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Alternating polyesteramides based on 1,4-butylene terephthalamide: 4. Alternating polyetheresteramides based on glycols (4NTglycol)

P. J. M. Serrano†[a], R. J. Gaymans[a,*] and L. Aerts[b]
[a]*University of Twente, PO Box 217, 7500 AE Enschede, Netherlands*
[b]*Dow Benelux N.V., PO Box 48, 4530 AA Terneuzen, Netherlands*
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Polyetheresteramides (PEEAs) have been synthesised in the melt from 1,4-butylene terephthalamide and ethylene or propylene glycols. The ethylene glycols were ethylenediol, diethylene glycol, triethylene glycol and tetraethylene glycol. The propylene glycols were 1,3-propanediol and the mixtures of 1,2- and 1,3-propylenediols, 1,2/1,3-propanediol, dipropylene glycol and tripropylene glycol. The melting temperatures of the PEEAs decreased with increasing length of the glycols. The ethylene glycols have higher melting temperatures than the 1,2/1,3-propylene glycols. The undercooling for these polymers determined at 20°C min^{-1} was low (20–35°C), suggesting a very high rate of crystallisation of the copolymers. Injection moulded samples were analysed with dynamic mechanical thermal analysis. The glass transition temperature for the ethylenediol polymer was 122°C and the T_g decreased with increasing glycol length to 42°C for the tetraethylene glycol. The T_g/T_m ratio for these polymers was high (0.69–0.70). The dimensional stability of these copolymers above the T_g was high. The diethylene glycol PEEA had a melting temperature of 262°C, a glass transition temperature of 103°C, a shear modulus at 150°C of 180 MPa, an undercooling of 28°C, a stress at break of 65 MPa and a modulus of 2.9 GPa. © 1998 Elsevier Science Ltd. All rights reserved.

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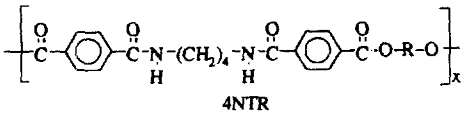
INTRODUCTION

Alternating polyesteramides (APEAs) are copolymers with a high order and a high dimensional stability. Particularly interesting are the polyesteramides based on 1,4-butylene terephthalamide and aliphatic diols[1,2].



4NTR

The melting temperature of these APEAs show with varying diol length a typical odd–even effect. Surprisingly, the copolymers with odd methylene length and also mixtures of diols are still highly crystalline materials which crystallise fast and have a high dimensional stability. Also remarkable about these APEAs is that with increasing irregularity in the diol sequence the T_g/T_m ratio increases from 0.65 to 0.74. A high T_g/T_m ratio is interesting, as for a particular melting temperature one has a high glass transition temperature.

If the diol in the 4NTR is replaced by a poly(tetramethylene oxide) with a molecular weight of 250 (PTMO$_{250}$)[3,4] one still has a polymer with interesting engineering plastic properties, a T_g of 43°C and a T_m of 185°C. With PTMO of a higher molecular weight the T_g is lowered to well below room temperature and these systems have interesting thermoplastic elastomer properties.

The melting temperatures of these polyesteramides (4NTR) depend on the type and length of the R unit and whether this R unit takes part in the crystallisation. The glass transition depends on the type and length of the R unit and whether there is 1,4-butylene terephthalamide present in the amorphous phase. In the long chain PTMO polymer no or very little 1,4-butylene terephthalamide is present in the amorphous phase.

Short chain ethers like diethylene glycol or dipropylene glycol are cheap compared with the longer diols. However, they are little used in engineering plastics as the polymers do not crystallise well. As ordering can still take place in the 4NTR system with uneven diols and mixtures of diols, it might also be possible that ordered systems can be obtained with short chain ethers. A drawback of ethers might be their thermal stability[5,6].

The aim of this study was to synthesise polyetheresteramides (PEEAs) of the type 4NTR with ethylene and propylene glycols and to evaluate their thermal properties. A comparison is made with the APEAs and PBT.

EXPERIMENTAL

Materials

1,2-Ethanediol and 1,3-propanediol were purchased from

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* To whom correspondence should be addressed
† Presently at General Electric Plastics bv, PO Box 117, 4600 AC Bergen op Zoom, Netherlands

Merck and used as-received (purity > 95%). The ethylene and propylene glycols were obtained from Dow Benelux NV and used without further purification. Propylene glycols consisted of a mixture of 1,2- and 1,3-propylene glycol. 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 synthesised as described earlier[7] and used without further recrystallisation.

Melt polycondensation

The preparation of the polymer consisting of T4T dimethyl and diethylene glycol 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 diethylene glycol (25.73 g, 242.5 mmol) was heated up 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 a reduced pressure (10–15 mmHg) was applied while raising the temperature to 250°C ($2°C\ min^{-1}$). After 10 min at 250°C a pressure of less than 1 mmHg was applied for 1 h. The reaction was stopped and the vessel was slowly cooled down to room temperature while maintaining the low pressure. The polymer was cooled with liquid nitrogen, ground in a Fritsch Pulverisette and subsequently dried in a vacuum oven at 60°C.

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 glycol/T4T dimethyl molar ratio was increased from 2.5 to 8.8. Furthermore, the reaction time at 15 mmHg was increased to 1 h.

Solid state post-condensation

The ground polymer (particle size < 1 mm) was dried overnight in vacuo at 80°C. The post-condensation 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 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 crystallisation 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 a calibration standard.

N.m.r.

Proton n.m.r. spectra were recorded on a Bruker AC 250 spectrometer at 250 MHz. Trifluoroacetic acid (TFA-*d*) was used as solvent without internal standard.

Injection moulding

Specimens of polymer 4NTdiethylene glycol 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. Before use, the polymer was dried for 48 h at 80°C in a vacuum oven. During injection moulding the polymer was kept under a nitrogen flow. Temperature settings were 335-320-310-300°C, whereas the mould temperature was 90°C. The complete cycle time was 18 s.

Processing

Test bars for the dynamic-mechanical thermal analysis (DMTA) test ($70 \times 9 \times 2\ mm^3$) were prepared on a Lauffer OPS 40 press at 30°C above the melting temperature of the polymers. During 5-1-4 min pressures of 0-5-10 bar were applied. The mould was cooled to room temperature ($40°C\ min^{-1}$), after which the specimen was released.

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 $1.8°C\ min^{-1}$. The glass transition temperature T_g was defined as the maximum of the loss modulus G''.

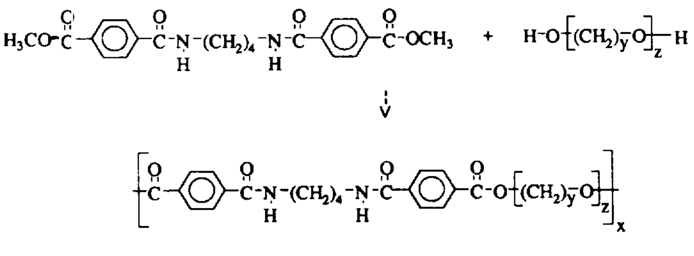
Tensile test

The tensile tests were performed at 20°C with a strain rate of $1\ mm\ min^{-1}$ on an Instron TT/CM, equipped with a 2 kN load cell and a strain gauge. All test bars were dried in vacuo at 80°C for 48 h.

RESULTS AND DISCUSSION

Introduction

The PEEAs (4NTglycol) were prepared by a melt polycondensation of dimethyl 1,4-butylene terephthalamide and ethylene ($y = 2$) or propylene ($y = 3$) glycols with $z = 1$–4.



4NTglycol

Table 1 Results of synthesis 4NTglycol PEEAs

Code	Glycol	P (mmHg)	$\eta_{inh}{}^{a}$ (dl g^{-1})	T^{b} (°C)	$\eta_{inh}{}^{c}$
4NT2	ethanediol	0.1	0.14	260	0.41
4NTde[d]	diethylene	0.2	0.67	230	1.69
4NTte	triethylene	1.5	0.58	—	
4NTtee	tetraethylene	2.0	0.37	—	
4NT3	1,3-propane	0.1	0.22	260	1.26
4NTmp	1,2/1,3-propanediol	1.5	0.15	235	0.16
4NTdp	dipropylene	2.5	0.35	—	
4NTtp	tripropylene	1.8	0.44	—	

[a] After melt polymerisation at 250°C
[b] Post-condensation temperature
[c] After solid-state post-condensation
[d] 1.3 l stainless steel reactor

Table 2 ^{1}H n.m.r. 4NTdiethylene glycol

Segment	Proton	Chemical shiftδ (ppm)
Diamide unit	aromatic protons	
	amide side	8.14
	ester side	8.43
	$NH-CH_2$	4.11
	$NH-CH_2-CH_2$	2.32
Diethylene glycol unit	$C(O)-O-CH_2$	5.08
	CH_2-O-CH_2	4.64

The propylene glycols consisted of mixtures of 1,2- and 1,3-propylene glycol. The thermal and mechanical properties were determined by means of d.s.c. and DMTA. Tensile tests were performed with the PEEA based on diethylene glycol.

Synthesis

The PEEAs were prepared similar to the synthesis of the 4NTm polyesteramides[1,2]. An excess of glycol was used to transesterify the dimethyl 1,4-butylene terephthalamide in the presence of a titanium catalyst. The transesterification temperature (180–220°C) was allowed to be higher than with the PBT synthesis as the dimethyl 1,4-butylene terephthalamide did not sublimate as easily as DMT[8,9]. Once the formation of methanol had stopped, the temperature was raised to 250°C and the pressure was reduced. Temperatures higher than 260°C would lead to thermal degradation and to a high degree of ester–amide interchange[1,10,11]. The results of the syntheses are given in *Table 1*.

The polymers with ethylenediol en propylenediol solidified during the polymerisation at 250°C. These polymers and the diethylene glycol polymer were post-condensed in the solid state to further increase the molecular weight.

The viscosities of the 1,2/1,3-propanediol, the dipropylenediol and the tripropylenediol were low after the melt polymerisation and remained low after the solid-state polymerisation. A possible reason for this is the lower reactivity of the 1,2-propanediol.

The 4NTglycol polymers were light brown in colour and further colouring took place on moulding. The inherent viscosity of 4NTde injection moulded at 310°C decreased from 1.69 to 0.92 dl g^{-1}. Such a decrease of the unstabilised polymer is in the same order of magnitude as the polyesteramides[1,2]. No degradation of the polymer 4NTde was found in TFA-*d* (7 days at room temperature).

The compositions were checked with ^{1}H n.m.r. A spectrum of 4NTde is given in *Figure 1* and the assignments in *Table 2*.

Melting behaviour

Upon heating, some PEEAs show two endothermic transitions. This was already observed for the APEA[1,2]. It is attributed to the arrangement of crystals[12,13]. Less perfect lamellae melt and recrystallise immediately into more stable lamellae.

The melting temperature of the 4NTglycol PEEAs decreases with increasing length of the glycol (*Figure 2* and *Table 3*).

The melting temperature shows a gradual decrease with increasing glycol length, and an odd/even effect is not observed. The T_m values of the ethylene glycol polymers are similar to the polyesteramides with mixtures of diols[2]. Furthermore, the melting temperature of the PEEAs based on propylene glycols is lower than the T_m of the ethylene-glycol-based polymers with a similar length. This is probably caused by the mixture of the 1,2- and 1,3-propylene glycols which give a very irregular packing. The 4NT3 polymer (linear) has a T_m in the same range as the T_m values of the ethylene glycol polymers. The 1,2/1,3-propylene glycol polymers apparently have a lower order than the ethylene glycol or mixture of diols polymers.

The polymers based on ethylenediol, ethylene glycols and 1,3-propanediol have a reasonable melting enthalpy, being in the same range of the 4NTm and 4NTm,p polymers. The 1,2/1,3-propylene glycol based polymers, however, have a lower ΔH_m. Possibly this is due to the mixture of the 1,2/1,3-propylene glycols, which results in a poorer chain packing and thus in a lower melting enthalpy. On cooling the 4NTmp and 4NTtp samples no recrystallisation exotherm was observed.

The undercooling ($T_m - T_c$) of most 4NTglycol polymers is small and comparable with the values of PBT and the 4NTm polymers. This suggests a very fast crystallisation of the PEEA copolymers, which is probably due to an ordering in the melt of the uniform T4T segments caused by hydrogen bonding[14–16].

DMTA

The DMTA tests were performed on melt-pressed samples. Owing to the low inherent viscosities of the 1,2/1,3-propylene-glycol-based polymers, no DMTA tests were possible except for 4NTtp. A typical DMTA graph is that of 4NTde (*Figure 3*). The results for the ethylene glycol polymers are shown in *Table 4*.

In most DMTA spectra a β-transition was visible at about

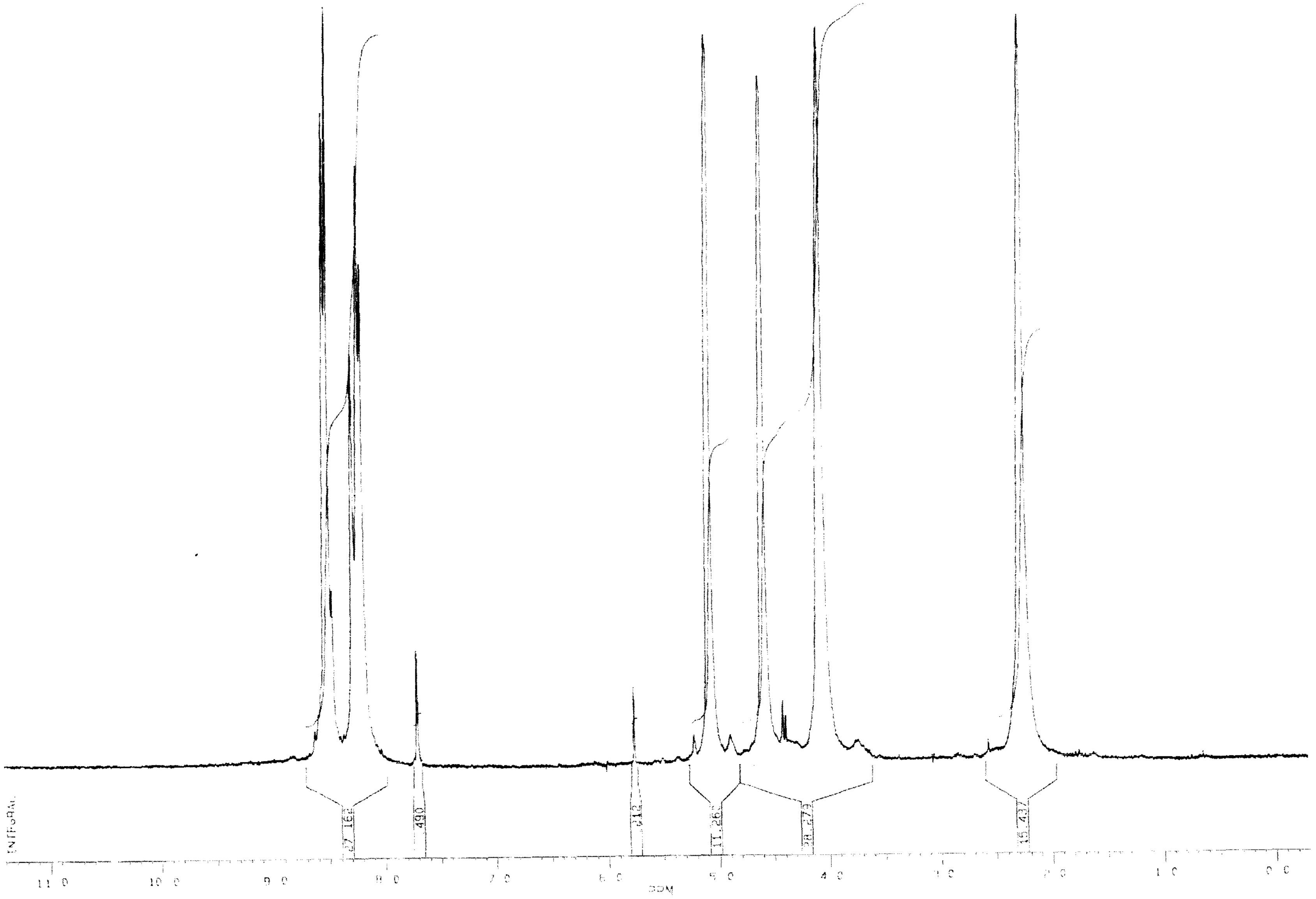


Figure 1 ^{1}H n.m.r. spectrum of 4NT diethylene glycol

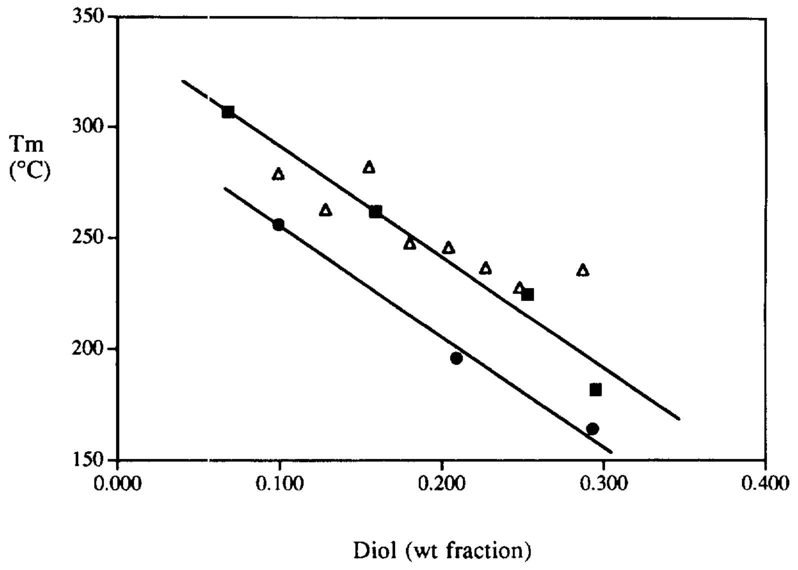


Figure 2 Melting temperature of polyesteramides *versus* weight fraction of diol: ■, ethylene glycol; ●, 1,2/1,3-propylene glycol; △, mixtures of diols[2]

Table 3 Thermal properties (d.s.c.) of 4NTglycol PEEAs. Heating and cooling rate 20°C min^{-1}

Code	Glycol	W_{glycol} [a]	T_m (°C)	T_c (°C)	$(T_m - T_c)$ (°C)	ΔH_m (J g^{-1})
4NT2	ethanediol	0.068	307	282	25	38.3
4NTde	diethylene	0.159	262	234	28	45.5
4NTte	triethylene	0.253	225	185	40	29.3
4NTtee	tetraethylene	0.295	182	150	32	6.8
4NT3	1,3-propane	0.099	298	251	47	39.8
4NTmp	1,2/1,3-propane	0.099	256	—	—	9.0
4NTdp	dipropylene	0.208	196	176	20	12.7
4NTtp	tripropylene	0.293	164	—	—	11.2

[a] Weight fraction of glycol without ester group

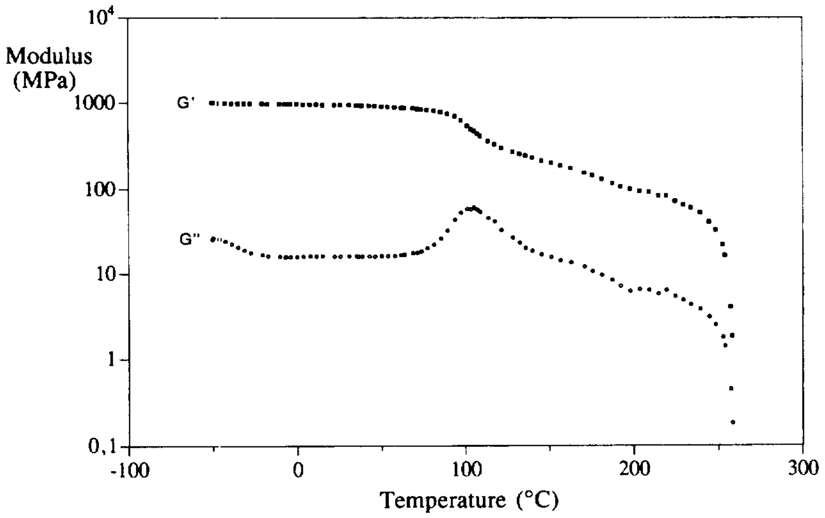


Figure 3 Torsion modulus of 4NT diethylene glycol at 1 Hz

−50°C. A transition at −50°C is often observed in aliphatic polyesters and non-hydrogen-bonded polyamides[17,18].

The α-transition T_g is located at much higher temperatures (*Table 4*) and decreases with increasing glycol length (*Figure 4*). The decrease with the ethylene glycol PEEAs is stronger than observed for the APEA samples prepared with mixtures of diols[2]. This suggests a higher flexibility of the ether segment.

The shear modulus of the PEEAs at 150°C are high and even higher than that of PBT.

As a measure for the stability of the physical cross-links by the crystalline phase, the slope of the G' modulus curve

Table 4 DMTA results of 4NTglycol PEEAs

Code	Glycol	W_{glycol} [a]	T_g (°C)	G'(150°C) (MPa)	$\Delta G'$	T_g/T_m
4NT2	ethanediol	0.068	122	—	—	0.68
4NTde	diethylene	0.159	103	180	2.4	0.70
4NTte	triethylene	0.233	71	101	2.3	0.69
4NTtee	tetraethylene	0.295	42	47	2.6	0.69
4NT3	1,3-propane	0.099	119	189	2.4	0.69
4NTmp	1,2/1,3-propane	0.099	—	—	—	—
4NTdp	dipropylene	0.208	—	—	—	—
4NTtp	tripropylene	0.293	—	—	—	—
PBT	butane	—	50	79	5.6	0.65

[a] Weight fraction of glycol without ester group

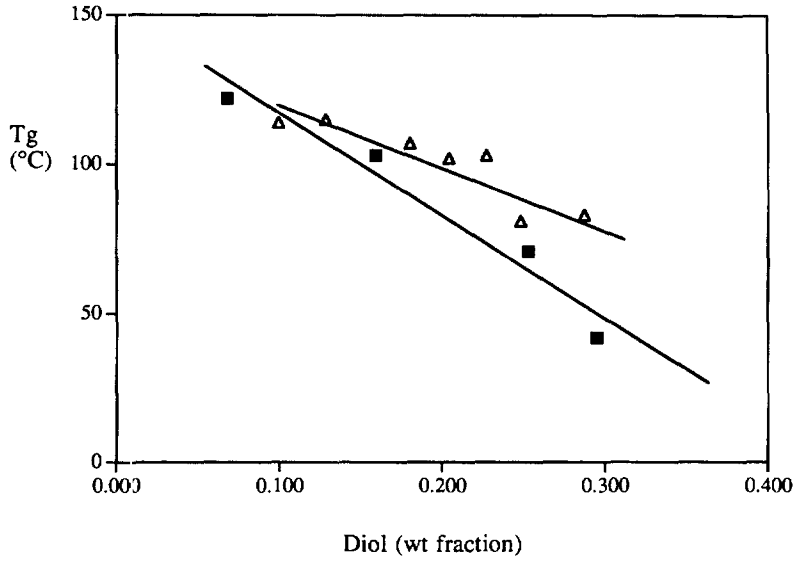


Figure 4 Glass transition temperature of ethylene-based PEEAs and APEAs with mixtures of diols[2] *versus* weight fraction of diol: ■, ethylene glycols; △, mixtures of diols

in the rubbery region ($\Delta G'$) is calculated. The decrease of the modulus above T_g is expressed in $\Delta G'$:

$$\Delta G' = \frac{G'_{T_g+40}}{G'_{T_{fl}-40}}$$

in which T_{fl} stands for the temperature at which the polymer starts to flow. The $\Delta G'$ values are given in *Table 4*. Small values of $\Delta G'$ mean that the storage modulus does not vary much between T_g and T_{fl}. The $\Delta G'$ values of these PEEAs are low and close to those for the polyesteramides[1,2]. From *Table 4* it is clear that the PEEAs have excellent dimensional stability above T_g and are considerably better than PBT.

The T_g/T_m ratio for the PEEAs is higher than 2/3. This indicates that the chemical compositions of the amorphous and crystalline phases are different from each other. The crystalline phase mainly consists of T4T segments. It almost seems that the glycol segments do not take part in the crystallisation.

Tensile test

Tensile tests were performed with polymer 4NTdiethylene glycol. The tensile samples were prepared by injection moulding. The fast crystallising 4NTdiethylene glycol polymer was easily injection mouldable and with short cycle times (18 s). The Young's modulus was determined at room temperature with a strain rate of 1 mm min^{-1}. The average value found is 2.9 GPa, with a stress at break of 65 MPa. The maximum strain was 3%, and all samples showed a brittle fracture surface. This indicates that the maximum stress was not reached. Probably the molecular weight of the polymer was too low for optimal properties. The value of the stress at break is lower than the corresponding value of the 4NT5,7 polyesteramide[2]. The Young's modulus, on the other hand, is comparable with 4NT5,7 and is between those of polyesters and polyamides.

CONCLUSIONS

Polycondensation of T4T dimethyl and ethylene or propylene glycols resulted in alternating PEEAs. The molecular weight of the 1,2/1,3-propylene-glycol-based polymers remained low. This was probably due to the low reactivity of the secondary alcohol group in the 1,2-propylene glycol. Post-condensation in the solid state increased the molecular weight of the ethylene glycol polymers. The thermal stability of 4NTde was comparable with APEAs, which suggests that the glycol group did not make these polymers more thermally unstable.

The melting temperature of the alternating polymers decreased almost linearly with increasing weight fraction of the glycols. The ethylene-based polymers showed a melting enthalpy comparable with the values of the APEAs. The 1,2/1,3-propylene-based polymers had a much lower ΔH_m. These copolymers had a remarkably high rate of crystallisation (small undercooling) and values comparable with the APEAs.

The glass transition temperature decreased with increasing length of the glycol segment. The T_g/T_m ratio was higher than 2/3. The decrease of the storage modulus between T_g and T_{fl} was small and was comparable with the APEAs.

Particularly noteworthy is the PEEA with diethylene glycol, as this polymer has excellent engineering plastics properties and is good melt-processable. The diethylene glycol PEEA had a melting temperature of 262°C, a glass transition temperature of 103°C, a shear modulus at 150°C of 180 MPa, an undercooling of 28°C, a stress at break of 65 MPa and a modulus of 2.9 GPa.

ACKNOWLEDGEMENTS

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