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Polymer 41 (2000) 2719–2725

polymer

Polyesteramides based on PET and nylon 2,T
Part 1. Synthesis of the bisesterdiamide

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Received 5 June 1999; received in revised form 1 July 1999; accepted 14 July 1999

Abstract

The synthesis of the bisesterdiamide T2T-dimethyl (one-and-a-half repeating unit of nylon 2,T) (benzoic acid, 4,4′-[1,2–ethanediyl-bis(iminocarbonyl)] bis-dimethyl ester, CAS no 7060-10-8) has been studied using dimethyl terephthalate (DMT) and 1,2-diaminoethane (DAE) as starting materials. T2T-dimethyl was synthesised in a solvent mixture of toluene/methanol at 65°C employing lithium or sodium methanolate as a catalyst. The progress of reaction was followed as function of time using liquid chomatrography and endgroup titrations. The products were analysed using ^{1}H NMR, ^{13}C NMR and differential scanning calorimeter. A high yield was obtained (90%), and after recrystallisation from NMP, the product was found to be of high purity. The pure T2T-dimethyl obtained had a melting onset of 312°C and a melting enthalpy of 165 J/g.

T2T-dimethyl was also synthesised in absence of a catalyst at 100°C and using *m*-xylene as solvent and at a high concentration of reactants. The yield of this reaction was relatively low (34%). The addition of phenol to the reaction mixture had little effect on the yield and purity of the product. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bisesterdiamide; 1,2-Diaminoethane; Dimethyl terephthalate

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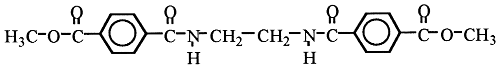
1. Introduction

Copolyesteramides have been studied extensively. If the amide containing segments in the copolymer are distributed randomly, the copolyesteramide is usually slow in crystallising, as well as having a low crystallinity [1,2]. If the amide containing segments are more ordered and in particular if they have a constant length, the copolyesteramides crystallise rapidly and have a high crystallinity [3]. Amide segments of uniform length are present in alternating polyesteramides and in polyesters modified with diamide segments. Copolyesteramides with uniform diamide segments can be prepared using bisesterdiamides. The purity of these bisesterdiamides is very important, as it affects the uniformity of the amide segment length in the polyesteramide, and thereby the crystallisation rate and the crystallinity [4,5]. We have studied copolyesteramides that have been made using bisesterdiamides based on terephthalic acid and 1,2-diaminoethane, called T2T-dimethyl (**1**). In T2T-dimethyl, the “T” stands for terephthalic acid, and “2” for the number of methylene groups present between the amide groups.



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T2T-dimethyl

A number of investigators have reported on the synthesis of bisesterdiamides [6–12]. Ciceri et al. [6] have synthesised T2T-dimethyl from dimethyl terephthalate (DMT) and 1,2-diaminoethane using lithium methanolate as a catalyst (0.14 mol lithium/mol diamine). The reaction was carried out in a solvent mixture of toluene and methanol (65–70°C) over a period of 5 h. The yield after recrystallisation from dimethyl formamide was 32% and the T2T-dimethyl obtained was found to have a melting temperature of 315°C.

Bussink et al. [7] also synthesised T2T-dimethyl from DMT and 1,2-diaminoethane, but in a solvent mixture of toluene and dimethyl formamide (50/50 volume fraction), using lithium methanolate as a catalyst (0.19 mol lithium/mol diamine). The reaction was carried out over 4 h at 140°C, the product had a melting temperature of 295°C and the yield obtained after washing was 82%.

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PII: S0032-3861(99)00485-1

Table 1
Influence of functional groups on chemical shifts in NMR of terephthalic protons and carbons of T2T-dimethyl in TFA-d

Code	Functional groups	^{1}H NMR δ (ppm)		^{13}C NMR δ (ppm)	
EE + eaE	Ester side	8.0–8.1	Doublet		
AA +eaA	Amide side	8.3–8.4	Doublet		
eaE	Ester side			132.8	Singlet
eaA	Amide side			129.8	Singlet
EE	Ester			132.2	Singlet
AA	Amide			130.4	Singlet

The reaction conditions of the amidation of DMT are dependent on the toluene/methanol ratio [8], the concentration of the reactants [9,10] and solubility of the diamide [9]. The amidation can also be carried out without a catalyst at high yield if diphenyl terephthalate is used as a starting material [11]. Next to Lithium alconalates Sodium alconalates have also been reported as catalysts in the amidation reaction [6,12]. The mechanism is assumed to be a base-catalysed ester aminolysis [13]. Jouffret and Madec [14] used phenol (5 wt%) at catalyst in the synthesis of nylon-6,6 starting from dimethyl adipate and 1,6-diaminohexane. Pure bisesterdiamides were obtained by recrystallisation from *N*-methyl-2-pyrrolidone [8].

As the purity of the bisesterdiamides is very important for the properties of the resulting polyesteramides [4,5], the aim of this study is to find a suitable synthetic route in order to obtain pure T2T-dimethyl at a high yield. As starting materials dimethyl terephthalate and 1,2-diaminoethane are being used.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), 1,2-diaminoethane (DAE), anhydrous toluene, anhydrous methanol, *N*-methyl-2-pyrrolidone (NMP) and phenol were obtained from Merck. *m*-Xylene was purchased form Fluka, and lithium and sodium were obtained from Aldrich. All chemicals were used as received. $LiOCH_3$ and $NaOCH_3$ were prepared by adding lithium or sodium to anhydrous methanol (1.25 M).

2.2. Synthesis of T2T-dimethyl

The CA index name for T2T-dimethyl is benzoic acid, 4,4′-[1,2-ethanediylbis(iminocarbonyl)] bis-dimethyl ester, no. 7060-10-8.

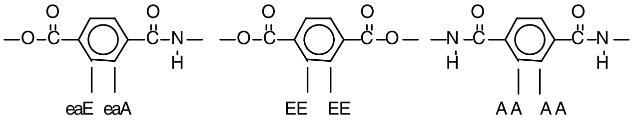


Fig. 1. Codes aromatic atoms of terephthalic group.

DMT (225 g, 1.16 mol) was dissolved in 900 ml toluene and 50 ml methanol at 65°C, in a 2 l flask, equipped with a mechanical stirrer, nitrogen inlet, condenser, and calcium chloride tube. When the DMT was dissolved, 20 ml of catalyst solution (1.25 M $LiOCH_3$ in methanol) was added and DAE (20 ml, 0.3 mol), previously dissolved in 100 ml toluene, was also added dropwise to the reaction mixture. The nitrogen flow was stopped to prevent the evaporation of DAE. Three hours after the start of the reaction, the temperature was gradually raised to 90°C and the methanol distilled. After a total reaction time of 24 h, the reaction was stopped and the white precipitate filtered off through a soxhlet extraction thimble. The obtained product was washed twice with hot *m*-xylene and then dried in a vacuum oven at 70°C overnight.

To further purify the product, T2T-dimethyl was recrystallised from NMP (50 g/l, 160°C) and washed twice with hot acetone. The purified product was then dried in a vacuum oven at 70°C overnight.

2.3. NMR

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

In determining the purity of T2T-dimethyl using ^{1}H and ^{13}C NMR, the chemical shifts of the aromatic atoms are used [9]. In Table 1 the chemical shifts of the different protons in T2T-dimethyl are given. Fig. 1 shows the peak assignment of the different protons of T2T-dimethyl.

The terephthalic ester-amide content X_{EA} can be calculated according to Eq. (3), using the integrals of peaks ester and amide peaks. If DMT remnants are present, the aromatic ester peak (EE) overlaps with ester peak of T2T-dimethyl (eaE). If the product has been well washed, this DMT-peak (EE) should be absent. Side products of the T2T-dimethyl synthesis, such as 2T2, T2T2 and T2T2T, have an AA-peak and increase the integral of the amide peak (eaA + AA). Impurities such as DMT and side products have an opposite effect on X_{EA}.

$$X_{EA} = \left(2 - \frac{AA + eaA}{EE + eaE}\right) \times 100\% \qquad (mol\%) \qquad (3)$$

^{13}C NMR is, in principle, less sensitive than ^{1}H NMR, but larger chemical shifts and single peaks are observed. For quantitative analysis with ^{13}C NMR only the integral of structurally similar carbon atoms may be compared, as the time between two pulses is not long enough for a complete relaxation of all carbon atoms. Table 1 shows the peak assignment and chemical shifts of some of the aromatic carbon atoms, and Fig. 1 gives the codes for the important aromatic carbon atoms.

The EE peak in ^{13}C NMR indicates the presence of DMT and AA peaks the presence of terephthalic diamides such as present in 2T2, T2T2 and T2T2T. The impurity content, such as the terephthalic diamide fraction (X_{AA}) and the DMT content (X_{EE}), can be determined by ^{13}C NMR analysis, using Eqs. (4) and (5):

$$X_{AA} = \frac{AA}{eaA + eaE + AA + EE} \times 100\% \qquad (\text{mol}\%) \qquad (4)$$

$$X_{EE} = \frac{EE}{eaA + eaE + AA + EE} \times 100\% \qquad (\text{mol}\%) \qquad (5)$$

2.4. DSC

DSC spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried samples of 2–5 mg were measured at a heating rate of 20°C/min up to a temperature of 330°C. The onset of the melting peak was taken as the melting temperature. The peak area was used to calculate the melt enthalpy.

2.5. HPLC

A Varian 2500 apparatus, Varian pump 2510, variable detector 2550, Valco injector of 10 μl loop and an integrator of the Merck Hitachi D2500 type were used for HPLC analysis which was performed using a Lichrospher 100 RP-8 1255 × 4 mm column. The samples were dried in a vacuum oven at 70°C overnight and dissolved in NMP (3–7 mg/ml). In another experiment, the wet samples were directly dissolved in NMP. The eluent was a mixture of acetonitrile/water (35/65 volume fraction) and the eluent flow rate was 1 ml/min. After 3 min the eluent was changed so that a mixture of 60% acetonitrile and 40% water would be reached in 55 min. Detection was performed with UV at 288 nm.

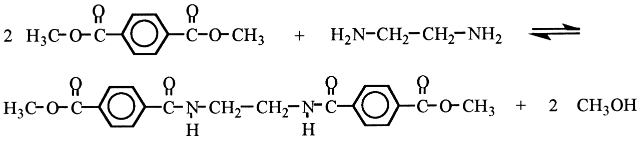
2.6. NH_2-endgroup concentration

The concentration of NH_2-endgroups was determined using a Metrohm titroprocessor type 636 with Ross glass electrodes. T2T-dimethyl was dissolved in water/phenol (85/15 volume fraction) and tetrabutyl ammonium hydroxide in isopropanol/methanol (0.1 M) was used as the titrant.

3. Results and discussion

3.1. Introduction

T2T-dimethyl was synthesised from DMT and DAE (**6**) using a solvent mixture of toluene and methanol, and employing lithium or sodium methanolate as a catalyst. The reaction was followed by HPLC analysis of reaction products and the influence of reaction conditions is studied.



(6)

A reaction scheme proposed by Serrano [9] for the synthesis of T4T-dimethyl has been adapted for T2T-dimethyl. It is assumed that the reaction starts with the fast formation of T2 (**7**), this monoamide then reacts with DMT to form T2T (**8**), finally T2T-dimethyl precipitates from the reaction mixture, thereby limiting any further reaction.

$$\text{DMT} + \text{DAE} \rightarrow \text{T2} \qquad (7)$$

$$\text{T2} + \text{DMT} \rightarrow \text{T2T} \qquad (8)$$

$$\text{T2} + \text{DAE} \rightarrow \text{2T2} \qquad (9)$$

$$\text{T2} + \text{T2} \rightarrow \text{T2T2} \qquad (10)$$

$$\text{2T2} + \text{DMT} \rightarrow \text{T2T2} \qquad (11)$$

$$\text{T2T} + \text{DAE} \rightarrow \text{T2T2} \qquad (12)$$

$$\text{T2T} + \text{T2} \rightarrow \text{T2T2T} \qquad (13)$$

$$\text{T2T2} + \text{DMT} \rightarrow \text{T2T2T} \qquad (14)$$

Different side reactions can occur during the T2T-dimethyl synthesis. The monoamide T2 may also react with DAE (**9**), itself (T2) (**10**) or T2T (**13**). To limit these

Table 2
HPLC Peak areas at different eluent times and amino-endgroup concentration of the T2T reaction products at different reaction times

Reaction time (h)	Peaks at different elution times (min) Peak areas in %.						NH_2 (mmol/g)
	2.8	3.2	3.5	4.2	5.4	9.7	
0.25			0.02	0.14	6	94	0.77
0.50	0.01	0.01	0.05	0.29	14	86	0.64
0.75	0.01	0.02	0.07	0.45	20	79	0.50
1.0	0.02	0.02	0.08	0.54	26	74	0.48
1.5		0.01	0.09	0.66	34	66	0.37
2.0		0.01	0.09	0.66	38	62	0.34
3.3		0.01	0.08	0.82	45	55	0.21
5.1		0.01	0.08	0.89	47	47	0.23
7.4		0.01	0.09	0.95	59	40	0.24
24		0.01	0.13	0.96	56	43	0.23

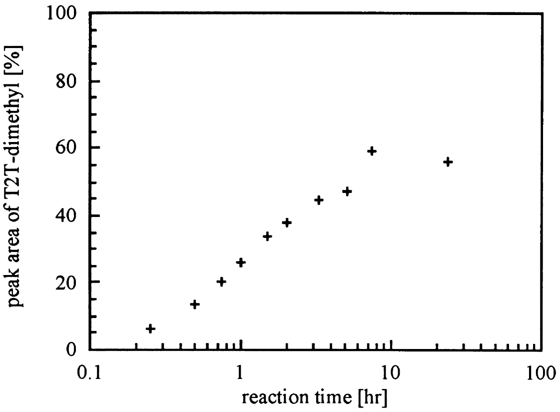


Fig. 2. HPLC peak area of T2T-dimethyl (5.4 min) versus the reaction time.

side reactions, the concentration of DMT should be much greater than the concentration of DAE, T2 and T2T-dimethyl. Therefore DAE is added dropwise in the presence of a large excess of DMT. Reactions (**11**) and (**14**) depend on the concentration of other side products, such as 2T2 (**9**) and T2T2 (**11** and **12**).

3.2. T2T-dimethyl synthesis

T2T-dimethyl, in common with other bisesterdiamides, can also be synthesised from DMT and DAE by using lithium methanolate as catalyst [6–9,11]. The synthesis was carried out using toluene and methanol as a solvent mixture. The progress of reaction was studied by taking samples from the reaction mixture at different reaction times. The samples were dried and analysed by HPLC and the amino-endgroup concentration determined (Table 2). In the HPLC-spectrum the T2T-dimethyl and DMT peak appear at 5.4 and 9.7 min, respectively.

Initially, after the addition of DAE, the reaction mixture remained clear with the first precipitate forming after 10–15 min. Fig. 2 shows the peak area of T2T-dimethyl versus the logarithm of the reaction time and Fig. 3 shows the peak area of the side products of the T2T-dimethyl synthesis and the amino-endgroup concentration plotted against the logarithm of the reaction time.

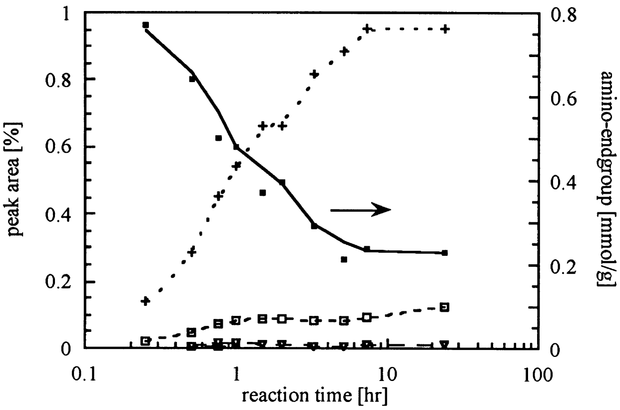


Fig. 3. HPLC Peak area of the side products of the T2T-dimethyl synthesis and amino-endgroup concentration versus the reaction time: (▽, 3.2 min; □, 3.5 min; +, 4.2 min; and amino endgroup concentration, ■.

The T2T-dimethyl concentration (5.4 min) increases with the logarithm of the reaction time, at the same time, a decrease of the DMT concentration (9.7 min) is observed. The amount of side products slightly increases with the logarithm of reaction time and this is particularly true for the 4.2 peak. After 7 h reaction time, the concentrations plateau and remain stable. A reaction time of 7 h is therefore sufficient. The suggested peak assignments are give in Table 2. The DMT decreases with time, the 2T2 is low and fairly constant with time, while the others (T2T, 2T2T and T2T2T) increase with the reaction time. According to the presented reaction scheme (**7**)–(**14**), a T2 peak should increase rapidly at the beginning of the reaction, and decrease upon further reaction. This peak is expected to appear earlier than those for T2T, 2T2, T2T2 and T2T2T in the HPLC-spectrum. However, no such peak is visible. One reason is perhaps that any T2 present has evaporated during the drying of the sample in the vacuum oven. Another reason could be that the peak appears in the noise signal at the beginning of the spectrum, and is therefore not visible. The sample, drawn after 15 min reaction time was analysed with ^{1}H NMR and a peak that is assumed to be of T2 was observed at 4.05 ppm ($R{-}CO{-}NH_2{-}CH_2{-}CH_2{-}NH_2$), as during such a short reaction time hardly any side products such as 2T2 or T2T2 are formed.

In a following experiment, the reaction mixtures samples were not dried, but dissolved directly in NMP and then kept in the refrigerator overnight for analysis the next day to limit any further reaction. The composition of the eluent fluid was then changed to 75% water and 25% acetonitrile, to delay the elution of products. However in these samples no T2 peak was detected either and we therefore conclude that the used HPLC-method is not suitable for the detection of T2.

The amino endgroup concentration decreased with increasing reaction time (see Fig. 3). However, the side products peaks increased with time. This decrease of the amino endgroup concentration could well be caused by the diminishing amount of T2. The amino-endgroup concentration after 15 min is 0.77 mmol/g. DAE is not expected to be present in the samples, as this is removed during the drying of the sample. The theoretical maximum amino endgroup concentration in the samples (when all the DAE has reacted to form T2) is 1.29 mmol/g and therefore the value of 0.77 mmol/g after 15 min reaction time suggests that at that moment, already 60% of the theoretical total amount of T2 has been formed. After a reaction time of 15 min, some DAE may not have yet reacted to form T2, and a small amount of T2 may also have reacted to form T2T.

It appears that the reaction starts by the fast formation of the monoamide T2, a catalyst being necessary for this step. This T2 partly precipitates and dissolves again to further

Table 3
Analysis after synthesis and washing and after recrystallisation from NMP

	HPLC				Endgr.	^{1}H NMR	^{13}C NMR		DSC	
	3.5 (%)	4.2 (%)	5.4 (%)	9.7 (%)	NH_2 (mmol/g)	X_{EA} (mol%)	X_{AA} (mol%)	X_{EE} (mol%)	T_m (°C)	ΔH_m (J/g)
Assignment	T2T2	T2T2T	T2T	DMT						
After synthesis	0.07	1.30	98	0.41	0.41	95	3	4	285	55
After recrystallisation	0.02	0.66	99	0.07	0.01	99	–	–	312	165

react, forming T2T. The rate-limiting step is the reaction of T2 with DMT in the formation of T2T. At the end of the reaction, the amino-endgroup concentration levels are 0.23 mmol/g, this being 18% of the theoretical amount of T2 that could be produced. Why this reaction has not proceeded to completion is not clear. It is possible is that T2 partly precipitates when being formed at the beginning of the reaction. The T2T-dimethyl then deposits at these T2 particles, encapsulating the T2 and thereby limiting any further reaction. It is necessary to remove T2 by recrystallisation, as it contains a free amino endgroup that will disturb subsequent polymerisation reactions. The increase in formation of T2T is logarithmic with time (see Fig. 2). The availability of T2 (by diffusion out of encapsulated particles and solving in the reaction mixture) is most likely the rate-limiting step. To increase the yield of the T2T-dimethyl synthesis, the T2 should be prevented from precipitating such that it no longer remains inactive. One way to achieve this is to select a solvent system in which T2 is better soluble.

The products, after synthesis (P) and after recrystallisation (PH) were also analysed by HPLC and by NMR and DSC (Table 3). The T2T-dimethyl was washed twice with *m*-xylene following synthesis, therefore all DMT should have been removed. After synthesis, the product was found to have a high amino endgroup content of 0.36 mmol/g, meaning that 13% of the DAE was in the T2 form (T2 having no influence on X_{EA}). T2 is the main impurity after synthesis. On recrystallisation, the peaks of the side products and the amino-endgroup concentration are found to decrease, such that almost all of the T2 is removed. However, some impurities still remain. The most important impurity after recrystallisation is the pentamer T2T2T. If the values of X_{EA}, X_{EE} and X_{AA} as measured by NMR are for the as synthesised sample are compared with the HPLC analysis it is observed that the HPLC method suggest a higher purity than NMR. After recrystallisation, the AA and EE peaks both disappear.

An other indication of the purity is the melting endotherm of the T2T-dimethyl. Fig. 4 shows the melting endotherms of T2T-dimethyl before and after recrystallisation. After recrystallisation, the melting temperature of T2T-dimethyl was sharp, had a higher melting temperature and a higher melt enthalpy (Table 3). The onset of the melting temperature being at 312°C, the melt enthalpy is 165 J/g and the maximum of the peak is at 317°C. Bussink et al. [7] found for a sample which had not been crystallised a melting temperature of 295°C. The T2T-dimethyl obtained by Ciceri et al. [6] after recrystallisation from dimethyl formamide, was pure according to elemental analysis and had a melting temperature of 315°C.

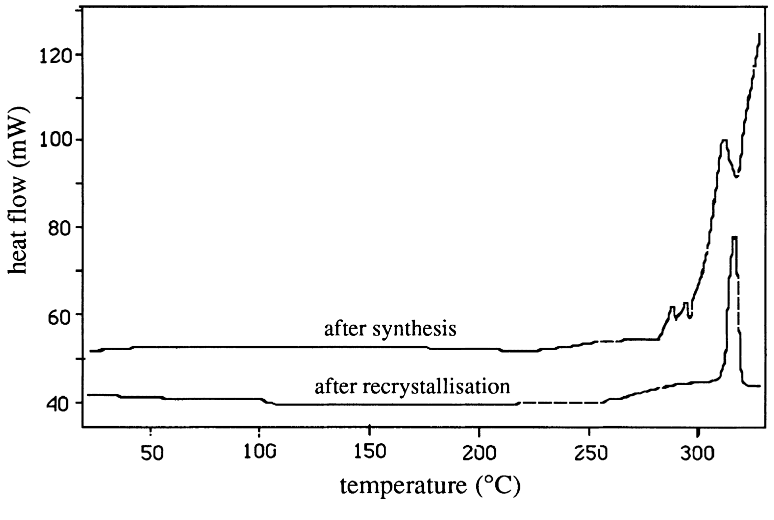


Fig. 4. DSC first heating scan of T2T-dimethyl, after synthesis and after recrystallisation from NMP.

Table 4
T2T-dimethyl synthesis using $LiOCH_3$ as catalyst, reaction time 7 h

Batch no	Methanol (ml)	T_{max} (°C)	Yield (%)	Yield[a] (%)	X_{EA}[a] (mol%)	T_m[a] (°C)	ΔH_m[a] (J/g)
1	45	90	73	36	96	312	162
2	70	90	80	43	99	311	175
3	95	90	85	50	95	303	171
4	120	90	70	37	97	306	165
5	145	90	86	38	97	304	168
6	70	65	81	46	99	312	165
7	70	65	88	46	99	313	166

[a] After recrystallisation.

3.3. Reaction conditions

The T2T-dimethyl synthesis has been further optimised. The reaction time was set to 7 h, as HPLC measurements indicated that this was sufficient. The influence of varying the reaction conditions such as the methanol content in the toluene–methanol mixture and the reaction temperature are shown in Table 4. The $LiOCH_3$ solution is included in the amount of methanol and T_{max} is the maximum temperature during the reaction.

The yield before and after recrystallisation does not change with the methanol content. The T_m decreases with an increasing amount of methanol, particularly when this exceeds 70 ml. The ΔH_m values obtained are constant for this series. Serrano et al. [8] also found that by increasing the amount of methanol, the purity decreased and they have suggested that the solubility of the monoamide is increased by methanol, increasing the amount of side products formed. According to the presented reaction scheme, increasing the T2 concentration increases the rate of reactions (**8**)–(**10**) and (**13**). Particularly the rate of reaction **10** is increased, the product of this self-reaction, T2T2, then being able to further react to form T2T2T. At methanol amounts lower than 50 ml, it becomes difficult to solve DMT at this temperature (65°C), as an increase of the methanol concentration also increases the solubility of DMT.

The reaction temperature was kept at 65°C for batches 6 and 7, this having no negative influence on the yield and purity of the resultant product. For batch 7, DAE was added all at once instead of dropwise. It was found that increasing the DAE concentration from effectively 0% (by adding dropwise) to 1.6 wt% did not adversely influence the formation of side products, probably due to the rapid reaction in the formation of T2.

3.4. Type of catalyst

In addition to lithium also sodium alcanolates have been used as catalyst for the amidation of esters [6,14]. These are effective promoters of the esters aminolysis, may have catalytic effects by acting as base catalysts [13]. They may also influence the solubility of the reaction products. Lithium- and sodium methanolate are used at relatively high concentrations for catalysts, 0.08 mol catalyst/mol amine (Table 5). An even higher amount (0.14 mol lithium/mol amine) has been used by Ciceri et al. [6]. The T2T-dimethyl batch, in which sodium methanolate was used as a catalyst, was recrystallised at a higher concentration (100 g/l) than the batch T2T-dimethyl synthesised with lithium methanolate as a catalyst (50 g/l), resulting in a higher yield after recrystallisation. The yield and purity of the batches using either lithium or sodium methanolate were comparable, indicating that sodium methanolate is also a suitable catalyst.

According to Jouffret and Madec [14], phenol is a good catalyst for the acid-catalysed amidation of esters. In their experiments the reactions were performed in the melt. The T2T-dimethyl synthesis was not carried out in the melt, as DAE is very volatile at the temperature required (melting temperature of DMT is 141°C). In addition at higher temperatures, alkylation of the diamine can occur [15]. Therefore the reaction was carried out in a minimal amount

Table 5
Influence catalyst on T2T-dimethyl synthesis using 0.3 mol diaminoethane

Catalyst	Solvent	Temperature (°C)	Yield (%)	Yield[a] (%)	X_{EA}[a] (mol%)	T_m[a] (°C)	ΔH_m[a] (J/g)
Li OCH_3 (0.024 mol)	Toluene/methanol (900/70 ml)	65	88	47	99	313	166
Na OCH_3 (0.024 mol)	Toluene/methanol (900/70 ml)	65	89	55	97	311	171
Phenol (50 ml)	*m*-Xylene (200/600 ml)	100	21	12	84	308	107
none	*m*-Xylene (200/800 ml)	100	34	9	81	306	96

[a] After recrystallisation from NMP.

of *m*-xylene (200 ml) at 100°C. As the reaction progressed the mixture became highly viscous and more xylene was added (400 ml). The overall yield of synthesis phenol method is low and the purity even after crystallisation not so high. For comparison also a synthesis was carried out have no catalyst. The yield of this synthesis was low too. The low yields may in part be due to the evaporation of DAE at 100°C. Adding phenol does not enhance the amidation reaction in this system.

4. Conclusions

T2T-dimethyl can be synthesised from DMT and DAE, in the absence of a catalyst at 100°C in *m*-xylene, the yields were however low. The addition of phenol to this system had little effect on yield and purity. The maximum yield of this reaction being a relatively low 34%.

By employing sodium or lithium methanolate as a catalyst using a solvent system of toluene and methanol, a high yield of T2T-dimethyl is obtained (90%). For a purity of >98% recrystallisation is necessary. The amount of methanol used in this system was found to enhance the solubility of the monoamide T2, resulting in a decrease in the purity of T2T-dimethyl. The reaction at 65°C and at a DAE concentration of 1.6 wt% did not occur in the absence of either a lithium or sodium methanolate catalyst. The reaction begins by the fast formation of T2, which partially precipitates, the rate limiting step probably being the re-dissolving of the T2, and its subsequent reaction with DMT to form T2T. After synthesis and washing, the main impurity in the obtained T2T-dimethyl is T2 (13%). One reason for this could be that T2T precipitates on T2 particles thus encapsulating the T2 and limiting any further reaction. Optimising the reaction conditions could well reduce this encapsulation of T2. On recrystallisation, most of the T2 is removed.

Acknowledgements

This work was financially supported by GE Plastics, Bergen op Zoom, the Netherlands. G. de Wit (GE Plastics) and J. Feijen (University of Twente) are acknowledged for fruitful discussions and valuable suggestions. W. Lengton (University of Twente) is acknowledged for developing and performing the amino endgroup concentration measurements.

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