΔT is the difference between the melting temperature (20°C min^{-1}) and the crystallization temperature at different cooling rates. This is a measure of the rate of crystallization. The melting temperature remains constant whereas the crystallization temperature decreases with increasing cooling rate.

For comparison, the values for PBT and modified PBT (20 mol% PEA) with similar inherent viscosities are also given. As can be seen, the undercooling is small and increases slightly with cooling rate. The 4NT6 copolymer thus crystallizes very fast. This can be seen by comparing the values of ΔT for 4NT6 with those of PBT and modified PBT, which are considered to be fast crystallizing polymers.

From *Table 3* it is clear that all the PEAs show a small ΔT. Even the polymers with an odd number of methylene groups in the diol have a small ΔT and a reasonable ΔH_m. This suggests a fast crystallization of all the 4NTm polymers. This is probably due to the uniform diamide segments. Possibly these diamide segments are ordered in the melt by hydrogen bonds[46,47]. A decreasing uniformity (higher relative amide non-uniformity fraction) increases the ΔT (*Figure 5*).

We also observed negative spherulites with optical light microscopy. Ramesh *et al.*[47] proposed that the existence of negative spherulites requires a pre-existing structure in the melt. These negative spherulites remained when cooling down the polymer, while the interspherulitic material crystallized in a granular form. The same phenomenon was observed by Khoury[48].

No liquid crystalline behaviour for the 4NTm PEAs was observed using the polarized light microscope. Aharoni[49], on the other hand, found liquid crystalline behaviour for PEAs prepared from bis(aminobenzoyl) alkanes and aliphatic dicarboxylic acids. The behaviour was observed only for polymers with more than four methylene groups in the diamine and three or more methylene groups in the diol.

Polymer 4NT5 has an extremely small ΔT. The reason for this is not known. Possibly because of the pentanediol, the polymer can easily form chain folded crystals (kinetically determined form) resulting in a fast crystallization. From computer simulations[50] it was found that 1,5-pentanediol introduced the lowest strain in a chain-folded crystal.

We have also synthesized PEAs consisting of T4T dimethyl and mixtures of 2,5-hexanediol/1,6-hexanediol with different compositions. Introducing 2,5-hexanediol in the chain was thought to give lamellae consisting of T4T segments exclusively since it will be difficult for the diol to crystallize. However, the polymer 4NT2,5-hexanediol was completely amorphous ($T_g = 75$°C (d.s.c.)) and became crystalline only after prolonged annealing at 150°C (48 h). The polymer has a low T_m of 170°C, but a reasonable melting enthalpy (33 J g^{-1}). The methyl groups in the 2,5-hexanediol probably hinder the crystallization of the T4T segments. The surprisingly low T_g might be caused by the low molecular weight ($\eta_{inh} = 0.20$ dl g^{-1}) and the presence of non-reacted 2,5-hexanediol.

The 4NT6 polymer with 20 mol% 2,5-hexanediol showed a somewhat smaller ΔT (27°), but also a much lower melting temperature (250°C) compared to 4NT6 (291°C). A T_g was no longer visible in the d.s.c. scan. The melting enthalpy was also lowered (20 J g^{-1}). The 2,5-hexanediol probably hinders the crystallization of the diol mixture (spacer groups). The presence of non-crystallizing spacer groups thus leads to lower melting temperatures and melting enthalpies. The undercooling seems to remain fairly constant. Moreover, the reactivity of the secondary alcohol is low, leading to low molecular weight polymers.

Uniformity of the amide segment. The introduction of randomness in the polyesteramides (higher X_{AA}/X_A values) lowers the melting and crystallization temperature, as can be seen in *Figure 5*. The same had already been found for T4T dimethyl[17]. The amide segments probably disturbed the crystalline order in the polymer by the formation of less perfect lamellae. This was studied through X-ray diffraction by Van Bennekom and Gaymans[18].

The formation of less perfect lamellae is also reflected in an increasing broadness of the initially sharp melting

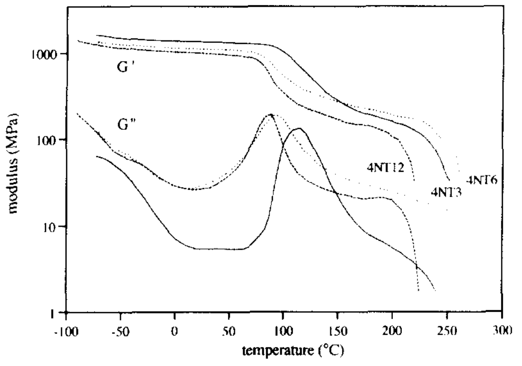


Figure 7 Typical d.m.t.a. scans of dry 4NTm PEAs (4NT3, 4NT6 and 4NT12)

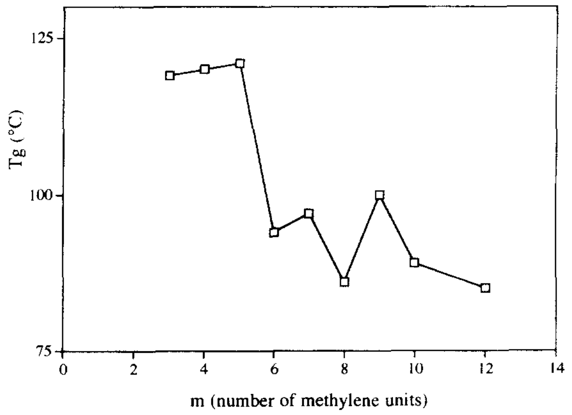


Figure 8 Glass transition temperature of 4NTm polyesteramides vs number of methylene groups (*m*) in the diol

Table 4 D.m.t.a. results for 4NTm polyesteramides and PBT

Code	Diol	T_g (°C)	G' at 150°C (MPa)	$\Delta G'$	T_g/T_m
4NT2	ethane		–	–	
4NT3	propane	119	189	2.4	0.69
4NT4	butane	120	176	2.2	0.67
4NT5	pentane	121	198	2.2	0.72
4NT6	hexane	94	174	2.5	0.65
4NT7	heptane	97	123	2.9	0.70
4NT8	octane	86	188	2.6	0.66
4NT9	nonane	100	116	2.4	0.71
4NT10	decane	89	160	2.3	0.70
4NT12	dodecane	85	103	2.1	0.69
PBT	butane	50	79	5.6	0.65

and crystallization peaks, the melting endotherm being broader than the crystallization exotherm (*Figure 6*). Prolonged residence time in the melt increases the loss of uniformity. The difference in broadness of the T_m and T_c peaks may be attributed to crystallization below T_c, leading to less perfect lamellae and thus to a somewhat broader melting peak.

Dynamic mechanical thermal analysis

D.m.t.a. tests were performed on a torsion pendulum apparatus. The storage modulus (resistance against the applied torque) and the loss modulus (dissipated energy) were determined. The glass transition temperature (T_g) is defined as the maximum of the loss modulus curve. The storage modulus above T_g was examined by defining the decrease of the modulus above T_g vs temperature. In *Figure 7* results for three typical examples of PEAs are given.

Usually, only the α-transition (T_g) was clearly visible in the spectrum of the loss modulus. However, sometimes a second peak (β-transition) was seen at about −60°C. This β-transition is attributed to interactions of amide linkages in the amorphous phase which are not involved in hydrogen bonds[10,51]. In a completely dry sample this transition is absent, but with increasing water content it becomes visible[52].

The values of the glass transition temperature of the 4NTm polyesteramides (*Table 4* and *Figure 8*) are higher than for the corresponding poly(alkylene terephthalates). This indicates that part of the amide linkages is in the amorphous phase, forming hydrogen bonds and thus restricting the mobility of the amorphous chains, which results in an increased T_g. This was verified by immersing a sample of 4NT6 in water at 75°C for 24 h. After this treatment the T_g decreased from 94 to 59°C. This T_g should be comparable to the T_g of an alkylene terephthalate polymer. It was expected to lie between the T_gs of poly(butylene terephthalate) and poly(hexamethylene terephthalate) (45 and 15°C)[53]. The higher T_g of 4NT6 after water treatment (59°C) suggests that the structure of the crystalline diamide phase also has an influence on the T_g.

Since only one T_g is found for these systems, the ester and amide segments have to be compatible in the amorphous phase.

From *Figure 8* it can be seen that the T_g of the PEAs decreases with increasing number of methylene groups in the diol. Introducing a longer flexible chain in the polymer will lower the T_g. Also, an odd–even effect was observed from 4NT4 up to 4NT12. This effect is reversed in comparison with the odd–even effect found for the T_ms. For shorter diols the T_g remained more or less constant. This behaviour is not clear at present. There might be a difference in the composition of the amorphous phase of the odd and even spacered polymers.

From solid-state n.m.r. analysis[29] it became clear that the PEAs with less than five methylene units in the diol have a more or less constant lamellar size which is smaller than the lamellar size of the other PEAs. With an equal crystallinity, this implies more tie points for the PEAs with shorter diols. Because of the higher concentration of tie points, the mobility of the shorter diol chains is reduced, which results in a higher T_g. Above five methylene groups, the size of the lamellae differs, with the chain length of the diol equal to the odd–even effect, the even diols having thicker lamellae. This is reflected in a lower T_g.

This odd–even effect for T_g is hardly observed in literature. Oertel[54] found a similar odd–even effect for polyester–polyurethane elastomers. The heat distortion temperature showed an odd–even effect with differing length of the diamine chain extender in the urethane segment.

The storage modulus below T_g is almost independent of temperature. However, it is higher for the polymers with shorter diols (butanediol and lower), as can be seen in *Figure 7* (4NT3). This difference is possibly due to a smaller secondary transition at lower temperatures. Sometimes this transition is not visible at all[55].

Above T_g the modulus decreases with temperature (*Figure 7*). Due to the crystallites which form an interconnected network, the modulus remains high up to the melting temperature. The level of the modulus above T_g is determined mainly by the volume fraction crystallinity. The crystalline regions act as a filler and as physical cross-links, holding the chains together. Due to the uniform segments, a good phase separation is obtained which results in a stable crystalline network. This was expressed in a gradual decrease of the modulus above T_g with temperature. This is, of course, important for high temperature applications. The decrease of the modulus with temperature is expressed by

$$\Delta G' = \frac{G'_{(T_g+40)}}{G'_{(T_{\mathrm{fl}}-40)}} \tag{8}$$

in which T_{fl} is the temperature of flow ($G' < 5\,\mathrm{MPa}$). The values of $\Delta G'$ for the PEAs as a function of the diol length are given in *Table 4*. Higher values of $\Delta G'$ mean a stronger decrease of the modulus. For comparison, also the value of a commercial engineering plastic, PBT, is given. It is clear from this table that the 4NTm polymers have a good dynamic mechanical behaviour above T_g. The values of $\Delta G'$ are between 2.1 and 2.9, indicating a similar dynamic mechanical behaviour of the polymers. Polymer 4NT7 has a somewhat higher value which might be caused by a high loss of uniformity (*Table 1*). During injection moulding the loss of uniformity may also increase, due to the high temperatures necessary to injection mould the PEAs. For example, the loss of uniformity of 4NT10 increased from 11.6 to 13.1%, while X_{AA}/X_A of 4NT6 increased from 2 to 5.3% (higher moulding temperature).

The values of T_g/T_m for most semi-crystalline homopolymers are close to 2/3[14,15]. The 4NTm polyesteramides with odd diols have a higher T_g/T_m ratio than the polyesteramides with even diols. This suggests that probably fewer odd diol spacers are in the crystalline phase. The odd diol PEAs behave less like homopolymers than the even diol based polymers. The high ratio of 4NT5 may be explained by the ease of chain folding of the pentanediol (see above). This will result in lamellae with a smaller thickness and in less incorporation of the diol in the crystal.

Bending test

Bending tests were performed with polymer 4NT6 at room temperature. The strain rate was relatively low ($1\,\mathrm{mm\,min^{-1}}$).

The flexural modulus for the material is about 2.9 GPa, which is in good agreement with the expected values for polyesters and polyamides. The expected Young's modulus can be calculated through equation (9). The value of G' at 25°C is 960 MPa, with a Poisson constant of 0.42 (nylon-6,6). This gives a Young's modulus of about 2.7 GPa, which is close to the value of the flexural modulus.

$$E = 2(1+v)G' \tag{9}$$

The flexural stress was 86 MPa with 2% strain. These values are better than the values for PBT and are comparable to those of polyamides.

Water absorption

It is well known that polyamides can absorb water up to 15 wt%[56]. The water is usually absorbed only in the amorphous part of the polymer. Crystalline regions seem to be less accessible for water. This water absorption results in a decrease in the T_g[57]. For the aliphatic polyamides this shift in T_g is from 60°C down to −35°C when saturated with water.

With polyesteramides the water absorption is expected to be lower because of the replacement of amide linkages by ester groups which hardly absorb water. The water absorption of the polymer 4NT6 was measured with dumbbell shaped specimens at 25°C in 100% relative humidity. The value of 1.6 wt% which was found is much lower than the value for nylon-4,T (15 wt%)[56]. The shift in T_g due to water absorption for 4NT6 is 35° (from 94° to 59°C). Because of this low water absorption, the dimensional stability of the polyesteramide 4NT6 is higher than that of nylon-4,T.

CONCLUSIONS

Alternating polyesteramides (PEAs) of the type 4NTm can be regarded as consisting of crystallizable diamide segments (T4T) with spacer groups (diols). Depending on the structure of the diol, these spacer groups take part in the crystallization. Alternating polyesteramides 4NTm have been prepared by polycondensation of T4T dimethyl and aliphatic diols in the presence of a titanium catalyst. Through solid-state postcondensation it was possible to enhance the molecular weight of the polymers. It was observed that during synthesis and postcondensation ester–amide interchange reactions occurred to some extent, resulting in some randomness in the alternating structure.

The melting temperature of the PEAs decreased with increasing number of methylene groups in the diol. The melting temperatures displayed an odd–even effect, indicating that the diols also crystallize as well as the T4T segments, in particular the even diols. The PEAs showed a double melting peak which disappeared at higher heating rates. This was attributed to the melting of less perfect lamellae and subsequently recrystallization into more perfect lamellae.

The thermal properties such as the melting and crystallization temperature decreased with decreasing uniformity of the diamide units. The alternating polymers crystallized fast (small undercooling) and the polymers showed a crystallization rate comparable with the crystallization rate of PBT, even for the polyesteramides with odd numbered diols.

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

The d.m.t.a. tests showed that the PEAs had high glass transition temperatures. The T_g appeared to decrease with increasing spacer (diol) length. For the T_g a reversed odd–even effect was found for the longer diols, suggesting that the amount of T4T in the amorphous phase is higher in the odd diol polymers and/or that due to the expected smaller lamellar size, more tie points are present in the odd spacered polymers (with equal crystallinities). The storage modulus above the T_g was high and remained fairly constant. The T_g/T_m ratio was slightly higher than 2/3. The polymers with odd diols have a higher T_g/T_m than those with even diols. This higher ratio for the odd diol polymers might be caused by a higher T_g because of a higher concentration of tie points and more T4T being present in the amorphous phase, but also by a lower T_m because of smaller lamellae.

The polyesteramide 4NT6 showed a flexural modulus of 2.9 GPa with a flexural stress of 84 MPa. The water absorption of 4NT6 (1.6 wt%) was very low.

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