

Polyesteramides based on PET and nylon 2,T Part 2. Synthesis and thermal stability

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Abstract

The synthesis and the thermal stability of polyesteramides based on PET and nylon 2,T (PETA) using DMT, T2T-dimethyl (*N,N'*-bis(*p*-carbo-methoxybenzoyl)ethanediamine) and 1,2-ethanediol as starting materials has been studied. The catalysts that were used are tetraisopropyl orthotitanate, manganese acetate, zinc acetate, antimony trioxide and caesium carbonate. After a short melt polymerisation at 270–290°C for 15 min, the molecular weight was increased under milder conditions by solid state postcondensation (220–250°C). The thermal properties, inherent viscosity, melt stability at 320°C in nitrogen of the resulting polymers (PET with 25 mol% amide) was studied. Using tetraisopropyl orthotitanate as a catalyst, a polymer is obtained with a reasonable molecular weight, but the polymer has a high degradation rate constant. Inactivation of the titanium catalyst by triphenyl phosphite decreased the degradation rate, but compared to the other polymers it is still high. By using manganese acetate and zinc acetate in combination with antimony trioxide, a polymer with a reasonably high molecular weight and with a low degradation rate constant is obtained. The degradation is mainly caused by manganese acetate, the transesterification catalyst. Increasing the diamide concentration in PET results in a lower molecular weight, this effect being noticeable at concentrations higher than 10 mol%. The thermal degradation rate of PETA increased with increasing diamide content. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyesteramides have been studied extensively [1–6]. Random copolyesteramides usually have a low order, even if the repeating units of the ester and amide segments appear to be isomorphous [1,2]. Polyesteramides can crystallise rapidly if the amide segments have an ordered structure as in alternating polyesteramides [3,4] and polyesteramides with uniform diamide segments [5,6]. Polyesteramides with uniform diamides can be prepared from bisesterdiamides and it is advantageous to use a bisesterdiamide with a structure similar to that of the polyester in which it is copolymerised.

Poly(ethylene terephthalate) (PET) is a semi-crystalline polymer with a high glass transition temperature (T_g) of 85°C and melting temperature (T_m) of 255°C. Compared to polyesters with a similar structure, polyamides have a

higher T_g and T_m and crystallise more rapidly. For example, nylon 2,T has a T_g of about 200°C and a T_m of 455°C [7]. It would be interesting to modify PET with T2T (one-and-a-half repeating unit of nylon 2,T) to produce a rapidly crystallising polyesteramide with a higher T_g and T_m than PET. The polyesteramide based on PET and T2T is called PETA (**1**).

The PETA polymers can be synthesised from dimethyl terephthalate (DMT), 1,2-ethanediol and bisesterdiamide units (T2T-dimethyl) [8]. Firstly there is a transesterification at 150–220°C and at atmospheric pressure, followed by a polycondensation at 260–290°C under a high vacuum. In the transesterification step, methanol is formed and distilled off, in the polycondensation step, ethanediol is stripped. The rate of transesterification and polycondensation can be considerably enhanced by the use of a catalyst and research has shown that acids and several organometallic compounds are able to catalyse these reactions very well. In addition titanium compounds are often mentioned as catalysts for the polyester synthesis [9]. Bussink et al. [5] have used a zinc/antimony catalyst combination for the synthesis of PETA, and inactivated the zinc catalyst after the transesterification step. They have synthesised PETA up to an amide content

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was found that 6NT6 degraded more rapidly than PHT, this being attributed to a destabilising effect of the amide linkage in the terephthalic para position of the ester bond. However, van Bennekom [19] found no significant difference in the thermal stability of PBT and PBT modified with 20 mol% of diamide segments. Niesten [20] studied the melt stability of PET and 4NT2, an alternating polyesteramide based on PET and 1,4-diaminobutane, at 320°C under a nitrogen atmosphere, the polymers being synthesised using a titanium catalyst. For 4NT2, the degradation rate was five times higher than that of PET, with very few amino endgroups being formed, showing that the chain scission is mainly being caused by the β -elimination of the ester segments.

In polyesteramides another type of degradation reactions are interchange ester–amide reactions. These reactions do not affect the molecular weight, but do disturb the uniformity of the amide units, resulting in a slower crystallisation rate and a lower crystallinity [4,19,21].

The aim of the work is to study the synthesis and degradation PETA with a high amide content. Several catalyst systems will be evaluated and also the possibility to inactivate the catalyst at the end of the reaction. Synthesised are PET, PETA having 10 mol% T2T and PETA having 25 mol% T2T.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), 1,2-ethanediol, all catalysts, triphenyl phosphite (TPPi) and triphenyl phosphate (TPP) were purchased from Merck and all chemicals were used as received. T2T-dimethyl was synthesised and purified as previously described [8].

2.2. Melt polymerisation of PETA

As an example, the preparation of PETA₂₅ (PET with 25 mol% T2T) is given. The reaction was carried out in a 250 ml stainless steel vessel with nitrogen inlet and mechanical stirrer. The vessel containing DMT (19.42 g, 0.10 mol), T2T-dimethyl (19.22 g, 0.05 mol), 1,2-ethanediol (37–40 g, 0.60–0.65 mol) and a transesterification catalyst were heated in an oil bath to a temperature of 180°C. After 40 min at 180°C, the temperature was raised to 290°C (15°C/10 min) over a period of 70 min. The polycondensation catalyst was then added, and after 10 min at 290°C the pressure was reduced within 5 min to 20 mbar. The pressure was then further reduced within 10 min to less than 1 mbar, and the vessel was then slowly cooled to room temperature, whilst maintaining the low pressure. In some cases the transesterification catalyst was inactivated with TPP before polycondensation and TPP was added at 270°C.

The amounts of the different catalysts used are as follows:

Ti(*i*-OC₃H₇)₄ (in 2 ml *m*-xylene): 0.043 g (0.15 mmol);

Mn(CH₃CO₂)₂·H₂O (in 3 ml 1,2-ethanediol): 0.019 g (0.076 mmol);

Sb₂O₃ (in 3 ml 1,2-ethanediol): 0.022 g (0.076 mmol);

Zn(CH₃CO₂)₂·2H₂O (in 3 ml 1,2-ethanediol): 0.017 g (0.076 mmol);

Cs₂CO₃ (in 4 ml 1,2-ethanediol): 0.025 g (0.076 mmol).

2.3. Solid state postcondensation

The polymer was ground in a Fritsch Pulverisette (particle size <1 mm) and subsequently dried in a vacuum oven at 70°C overnight. Over a period of 24 h, the polymer was postcondensed in the solid state at a reduced pressure (0.1 mbar) in a glass tube which was placed in an oven at 220–250°C.

2.4. Viscometry

The inherent viscosity of the polymers was determined at a concentration of 0.1 g/dl in *p*-chlorophenol at 45°C, using a capillary Ubbelohde 1B.

2.5. NMR

Proton NMR and proton decoupled ¹³C NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 and 62.9 MHz, respectively, using deuterated trifluoroacetic acid (TFA-d) as a solvent without an internal standard. ¹³C NMR scans were recorded with an acquisition time of 2.097 s and a 45° pulse. The amide concentration of the polymers was determined by ¹H NMR. With ¹³C NMR, the uniformity of the amide segment length was measured.

2.6. Differential scanning calorimetry

DSC spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried polymer sample (2–5 mg) of was measured at a cooling and heating rate of 20°C/min. Firstly, the sample was rapidly heated to 340°C (80°C/min) and after 1 min, cooled down to 20°C (20°C/min). The maximum of the cooling scan was taken as the crystallisation temperature (*T_c*). After a further 2 min, the sample was heated for a second time up to 290°C, the maximum of the second heating scan being taken as the melting temperature (*T_m*), the peak area was used to calculate the enthalpy (ΔH_m).

2.7. Dynamic mechanical analysis

Samples for the dynamic mechanical analysis (DMA) test (70 × 9 × 2 mm³) were prepared on an Arburg H manual injection moulding machine. The polymers were pre-melted in a mini-extruder and quenched in a water bath and dried prior to injection moulding. The barrel temperature of the injection moulding machine was set at 50°C above the melting temperature of the polymer and the mould temperature was 150°C. The mould was opened after 2 min.

Table 1
Results of synthesis and degradation studies of PETA₂₅, synthesised with different catalyst systems

| Batch no. | Catalyst (mmol/g) | $\eta_{\text{inh}}^{\text{bp}}$ (dl/g) ^a | T_{m}^{bp} (°C) | η_{inh} (dl/g) | T_{m} (°C) | T_{c} (°C) | T_{g} (°C) | T_{fl} (°C) | $G'(150^{\circ}\text{C})$ (MPa) | k_0 (g/dl min) |
|-----------|--------------------|---|---------------------------------|----------------------------|---------------------|---------------------|---------------------|----------------------|---------------------------------|-------------------|
| 1 | Ti 0.0048 | 0.11 | 269 | 0.55 | 269 | 234 | 102 | 274 | 174 | |
| 2 | Ti 0.0057 | 0.18 | 268 | 0.65 | 268 | 228 | | | | 1.14 |
| 3 | Ti 0.0047 | 0.12 | 257 | 0.67 | 276 | 242 | | | | 0.37 ^b |
| 4 | Cs 0.018 | 0.12 | 266 | 0.38 | 279 | 241 | | | | 0.29 |
| 5 | Cs 0.018 | | | 0.35 | 273 | 241 | 110 | 283 | 225 | |
| 6 | Cs 0.035 | 0.13 | 273 | 0.36 | 269 | 235 | | | | 0.27 |
| 7 | Mn 0.0020 | 0.19 | | 0.44 | 271 | 239 | 112 | 279 | 181 | |
| 8 | Mn 0.0021 | 0.14 | 255 | 0.43 | 274 | 240 | | | | 0.29 |
| 9 | Mn/Sb ^c | 0.28 | 265 | 0.64 | 278 | | | | | 0.29 |
| 10 | Mn/Sb ^c | 0.26 | 264 | 0.83 | 274 | 243 | 110 | 278 | 185 | |
| 11 | Zn/Sb ^c | 0.16 | 268 | 0.57 | 280 | 244 | | | | 0.24 |
| 12 | Zn/Sb ^c | 0.15 | 268 | 0.64 | 282 | 247 | 109 | 280 | 182 | |
| 13 | Zn/Sb ^d | 0.18 | 287 | 1.12 | 287 | 247 | 108 | 279 | 172 | |
| 14 | Zn/Sb ^d | 0.40 | 268 | 0.86 | 274 | 244 | | | | 0.80 |

^a bp: before solid state postcondensation.

^b Inactivated with 16-fold excess of TPPi.

^c Approximately 0.0023 mmol/g for both catalysts.

^d Zn (0.020 mmol/g), 1.8-fold excess TPP, 0.0053 mmol/g Sb₂O₃ [5].

A Myrenne ATM3 torsion pendulum was used at a frequency of approximately 1 Hz and the storage modulus G' and the loss modulus G'' were measured versus the temperature. The dried samples were first cooled to -100°C and subsequently heated at a rate of $1^{\circ}\text{C}/\text{min}$. The maximum of the loss modulus was taken as the glass transition temperature and the flow temperature (T_{fl}) defined as the temperature where the storage modulus reaches 15 MPa.

2.8. Melt degradation

Melt degradation was carried out in a 4cc DSM res RD11H-1009-025-4 corotating twin screw mini-extruder. Prior to this the polymer (5 g) was dried in a vacuum oven at 70°C overnight. Extrusion experiments were carried out at 320°C with a constant screw speed of 50 rpm. The residence times varied from 5 to 60 min. During extrusion, the polymer was maintained under a nitrogen flow. The extrudate was cooled in water.

2.9. COOH-endgroup analysis

The concentration of COOH endgroups was determined using a Metrohm titroprocessor type 636 with Ross glass electrodes. The polymers were dissolved in benzyl alcohol and titrated with tetrabutyl ammonium hydroxide (0.1 M).

2.10. UV absorbance

The UV absorbance was measured with a UVIKON 930 spectrophotometer (Kontron Instruments) from 300 to 400 nm, polymer solutions were prepared in *p*-chlorophenol at a concentration of 0.1 g/dl. The maximum of the absorption curve was at 315–320 nm.

3. Results and discussion

This study is concerned with the synthesis and degradation of PETA. Several catalyst systems were evaluated for their effect on the synthesis and thermal degradation of PETA₂₅ (PET modified with 25 mol% T2T). In addition, the influence of the amide concentration on the degradation of PETA was studied. The melt polymerisation is at a high temperature (290°C) and the time at this high temperatures should be limited as much as possible. The polymerisation of the polyesteramides was using a very short melt polymerisation time in combination with solid state postcondensation [3,22]. The influence of the solid state postcondensation conditions on the molecular weight, melting temperature and colour of PETA was investigated.

3.1. Synthesis and degradation of PETA₂₅ using different catalyst systems

Several different catalysts and catalyst systems have been used for the synthesis of PETA₂₅ and were evaluated for their effect on the inherent viscosity and thermal properties of the resulting polymers. The melt stability was studied at 320°C under a nitrogen atmosphere. By viscometry the decrease in inherent viscosity is measured, and the degradation rate constant k_0 calculated (see Eq. (3)). The results of the synthesis and degradation experiments are presented in Table 1. The amount of catalyst used is given in mmol per gram of polymer. Firstly, the synthesis results are discussed, followed by the results of the degradation experiments.

When tetraisopropyl orthotitanate ($\text{Ti}(i\text{-OC}_3\text{H}_7)_4$) is used as a catalyst, it is possible to obtain a reasonable molecular weight of PETA₂₅, however the melting temperature (T_{m}), glass transition (T_{g}) and flow temperature (T_{fl}) are rather low in comparison with the other batches. The amount of

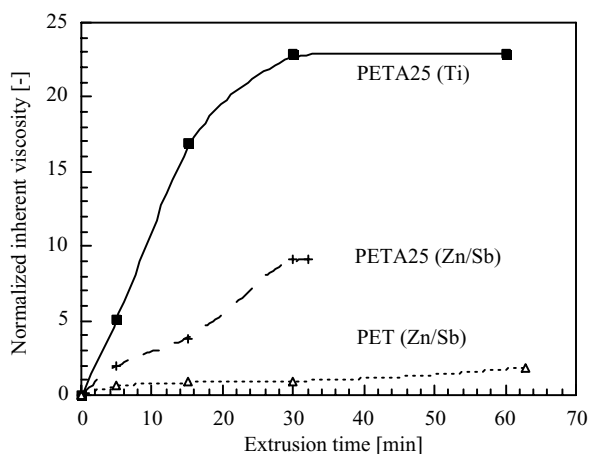


Fig. 1. Normalised inherent viscosity versus the extrusion time at 320°C under a nitrogen atmosphere of PET and PETA₂₅.

caesium carbonate was increased in going from batch 4 to 6 and the thermal properties of these polymers were found to be good. However, no high molecular weight polymer was obtained using caesium carbonate as a catalyst. Comparing the batches synthesised using manganese (batches 7 and 8) and manganese/antimony (batches 9 and 10) as catalysts, it can be seen that adding antimony increases the molecular weight of the polymer obtained, showing that manganese is not an efficient catalyst for polycondensation. When zinc acetate (batches 11 and 12) is used as a transesterification catalyst instead of manganese acetate (batches 9 and 10), a higher melting temperature is obtained but the inherent viscosity is slightly lower. Higher inherent viscosities can be obtained using the zinc/antimony system, by applying higher catalyst concentrations (batches 13 and 14).

When using manganese acetate and caesium carbonate as catalysts, it is not possible to obtain a high molecular weight polymer but in using titanium, zinc/antimony and manganese/antimony catalysts a reasonable inherent viscosity is obtained (0.7–0.8 g/dl).

PETA₂₅ had a T_m between 275 and 280°C, and a T_c of 240°C. Using titanium as a catalyst, lower values for T_m and T_c were obtained. With caesium carbonate and manganese acetate as catalysts, the T_m values of the resulting polymers were also low. This is probably caused by the lower molecular weight. The undercooling ($\Delta T = T_m - T_c$) is in the range of 35–40°C for all the batches of PETA₂₅, however, the peaks in the DSC spectrum of PETA₂₅ are low and broad, this means that the T_m , T_c , and therefore ΔT are not very accurately measured.

PETA₂₅ had a T_g of approximately 110°C for all batches, with the exception of the batch synthesised using $Ti(i-OC_3H_7)_4$ as a catalyst ($T_g = 102^\circ C$). The flow temperature (T_{fl}) as measured by DMA, indicates the onset of melting. At the T_{fl} of PETA₂₅, approximately at 280°C, G' decreases sharply and therefore T_{fl} can be more accurately measured than T_m (by DSC). The torsion modulus at 150°C, $G'(150^\circ C)$, is a measure for the modulus of the rubbery

plateau, for PETA₂₅, $G'(150^\circ C)$ having a value of approximately 180 MPa, excepting the polymers synthesised with caesium carbonate as a catalyst. This may be caused by a higher crystallinity as a result of the lower molecular weight of these polymers.

The catalysts used also influenced the degradation rate of PETA₂₅. The amount of ester–amide interchange was determined with ¹³C NMR, but there were no detectable large amide segments present in any of the polymers. Thus under the used reaction conditions the amide units remain uniform in length in PETA₂₅.

Melt degradation of PETA₂₅, performed under a nitrogen atmosphere in a corotating twin screw extruder in the presence of different catalyst systems, was studied. The polymers were extruded at 320°C for different residence times (5, 15, 30, and 60 min) and it was found that the molecular weight, and thus the inherent viscosity were lowered by β -elimination. The effect of extrusion time on the molecular weight is therefore measured by viscometry, the normalised inherent viscosity being calculated according to the following equation:

$$\text{Normalized inherent viscosity} = \frac{1}{\eta_t} - \frac{1}{\eta_0} = k_0 t \quad (3)$$

in which η_0 is the inherent viscosity before extrusion, η_t is the inherent viscosity after extrusion time t and k_0 is the degradation rate constant. For PBT, there is a linear increase of the normalised inherent viscosity at 260°C [23]. The same increase in the normalised inherent viscosity of different polymers does not necessarily mean the same decrease in molecular weight. Therefore this method is not adequate enough to compare the degradation rate of different polymers. However, it is useful for studying the effect of different catalyst systems on degradation rate of the same polymer.

Fig. 1 is an example where the normalised inherent viscosity is plotted versus the degradation time of PET (Zn/Sb), PETA₂₅ (Ti) and PETA₂₅ (Zn/Sb), the first two measured points being the most reliable. At longer extrusion times, the extrudate is not completely soluble in the *p*-chlorophenol and also crosslinking via the vinyl groups may occur, thereby causing an increase in the inherent viscosity. To determine the k_0 value, a line was drawn through $t = 0$ and the first two measured points and this value was calculated according to Eq. (3).

Table 1 gives the k_0 values of the degradation rate at 320°C in nitrogen for PETA₂₅, synthesised using different catalyst systems. For PETA₂₅, synthesised with a titanium catalyst, the highest degradation rate constant (k_0) was found and adding the inactivator TPPi greatly influenced the degradation. However, it still maintains a higher degradation rate constant than in the other polymer batches using different catalysts. Comparison of the polymer batches synthesised using manganese and manganese/antimony as catalysts, shows that the antimony catalyst does not negatively influence the degradation rate, the degradation rate

Table 2

Degradation rate constants of PET, PETA₁₀, PETA₂₅ and 4NT2 at 320°C under a nitrogen atmosphere, determined with COOH-endgroup analysis (k_{COOH}) and viscometry (k_0)

| Polymer (mmol/g) | Amount of catalyst (mmol/g min) | k_{COOH} (g/dl min) | k_0 | Reference |
|--------------------|---------------------------------|------------------------------|-------|-----------|
| PET | Zn 0.0020/Sb 0.0019 | 0.0023 | 0.05 | |
| PETA ₁₀ | Zn 0.0023/Sb 0.0025 | 0.0207 | 0.24 | |
| PETA ₂₅ | Zn 0.0023/Sb 0.0022 | 0.0404 | 0.24 | |
| PET | Ti 0.010 | 0.0027 | 0.05 | 32 |
| 4NT2 | Ti 0.0050 | 0.0345 | 0.25 | 32 |

being mostly caused by the transesterification catalyst. PETA₂₅, synthesised with caesium carbonate was found to have a low k_0 value, the amount of caesium having no influence on the degradation rate. The lowest degradation rate constant was obtained using the zinc/antimony catalyst system, in addition the highest T_m and T_f values were obtained with this system. Therefore the zinc/antimony combination was chosen to be the most suitable catalyst system for PETA synthesis.

The last two batches (13 and 14) were synthesised as described by Bussink et al. [5], i.e. compared to the catalyst amounts used for batches 11 and 12, a 10-fold higher amount of zinc acetate was used, which was then inactivated with an excess of triphenyl phosphate (1.8-fold), and a 2.5-fold higher amount of antimony trioxide was applied. In using this system, a high inherent viscosity was obtained (>1 dl/g) in addition to high T_m and T_c values. Although the zinc catalyst was inactivated following transesterification, the degradation rate of the resulting polymer was still much higher compared to batch 11, this being synthesised using a lower amount of the zinc and antimony catalysts. Thus it appears that with a higher catalyst concentration, the degradation rate is also higher. This suggests that the inactivation was suboptimal.

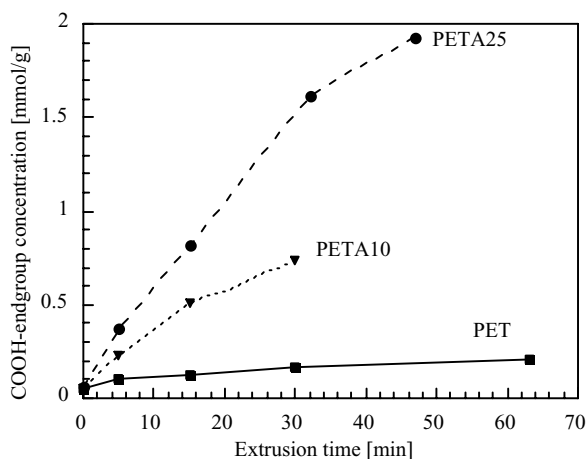


Fig. 2. COOH-endgroup concentration versus the extrusion time at 320°C under a nitrogen atmosphere of PET, PETA₁₀ and PETA₂₅, synthesised with Zn/Sb.

3.2. Influence of amide concentration on the degradation of PETA

To study the influence of the amide concentration of PETA on the degradation rate, PET and PETA₁₀ were also melt degraded at 320°C under a nitrogen atmosphere. PET and PETA₁₀ were synthesised using the same amounts of zinc acetate and antimony trioxide as previously used for PETA₂₅ (batches 11 and 12) and the degradation rate constant k_0 determined from viscometry results of the degraded polymers (Table 2). It was found that the introduction of amide bonds into PET leads to a higher degradation rate. To study this effect more closely, the COOH endgroup concentration of the degradation products of PET, PETA₁₀ and PETA₂₅ was determined. Fig. 2 plots the COOH-endgroup concentration versus the degradation time.

The increase in COOH-endgroups for PET, PETA₁₀ and PETA₂₅ is approximately linear with time, as the formation of COOH endgroups via(β-elimination is a first-order reaction [22]. Straight lines have been fitted through these data points, with a value of the correlation coefficient r of 0.95, 0.98 and 0.99 for PET, PETA₁₀ and PETA₂₅, respectively. Pilati [24] supposed that the linear relation of COOH-formation with time excluded a possible (auto) catalytic effect of the carboxylic acid groups. The degradation constant was calculated by taking the slope of the lines in Fig. 2 (Table 2), the slope of the PETA₂₅ line being twice as high as that of PETA₁₀ and almost 18 times higher than that of PET. With longer degradation times, the secondary degradation reactions become more important. For example, crosslinking through the formed vinyl groups may occur, causing an increase in inherent viscosity, therefore the k_{COOH} value is probably more meaningful than the k_0 value.

The degradation rate of PET is increased by the incorporation of amide segments, as both the k_0 and k_{COOH} values found for PETA₁₀ and PETA₂₅ are higher as compared to PET. Niesten [20] found that the values of the degradation rate constants for 4NT2 and PET synthesised using a titanium catalyst were within the same order. The expected higher degradation rate for PET synthesised with a titanium catalyst, compared to PET synthesised with a zinc/antimony catalyst combination, was not observed. For k_{NH_2} a value of 0.0004 mmol/g min was found, illustrating that very little β-elimination of the amide segments had occurred. It

Table 3

Influence of solid state postcondensation temperature (T_{pc}) on the properties of PET, PETA₁₀ and PETA₂₅. Postcondensation time is 24 h, pressure is 0.1 mbar

| Polymer (mmol/g polymer) | Zn/Sb (°C) | T_{pc} (mol%) | Amide (°C) | T_m (°C) | T_c (°C) | ΔT (°C) | η_{inh} (dl/g) |
|--------------------------|---------------|----------------------|------------|------------|------------|-----------------|---------------------|
| PET | 0.0023/0.0026 | – | – | 235 | 182 | 53 | 0.11 |
| | | 220 | – | 258 | 200 | 58 | 0.52 |
| | | 230 | – | 256 | 200 | 56 | 0.76 |
| PETA ₁₀ | 0.0023/0.0025 | – | 9 | 232 | 184 | 48 | 0.06 |
| | | 230 | 9 | 260 | 205 | 55 | 0.69 |
| | | 240 | 9 | 259 | 201 | 58 | 0.93 |
| PETA ₂₅ | 0.0023/0.0025 | – | 22 | 246 | 226 | 23 | 0.22 |
| | | 230 | 23 | 265 | 229 | 36 | 0.69 |
| | | 240 | 22 | 263 | 229 | 34 | 0.73 |
| | | 240/250 ^a | 23 | 272 | 234 | 38 | 0.92 |

^a 4 h at 240°C, 20 h at 250°C.

appears that the incorporation of amide segments has a stronger influence on the rate of degradation than the catalyst system used.

According to Pilati [18], the presence of the amide bond in the terephthalic *para* position destabilises the ester bond, as the amide bond is less electron withdrawing than the ester bond. This could explain why the degradation is increased by the incorporation of diamide segments, and why it depends on the concentration of diamide segments. However van Bennekom [19] observed no increased degradation rate on modifying PBT with diamides.

By the incorporation of amide bonds, the water absorption of the polymer is increased [25]. Due to the presence of amide bonds, it may be harder to remove all the water by vacuum drying. In principle the increased degradation may be a result of the presence of water. Batch 14 of PETA₂₅ was thoroughly dried (48 h, 110°C) and then melt degraded at 320°C for 5 min. The k_0 value was still very high, indicating that no thorough drying is not the reason for the increased degradation of PETA compared to PET.

3.3. Solid state postcondensation

Following melt polymerisation, the molecular weight of the prepolymer is increased by solid state postcondensation, this usually takes place at 20–30°C below the melting temperature [9]. It should also not be carried out at temperatures higher than 250°C, at this temperature, ester–amide interchange becomes important [3]. So far the solid state postcondensation of PETA₂₅ was performed at 230°C. For PET, PETA₁₀ and PETA₂₅ the postcondensation temperature was optimised, at a standardised postcondensation time of 24 h and pressure of 0.1 mbar. Polymer samples (5 g) were postcondensed at a number of different temperatures (T_{pc}) (Table 3). The amide content was determined by ¹H NMR, using the aromatic ester and amide peaks.

For PET, a T_{pc} of 230°C results in a higher molecular weight than at 220°C, the differences in T_m and T_c were negligible. For PETA₁₀, the highest molecular weight was obtained at 240°C, however the T_m and T_c were slightly lower compared to PETA₁₀ postcondensed at 230°C. The

combination of 4 h at 240°C and 20 h at 250°C appeared to be the best for PETA₂₅, resulting in the highest T_m and T_c as well as inherent viscosity. All of the polymers became more coloured when going to higher postcondensation temperatures.

Following polymerisation, PETA₂₅ already has a yellow coloration, during solid state postcondensation, the polymer darkens further. In addition, when going to higher postcondensation temperatures, the product becomes darker still. According to Edge et al. [26] the coloured species in melt degraded PET arise from the hydroxylation of the terephthalate ring and the formation of unsaturated ester and quinoid species. To achieve a less coloured product, a postcondensation temperature of 230°C should be used. Two polymer batches of PETA₂₅, synthesised as described by Bussink et al. [5], were postcondensed under different pressures at a temperature of 230°C. Normally, a vacuum of 0.1 mbar is applied, this being the highest obtainable vacuum with the equipment used. The postcondensation pressure was increased by two different strategies. In the first method, a nitrogen flow was passed over the polymer particles under a low vacuum, the pressure being varied by the increasing the nitrogen flow. In the second method, the nitrogen flow was led directly into the vacuum pump. The postcondensation tube was flushed with nitrogen before starting the solid state postcondensation. The colour was measured by UV absorbance. Table 4 shows the effect of postcondensation pressure on the colour, inherent viscosity, T_m and T_c for the polymers.

The polymers in series I, exhibit approximately the same inherent viscosity and colour, independent of the nitrogen flow, excepting the measurement at a pressure of 100 mbar, the polymer obtained at this point having a lower molecular weight. Ethanedilol is best removed by applying a high vacuum, possibly by using a low nitrogen flow.

The inherent viscosity of the polymers of series II seems to fall at a lower vacuum. As the condensation products such as ethanedilol or water are not removed as rapidly, the build up in molecular weight will be controlled by the diffusion of ethanedilol. Up to a pressure of 100 mbar there is hardly any colour change, a significant effect on the colour develops

Table 4
Effect of pressure during solid state postcondensation of PETA₂₅ at 230°C, 24 h

| Pressure (mbar) | Method | η_{inh} (dl/g) | Absorbance | T_m (°C) | T_c (°C) | ΔT (°C) |
|-----------------|-----------------|---------------------|------------|------------|------------|-----------------|
| bp ^a | | 0.40 | 0.177 | 268 | 240 | 28 |
| 0.1 | I ^b | 0.86 | 0.176 | 274 | 244 | 30 |
| 5 | I ^b | 0.81 | 0.189 | 278 | 244 | 34 |
| 10 | I ^b | 0.86 | 0.192 | 274 | 240 | 34 |
| 100 | I ^b | 0.56 | 0.182 | 266 | 240 | 26 |
| bp ^a | | 0.17 | 0.179 | 273 | 240 | 33 |
| 0.1 | II ^c | 0.64 | 0.189 | 272 | 236 | 36 |
| 5 | II ^c | 0.71 | 0.192 | 274 | 238 | 36 |
| 100 | II ^c | 0.55 | 0.193 | 269 | 237 | 32 |
| 1000 | II ^c | 0.49 | 0.211 | 266 | 229 | 37 |

^a bp: before solid state postcondensation.

^b I: Nitrogen flow led over the polymer particles.

^c II: Nitrogen flow led into the vacuum pump.

when the degradation and condensation products are not removed (at 1000 mbar).

Comparing both polymer series, it appears that a higher molecular weight and a less coloured PETA₂₅ can be obtained by leading a nitrogen flow over the polymer particles instead of directly into the vacuum pump. However, the best way is to apply a vacuum of 0.1 mbar (or lower), possibly using a low nitrogen flow.

4. Conclusions

Different catalyst systems have been tested in the PETA synthesis. In using titanium compounds as a catalyst, polymers with a reasonable molecular weight were obtained but with a low melting temperature as compared to other batches. PETA₂₅ synthesised with a titanium catalyst also yielded the highest degradation rate. However, by inactivating the titanium catalyst before processing with triphenyl phosphite the degradation rate of the polymer was significantly lowered. Using caesium carbonate as a catalyst results in a low molecular weight polymer, although the amount of caesium carbonate did not influence the obtained properties or the melt stability.

A combination of a transesterification catalyst such as manganese or zinc acetate, and a polycondensation catalyst such as antimony trioxide, results in a low degradation rate of the obtained polymers, the degradation mainly being caused by the transesterification catalyst. As degradation also occurs during polymerisation and solid state postcondensation, a higher molecular weight polymer could be obtained than with the other catalysts. The highest melting and flow temperatures were obtained using the zinc/antimony catalyst system.

When increasing the amounts of zinc acetate and antimony trioxide, a high molecular weight and a high melting PETA₂₅ could be synthesised. However the melt degradation rate of the polymer was increased due to the presence of a higher amount of catalysts. Inactivation of the zinc

catalyst after the transesterification was not sufficient to suppress the higher rate of degradation. As the zinc catalyst inactivation is as yet suboptimal, a more detailed study of the inactivation is relevant. The degradation of PET is enhanced by the incorporation of amide segments, i.e. with increasing amide content, the degradation rate constant is also increased.

For PET, PETA₁₀, and PETA₂₅ the highest molecular weights were obtained at a postcondensation temperature of 230, 240, and 240°C (4 h)/250°C (20 h), respectively. Using these solid state temperatures, led to not only a higher molecular weight polymer, but also a darker coloration. Reducing the solid state postcondensation pressure, caused a decrease of molecular weight of PETA₂₅ when the pressure was over 100 mbar, at this point the diffusion of ethanediol then becomes the limiting step. When the condensation and degradation products were not removed during solid state postcondensation (1000 mbar), PETA₂₅ became quite dark. Applying a nitrogen flow to remove the condensation products, caused a lowering of the molecular weight at pressures over 100 mbar. The best overall results were obtained using a high vacuum (0.1 mbar) and possibly a low purge gas (nitrogen) flow. Using these polycondensation conditions the amount of ester–amide interchange taking place was minimal.

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