Polymer Vol. 39 No. 23, pp. 5773–5780, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(97)10389-5

Alternating polyesteramides based on 1,4-butylene terephthalamide: 1. Synthesis of the bisesterdiamide

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(Accepted 20 November 1997)

The bisesterdiamide T4T dimethyl (one and a half repeat units of 1,4-butylene terephthalamide, nylon-4,T) (benzoic acid, 4,4′-[1,4-butanediylbis(iminocarbonyl)]bis-, dimethyl ester, CAS no. 1028 10-33-3) has been synthesized from an excess of dimethyl terephthalate and 1,4-butanediamine. Lithium methanolate was used as a catalyst. Different solvents have been used to optimize the yield and purity. A pure product could be obtained by recrystallization from hot NMP. D.s.c. and n.m.r. analyses were used to determine the purity of the product. The melting temperature of the T4T dimethyl ($T_m = 265°C$) decreased with increasing loss of uniformity. The T4T dimethyl showed a transition in the crystalline structure upon heating at 160–175°C. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: bisesterdiamide; 1,4-butanediamine; dimethyl terephthalate)

INTRODUCTION

Alternating polyesteramides are usually prepared by a two step synthesis. First, well-defined monomers are prepared which react in a second step to an alternating polyesteramide[1].

In this way a polymer with a regular structure is obtained. A one step synthesis in which all the monomers are reacted at the same time usually yields a polymer of low order[2]. The irregular structure hinders the ordering in a crystalline structure[3,4].

As a result of this the modulus above the glass transition temperature (T_g) is lowered. A strictly alternating copolymer thus might have a high crystallinity and a high modulus.

In order to obtain a strictly alternating polyesteramide it is necessary to perform the synthesis with pure preformed monomers. There are various methods to synthesize the preformed monomers for alternating polyesteramides. It is advantageous to form the amide linkage first and the ester linkage in a later stage. The amide bond is more stable and remains virtually unaffected during the esterification and polymerization.

Starting with, for example, a diamine, different reactions are possible to synthesize the amide segment. In general:

$$2R_2OOC - R_1 - COX_1 + H_2N - R_3 - NH_2 \rightarrow R_2OOC - R_1 - CONH - R_3 - HNOC - R_1 - COOR_2 + 2HX_1 \quad (1)$$

Easy to use are the diacids of which one acid group has been esterified and the other converted to an acyl chloride. Other possibilities are the reaction of a dicarboxylic acid with a diamine or the reaction of a mono ester dicarboxylic acid with a diamine. Reacting these preformed diamides with diols will give alternating polyesteramides.

Williams *et al.*[5] reported the synthesis of the polyesteramide based on 1,6-hexanediol and *N*,*N*′-bis(*p*-carbomethoxybenzoyl)hexanediamine (T6T dimethyl). This bisesterdiamide was prepared from 4-methoxycarbonyl benzoyl chloride and 1,6-hexanediamine[6]. The half acid chloride ester was added dropwise to a 1,6-hexanediamine/pyridine solution at room temperature. After the addition was completed, the mixture was poured into an ice water slurry. The product was recrystallized from ethanol. This reaction route gave pure diamide segments. Goodman and Starmer[7] were able to prepare similar bisesterdiamides. They reacted 4-ethoxycarbonyl benzoyl chloride with 1,6-hexanediamine. A solution of ethoxycarbonyl benzoyl chloride in toluene was added dropwise to a mixture of 1,6-hexanediamine in water and toluene. Then, a solution of sodium hydroxide in water was added dropwise. After the reaction had finished, the precipitate was washed with hot water. The pure bisesterdiamide was obtained after recrystallization from butanol.

Manzini *et al.*[8] synthesized *N*,*N*′-bis(*p*-carbobutoxybenzoyl)dodecanediamine (T12T dibutyl) from di-*n*-butyl terephthalate and 1,12-dodecanediamine. The reaction was carried out in the melt at 210°C for 5 h. After precipitation from *n*-butanol the product was washed with acetone. Recrystallization from *n*-butanol was necessary to obtain the pure product.

A lithium-catalysed synthesis for T6T dimethyl was reported by Snam Progetti[9]. Starting materials were 1,6-hexanediamine and dimethyl terephthalate (DMT) dissolved in a methanol/toluene mixture at 65°C. The catalyst, LiOCH3, was added in a relatively large amount (30 mol% Li/mol diamine). An excess of DMT (10 mol DMT/mol diamine) was used to avoid further reaction of the T6T dimethyl. The product was washed twice with toluene and twice with hot methanol. The bisesterdiamide was obtained in a yield of 93% and was without further purification polymerized with diols.

Gaymans and de Haan[10] and van Bennekom[11] synthesized T4T dimethyl (*N*,*N*′-bis(*p*-carbomethoxybenzoyl)butanediamine) in a similar way as the T6T dimethyl described by Snam Progetti (reaction 2). However, they used a smaller excess of DMT over 1,4-butanediamine (4,7 mol DMT/mol

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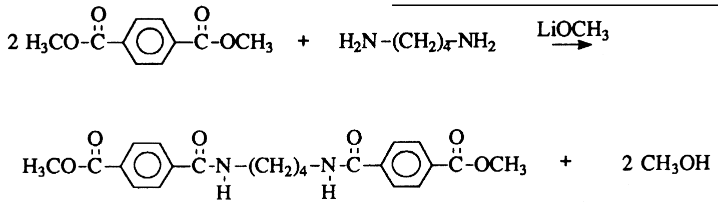
diamine) and a lower lithium concentration (6.5 mol% Li/mol diamine). These conditions were shown to be as effective as the larger excess used by Snam Progetti. A pure product was obtained after recrystallization from hot *N*-methyl-2-pyrrolidone[11].



(2)

T4T dimethyl

Matthijssen[12] used diphenyl terephthalate to synthesize T4T diphenyl (*N*,*N*′-bis(*p*-carbophenoxybenzoyl)butanediamine). The diphenyl terephthalate (DPT) was prepared by reaction of dimethyl terephthalate with phenyl acetate in *m*-xylene in the presence of a titanium catalyst. The reaction was carried out at 185°C for 24 h. An excess of diphenyl terephthalate was then reacted with 1,4-butanediamine in *m*-xylene (4.8 mol DPT/mol diamine). The product was formed in 6 h at a temperature of 119°C. Without catalyst, the yield was 88%.

Since the purity of the bisesterdiamides is very important for the preparation of strictly alternating polyesteramides, the reaction conditions for the preparation of pure T4T dimethyl were studied. Starting materials were dimethyl terephthalate and 1,4-butanediamine in a methanol/toluene mixture. Lithium methanolate was used as a catalyst.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), 1,4-butanediamine (BDA), anhydrous toluene and anhydrous methanol, *m*-xylene, *n*-butanol and *N*-methyl-2-pyrrolidone (NMP) were obtained from Merck. Lithium was purchased from Aldrich. BDA and *n*-butanol were distilled prior to use. $LiOCH_3$ was prepared by adding lithium to anhydrous methanol (1.25 M).

Synthesis of T4T dimethyl

The CA index name for T4T dimethyl is benzoic acid, 4,4′-[1,4-butanediylbis(iminocarbonyl)]bis-, dimethyl ester, CAS no. 1028 10-33-3. Three different synthetic routes were studied:

Route I. DMT (275 g, 1.42 mol) was dissolved in 1000–1100 ml anhydrous toluene and 310 ml anhydrous methanol (60°C) in a 2 l flask, equipped with mechanical stirrer, condenser, calcium chloride tube and nitrogen inlet. After addition of 12–20 ml of the solution of $LiOCH_3$ in methanol, the temperature was raised to 65°C. Then, BDA (34 ml, 0.34 mol), dissolved in 150 ml toluene and 10 ml methanol was added dropwise for 5 h. Once the BDA addition had started, the nitrogen flow was stopped to avoid the evaporation of BDA. After a total reaction time of 44 h at 65°C, the white precipitate was separated by hot filtration over a glass funnel, pore size 4. The product was purified by soxhlet extraction with toluene for 24 h and subsequently dried in a vacuum oven at 70°C for 24 h.

Route II. DMT (275 g, 1.42 mol) was dissolved in 1250 ml anhydrous *m*-xylene (90°C) in a 2-l flask, equipped with mechanical stirrer, condenser, calcium chloride tube and nitrogen inlet. After addition of 14 ml of the solution of $LiOCH_3$ in methanol, BDA (34 ml, 0.34 mol), dissolved in 150 ml *m*-xylene, was added dropwise in 4 h. During this addition the nitrogen flow was stopped and the temperature was raised to 110°C (5°/h). After 20 h reaction at 110°C, the white precipitate was separated by hot filtration over a glass funnel (pore size 4), purified by soxhlet extraction with toluene for 24 h and subsequently dried over night in a vacuum oven at 70°C.

Route III. DMT (275 g, 1.42 mol) was dissolved in 1100 ml anhydrous toluene and 85 ml anhydrous methanol (60°C) in a 2-l flask equipped with stirrer, condenser, calcium chloride tube and nitrogen inlet. After addition of 10–20 ml of the solution of $LiOCH_3$ in methanol, the temperature was raised to 65°C. BDA (34 ml, 0.34 mol), dissolved in 150 ml toluene and 10 ml methanol was added dropwise for 5 h while the nitrogen flow was stopped. After 3 h from the start of the BDA addition, the temperature was gradually increased up to 90°C (5°/h) while methanol was stripped off. After a total reaction time of 24 h the reaction was stopped. The white precipitate was filtered through soxhlet extraction thimbles and washed twice in hot *m*-xylene (100°C) to remove the DMT. Subsequently, the product was dried in a vacuum oven at 70°C for 24 h.

Recrystallization

Sometimes a recrystallization step was necessary to purify the T4T dimethyl. The product was recrystallized from hot *N*-methyl-2-pyrrolidone (50 g/l at 160°C) and washed twice in hot acetone. The purified T4T dimethyl was dried overnight in a vacuum oven at 60°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 3–5 mg with heating and cooling rates of 20°C/min. The onset of the peak of the first scan was taken as the transition temperature T_m or T_c and the area under the curve as the melting enthalpy 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. Deuterated 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 sec and a 45° pulse.

Li-determination

The lithium concentration was measured by atomic flame emission spectroscopy (AES) using a Varian AA6. Prior to the analysis, the sample (100 mg) was hydrolysed under acidic conditions (mixture of concentrated sulphuric and nitric acid) to disclose trapped lithium. The lithium was atomized by introducing the solution into a flame. The amount of lithium was determined by using lithium reference solutions.

Optical microscopy

The T4T dimethyl powder was placed in between two glass slides and analysed using a Leitz Ortholux II pol-BK optical microscope equipped with 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.

RESULTS AND DISCUSSION

HT4T dimethyl has been synthesized according to the patent of Snam Progetti[9]. 1,4-Butanediamine was added to DMT, dissolved in a mixture of methanol/toluene. An excess of DMT was used to promote the formation of pure T4T dimethyl (4.2 mol DMT/mol BDA). Lithium methanolate was used as a catalyst.

The T4T dimethyl precipitated in the reaction mixture at 65°C. After 24–48 h the white precipitate was filtered off through a glass funnel or a soxhlet extraction thimble. The precipitate contained T4T dimethyl and T4T4(T) besides DMT and T4 which had precipitated during the filtration step. Dimethyl terephthalate was removed by soxhlet extraction with toluene or by washing in hot *m*-xylene. The T4T dimethyl could be purified by recrystallization from hot NMP.

It is assumed that the reaction starts with the fast formation of the intermediate T4 (3). This product precipitates partly and dissolves again to react with DMT to give T4T dimethyl (4). The reactivity of both amine endgroups is considered to be equal. Furthermore, it is assumed that reaction of one endgroup does not influence the reactivity of the other endgroup.

$$\mathrm{DMT} + \mathrm{BDA} \rightarrow \mathrm{T4} \qquad (3)$$

$$\mathrm{T4} + \mathrm{DMT} \rightarrow \mathrm{T4T} \qquad (4)$$

In these equations T stands for a terephthalate group and 4 for a 1,4-butanediamine group.

As soon as T4T dimethyl is formed, it precipitates from the reaction mixture and further reaction is limited. Other reactions that may take place are:

$$\mathrm{T4} + \mathrm{BDA} \rightarrow \mathrm{4T4} \qquad (5)$$

$$\mathrm{T4} + \mathrm{T4} \rightarrow \mathrm{T4T4} \qquad (6)$$

$$\mathrm{4T4} + \mathrm{DMT} \rightarrow \mathrm{T4T4} \qquad (7)$$

$$\mathrm{T4T} + \mathrm{BDA} \rightarrow \mathrm{T4T4} \qquad (8)$$

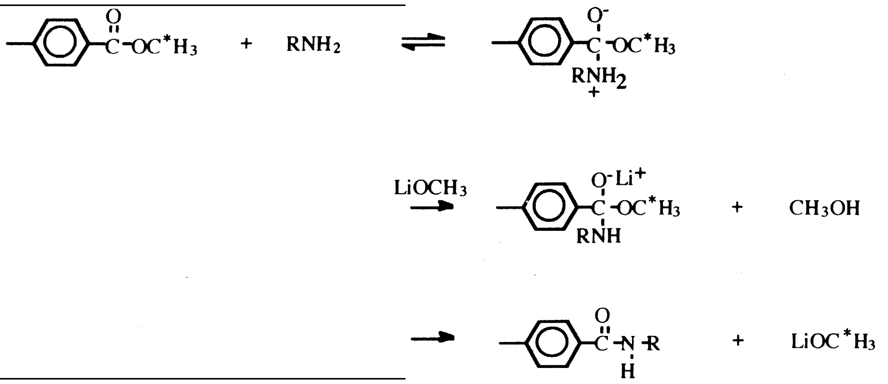
$$\mathrm{T4T} + \mathrm{T4} \rightarrow \mathrm{T4T4T} \qquad (9)$$

$$\mathrm{T4T4} + \mathrm{DMT} \rightarrow \mathrm{T4T4T} \qquad (10)$$

A fast reaction of BDA with DMT is desirable (3). The formed T4 is only partially soluble in the methanol/toluene mixture. The solubility of this component determines the rate of reaction (4), but also of (5) and (6). Reaction (5) is slow compared to (4) if the concentration of BDA is low compared to DMT. For this reason, a large excess of DMT is used and BDA is added dropwise. Reaction (6) is expected to be slow compared to (4) if the concentration of the soluble T4 is low compared to DMT. Reaction (7) is not important since reaction (5) hardly takes place. If all the BDA reacts (3), then reaction (8) will not be important either. Reaction (9) is dependent on the solubility of the T4T dimethyl. Reaction (10) is dependent on the reactions (6), (7) and (8). Thus, the poor solubility of the T4 and the excess DMT limit the formation of T4T4 (6).

Catalysis by $LiOCH_3$

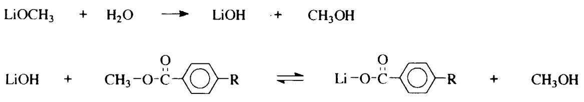
Lithium compounds are known to have a catalytic effect on the amidation reaction[9]. The mechanism is assumed to be a base-catalysed ester aminolysis. The nucleophilic attack of the diamine on the carbonyl carbon is followed by the formation and decomposition of a tetrahedral intermediate[13]. With poor leaving groups, the catalysed decomposition becomes kinetically important. In a number of amidation reactions the proton transfer is the rate-determining step, which explains the importance of the alcoholate counter ion.



(11)

When water is present in the system, lithium hydroxide can be formed (12), which can react further with dimethyl terephthalate to lithium terephthalate (13)[14] These compounds are not catalytically active. This also explains the large amount of LiOCH3 sometimes used to get a high reaction rate[10,11]. Thus, it is important that the catalyst is freshly prepared and that the reaction medium is anhydrous.

$$\mathrm{LiOCH_3} + \mathrm{H_2O} \rightarrow \mathrm{LiOH} + \mathrm{CH_3OH} \qquad (12)$$



(13)

$$\mathrm{LiOCH_3} + \mathrm{H_2O} \rightarrow \mathrm{LiOH} + \mathrm{CH_3OH}$$
$$\mathrm{LiOH} + \mathrm{CH_3{-}O{-}\overset{O}{C}{-}C_6H_4{-}R} \rightleftharpoons \mathrm{Li{-}O{-}\overset{O}{C}{-}C_6H_4{-}R} + \mathrm{CH_3OH}$$

Purity

The purity of the T4T dimethyl has been studied by DSC and by triad analyses of ^{1}H n.m.r. and ^{13}C n.m.r. spectra.

N.m.r. The chemical shifts of the aromatic protons and carbons depend on the para substituted amide and ester groups. The codes and chemical shifts of the important nuclei are given in *Figure 1* and in *Table 1*.

^{1}H n.m.r. In the proton n.m.r. spectra impure products

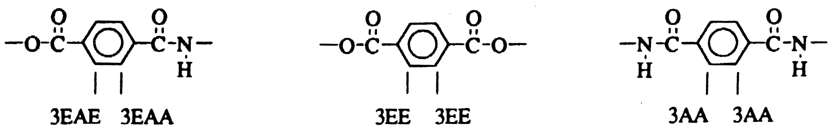


Figure 1 Codes for the different triads used in the n.m.r. analyses

Table 1 Chemical shift of terephthalic protons and carbons of T4T dimethyl in TFA-d. Influence of neighbouring R groups: R_1-T-R_2

Code	R_1	R_2	δ (ppm)	^{1}H n.m.r.	δ (ppm)	^{13}C n.m.r.
3EAE	Ester	Amide	8.30 + 8.34	Doublet	132.6	Singlet
3EAA	Amide	Ester	7.98 + 8.02	Doublet	129.8	Singlet
3EE	Ester	Ester	8.28	Singlet	132.0	Singlet
3AA	Amide	Amide	8.05	Singlet	130.4	Singlet

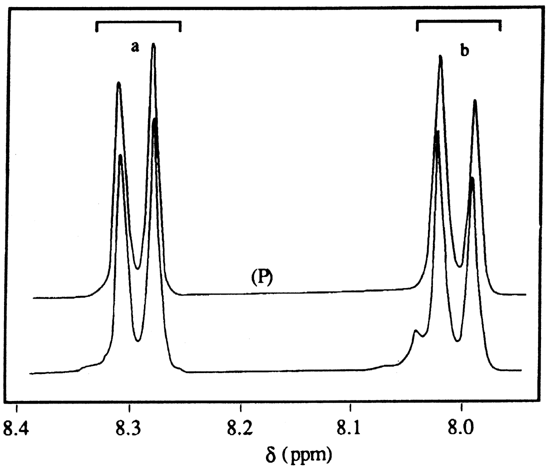


Figure 2 Expanded part of ^{1}H n.m.r. spectra of purified (P) and non-purified T4T dimethyl

(T4T4...) will lead to a 3AA proton peak which will have approximately the same chemical shift as the 3EAA peak, whereas the 3EE peak of residual DMT will overlap with the 3EAE peak. Typical ^{1}H n.m.r. spectra of purified and non-purified T4T dimethyl are given in *Figure 2*.

The terephthalic esteramide content X_{EA} can be calculated by integration of the three protons:

$$E_{EA} = \left(2 - \frac{b}{a}\right) \times 100\% \text{ (mol\%)} \qquad (14)$$

in which *b* is the total integral of 3EAA and 3AA protons and *a* the integral of 3EAE protons. The ratio *b*/*a* can be disturbed by the presence of DMT. However, it is assumed that after extraction or washing and recrystallization no DMT is present anymore. This has been verified by ^{13}C n.m.r.

^{13}C n.m.r. Another, more accurate method to determine the terephthalic esteramide content is by means of ^{13}C n.m.r. (*Figure 3*). Although ^{13}C n.m.r. is less sensitive than ^{1}H n.m.r., the obtained values are more reliable since the carbon atoms show distinct single peaks with different chemical shifts. Because of possible differences in relaxation times only structurally similar carbon atoms were compared[15]. The amide block fraction (X_{AA}/X_A) has been calculated via the integrated peaks of the three carbon atoms (*Table 1*):

$$\frac{X_{AA}}{X_A} = \frac{3AA}{3AA + 3EAA} \times 100\% \text{ (mol\%)} \qquad (15)$$

As can be seen in *Figure 3*, no 3EE peak is present in the ^{13}C n.m.r. spectrum of non-purified T4T dimethyl. This means that there is no DMT present which could disturb the value of the esteramide content X_{EA} obtained through equation (14).

It is also clear that amide–amide sequences are present in the non-purified product (3AA peak). These may be caused by the presence of T4T4, 4T4 or higher oligomers. Van Bennekom[11] showed by NH_2-endgroup analysis that the main side product causing this 3AA peak was T4T4.

After recrystallization from hot NMP the 3AA peak has disappeared (*Figure 3*). This means that amide–amide sequences are absent. In this way pure T4T dimethyl could be obtained. The filtration residue was investigated further with ^{13}C n.m.r. The spectrum showed a large 3AA peak besides a small amount of T4T dimethyl peaks, indicating that at least T4T4 was present.

D.s.c.

A typical thermogram for T4T dimethyl is given in *Figure 4*. Both the purified as well as the non-purified T4T dimethyl show two transition endotherms. The main transition peak is considered to be the isotropic melting peak. After recrystallization from hot NMP this peak shifts to higher temperatures and sharpens (*Tables 2* and *3*). Also the melting enthalpy increases after purification. Since both the melting temperature and the melting enthalpy are very sensitive to impurities, these two values are also taken into account when determining the purity of T4T dimethyl.

Synthesis

Different routes to synthesize T4T dimethyl have been investigated to obtain a pure bisesterdiamide in a high yield. Starting with the synthesis route for T6T dimethyl as described in the patent from Snam Progetti[9], a bisesterdiamide was obtained with an amide block fraction (X_{AA}/X_A) of 5 mol% (T4T-1, *Table 2*). In this reaction an excess of DMT was used (10 mol/mol diamine) and also a large amount of $LiOCH_3$ (30 mol%/mol diamine). The yield of T4T dimethyl was 63%. This was lower than the yield reported for the T6T dimethyl (95%). Increasing the reaction time and decreasing the amount of $LiOCH_3$ resulted in a higher yield, but also in a higher impurity level (compare T4T-1 with T4T-2). Due to the longer reaction time, reactions (9) and (10) could take place.

Because of this low yield and these impurities, other routes have been studied to optimize the yield and purity and to decrease the excess of DMT and the high concentration of $LiOCH_3$.

Table 2 Results of different T4T dimethyl syntheses. Concentrations of DMT (1.05 mol/l) and BDA (0.25 mol/l) were kept constant in all experiments

Batch	Method	Toluene (ml)	Methanol (ml)	Butanol (ml)	$LiOCH_3$*	Time (h)	Temp. (°C)	Yield (wt%)	X_{EA} (mol%)	X_{AA}/X_A (mol%)	*Tm* (°C)	Δ*Hm* (J/g)
T4T-1[a]	—	1084	361	—	30.0	6.5	65	63	96	5	258	142
T4T-2[b]	—	1250	310	—	5.6	40	65	80	90	11	252	111
T4T-3[c]	—	1000	310	—	4.4	42	65	70	—	10	250	112
T4T-4	I	1250	310	—	5.9	40	65	83	94	7	255	117
T4T-5	I	1200	90	—	5.9	48	65	85	98	4	260	145
T4T-6	I	1250	—	40	5.6	24	100	55	97	9	250	110
T4T-7	I	1250	10	15	7.4	24	85	82	96	5	254	124
T4T-8[d]	I	1000	25	—	5.0	7.5	102	60	95	6	253	118
T4T-9[e]	II	—	—	—	5.9	24	110	25	98	1	259	145
T4T-10	III	1250	95	—	5.3	24	65/90	94	98	3	265	152
T4T-11	I	1250	95	—	14.4	6.5	65	65	98	2	264	159

*mol% $LiOCH_3$/mol BDA

[a] Synthesis according to [9]

[b] BDA added all at once

[c] BDA added in five equal portions

[d] Route I at a pressure of 2.9 bar

[e] In *m*-xylene

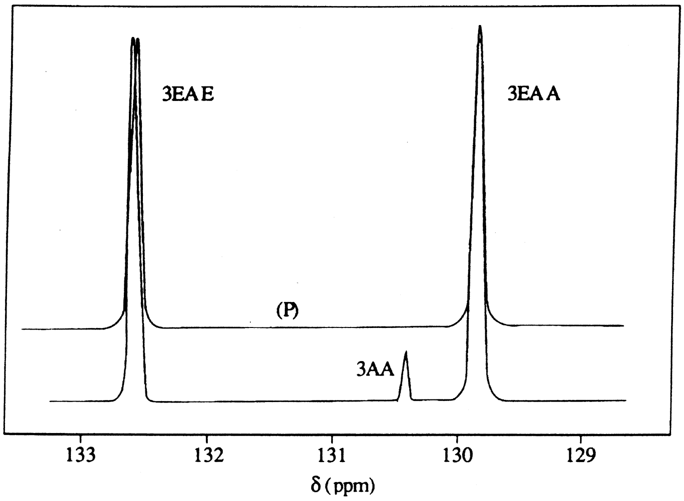


Figure 3 Expanded part of ^{13}C n.m.r. spectra of purified (P) and non-purified T4T dimethyl

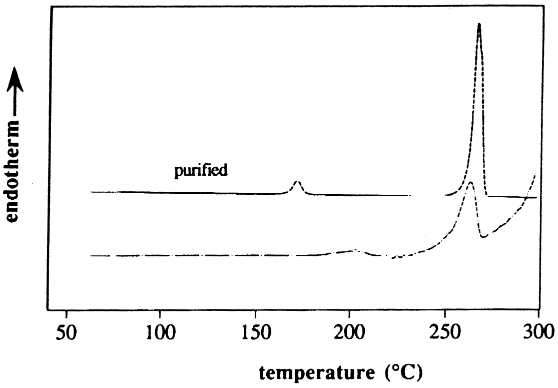


Figure 4 D.s.c. thermograms of purified (recrystallized) and non-purified T4T dimethyl

Table 3 Results of recrystallization of T4T dimethyl from hot NMP

Batch	Yield* (wt%)	X_{EA} (mol%)	X_{AA}/X_A (mol%)	*Tm* (°C)	Δ*Hm* (J/g)
T4T-3p	60	96	3	257	141
T4T-5p	64	100	0	263	158
T4T-10p	65	100	0	265	176

Recrystallization of T4T-3, T4T-5 and T4T-10, respectively

*Overall yield (synthesis and recrystallization)

BDA addition. To reduce the side reactions (5) and (6), DMT was used in a large excess, yielding a high DMT/BDA ratio and a high DMT/T4 ratio. Reaction (5) is limited if the DMT/BDA ratio is high and reaction (6) is limited if the DMT/T4 ratio is high. It is desirable to obtain these conditions of large excess without using a large amount of DMT. This could be achieved by slowly adding BDA. If the rate of addition is slower than the reaction rate, the BDA concentration will be low.

In T4T-3 the BDA was added in five equal portions. Comparing the results with those of T4T-2, where all the BDA is added at once, only little improvement is obtained. The purity could be increased by adding the BDA dropwise for 4–5 h (compare T4T-4 with T4T-2). In this way, the instantaneous excess of DMT over BDA in the reaction mixture was increased enormously in the first hours, while using a smaller amount of DMT compared to earlier syntheses[9,10] (during the reaction the ratio decreased from 283 to 148 mol DMT/mol BDA). Thus, the effect of dropwise addition of BDA to the reaction mixture is a less contaminated product.

Solvent system. Lowering the T4 concentration during the reaction is another method to decrease the amount of

T4T4 and products with higher molecular weights. This could be achieved by changing the polarity of the reaction medium. In T4T-5, for example, where smaller amounts of methanol (90 ml) were used, a white suspension was formed after a few minutes. With higher amounts of methanol (310 ml, T4T-4) it took up to 1 h before the formation of a white precipitate, probably T4, was visible. This suggests that methanol improves the solubility of T4 in toluene. The amide block fraction decreased with decreasing methanol concentration, as can be seen in *Table 2* (T4T-4 and T4T-5). However, at least 90 ml methanol should be present in the reaction mixture to keep the DMT in solution.

The replacement of methanol by butanol allowed higher reaction temperatures (T4T-6 and T4T-7). This favours a fast reaction of T4 with DMT to yield T4T dimethyl. However, the higher temperatures did not lead to higher selectivities. Probably, the solubility of T4 was also enhanced, resulting in a larger concentration of T4 in solution. At these higher reaction temperatures also some ester interchange occurred, which means that some methyl endgroups were replaced by butyl endgroups. This, together with the longer amide blocks, disturbed the structural order of the product, resulting in a lower melting enthalpy and melting temperature of the T4T dimethyl. Besides this, the T4T dibutyl itself has a lower melting enthalpy and temperature because of the longer alkyl endgroups. We, for example, have synthesized pure T4T didodecyl which had a Tm of only 196°C and a ΔHm of 112 J/g.

Another method that allows increase in the temperature while still using methanol is a reaction at high pressure. T4T-8 was made in this way. The reaction was carried out at a pressure of 2.9 bar for 6 h with only 25 ml methanol. The high reaction temperature (102°C) led to a reasonable yield of T4T dimethyl in a short time. But the purity was not higher than with the butanol reactions.

The batch T4T-9 has been synthesized in *m*-xylene at 110°C. Because of the low polarity of the solvent, pure T4T dimethyl was formed. However, the yield under these conditions was low. In the absence of methanol the catalyst did not seem to be active. Only at the beginning some methanol was present which was stripped off during the further reaction.

In agreement with earlier findings concerning the methanol concentration, the next step was the removal of methanol during the reaction by gradually increasing the reaction temperature (T4T-10). This increased the purity of the T4T dimethyl and, at the same time, increased the yield considerably. The T4 intermediate is probably only for a short period in solution, reacting fast to form T4T dimethyl. No products with higher molecular weights or other complexes could be formed (e.g. Li complexes (13)). This resulted in a high yield and, because of the higher reaction temperatures, in shorter reaction times (less than 24 h). This also suggests that methanol is only necessary in a large amount at the beginning of the reaction to quickly form T4. In the second stage of the reaction only a small amount of methanol may be necessary to convert T4 into T4T dimethyl.

The foregoing experiments suggest that the reaction of BDA with DMT proceeds well in a solvent mixture with a reasonable methanol concentration. However, to limit the formation of products with higher molecular weights, the methanol concentration should be low. Thus, at the beginning of the reaction the methanol concentration should be higher than at the end. In experiment T4T-10 the temperature of the reaction medium was gradually increased from 65 to 90°C, thereby decreasing the methanol concentration. As a result of this, the amount of higher amides was low and the melting enthalpy of the product was high. Surprisingly the yield was high too.

Catalyst. The amount of lithium catalyst used in the 'Snam Progetti' experiment was very high (T4T-1). This seemed to be necessary because of the presence of water in the system. The lithium reacted with water and formed lithium terephthalate complexes ((12) and (13)). Probably, a smaller amount of lithium can be used when no water is present. In our system the water content was estimated to be about 10 mmol at maximum. This implies that if the system was completely dry, less than 5 mmol of $LiOCH_3$ would be sufficient. This would also lead to less residual lithium in the product.

Without adding BDA no white precipitate was formed, thus the lithium complexes which might be formed were soluble or at least were only present in small amounts (reaction (12) and (13)). According to Cognigni *et al.*[14] the solubility of lithium terephthalate is 7 mmol/l in a 10/90 vol% methanol/toluene mixture. As in our experiments no white precipitate was detectable before BDA was added, less than 9.4 mmol water was present in our system (in about 1.3 l).

It was observed that the reaction slowed down in time. Adding fresh catalyst during the reaction increased the rate again and thus the yield. The reaction time could be shortened when a much higher lithium concentration was used (T4T-11). The purity of the product was higher compared to T4T-1 because of the lower methanol concentration. It is also clear from *Table 2* that the yield does not increase linearly with time.

From the reaction in *m*-xylene without methanol it can be concluded that the alcoholate ion is important for the catalytic mechanism. Without methanol the reaction stopped, once the methanol from the $LiOCH_3$ solution had evaporated (T4T-9). Another alcoholate counter ion could be used also, although this led to a lower reaction rate and yield (T4T-6). Adding a small amount of methanol to the butanol reaction mixture increased the reaction rate and thus the yield (T4T-7).

The catalyst concentration in the reaction medium was 367–615 ppm (calculated for the solid part, DMT and T4T dimethyl). After washing with *m*-xylene or toluene, the lithium concentration in the reaction product was still 170 ppm. A further reduction could be obtained by recrystallization from hot NMP. The lithium cation interacted with NMP by dipole–dipole interaction or by covalent bonding and was excluded from the growing crystallites. In this way the amount of lithium residues could be decreased to 20–30 ppm.

From the ^{1}H n.m.r. analyses of the different T4T dimethyl batches it became clear that with longer reaction times the X_{AA}/X_A increases which means that main impurities were products with a high molecular weight. Probably the T4 had enough time to react further to T4T4 and T4T4T. Reducing the reaction time decreased the amount of amide–amide sequences, but increased the amount of impurities such as T4 and cyclic endgroups (a small extra peak was visible at 3.4 ppm).

A balance must be sought between the yield and the purity of the product. Shorter reaction times result in a low yield with a reasonable purity, longer reaction times give a higher yield but a lower purity.

Recrystallization

A purification step was necessary since most of the products still contained some impurities. Recrystallization of the product from hot NMP (160°C) removed the side products such as T4, T4T4 and cyclic endgroups. This purification step increased the melting temperature and melting enthalpy significantly (*Table 3*). However, the procedure was time consuming and lowered the yield considerably. Furthermore, the impurities were only removed to a certain extent. When a sample contained a high concentration of side products, only part of these products were removed (compare T4T-3 and T4T-3p with T4T-10 and T4T-10p). With a second recrystallization step further purification was possible.

Thermal properties

As mentioned before, two transition endotherms are present in the d.s.c. thermogram of T4T dimethyl, the second being the melting peak. The first transition peak at 160–175°C is probably caused by a transition in the crystalline structure as it could not be detected anymore in a second heating cycle (*Figure 5*). This is a phenomenon well known for nylon-6,6[16,17]. During heating, the triclinic structure changes to a pseudo hexagonal structure at a certain temperature. This is the so-called Brill temperature[18]. Crystallization occurs in hexagonally packed chains which rearrange during further cooling in a triclinic structure[19]. The transition peak is often not present anymore in the d.s.c. scan on reheating. It can, however, still be made visible with X-ray measurements[20], in the first as well as in the second heating run. Since T4T dimethyl shows a similar behaviour, we assume that at 160–175°C also a transition in the crystalline structure takes place although this is not investigated with X-ray diffraction.

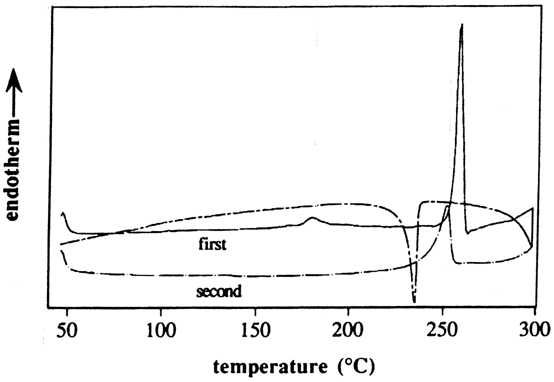


Figure 5 First and second heating scan of purified T4T dimethyl

The spherulitic structure of the T4T dimethyl could be changed by using different solvents from which it precipitated. When using polar solvents (methanol/toluene mixture and NMP) the transition peak was noticeable upon heating and the T4T dimethyl probably crystallized in the favoured triclinic structure. When non-polar solvents (*m*-xylene and toluene) were used, no transition peak was visible upon heating the sample and the hexagonal structure was formed.

This transition in the crystalline structure could be observed by cross polarized light microscopy. The samples, precipitated in polar solvents, showed a change in colour at the transition temperature while the samples precipitated in non-polar solvents did not. A melt pressed sample did not show any colour change either.

In *Figure 6* the melting temperature of T4T dimethyl is given as a function of the relative amide block fraction. The melting temperature decreases with increasing amide block fraction. The longer amide blocks disturb the regular packing of the T4T dimethyl and thus lower the enthalpy and the melting point. Similar graphs can be plotted for T_m *versus* 1-X_{EA} and ΔH_m *versus* 1-X_{EA} or X_{AA}/X_A.

The purity of the product was determined by several methods. The sensitivity of ^{1}H and ^{13}C n.m.r. analysis by themselves is only 2–3%. We found that the melting temperature and melting enthalpy gave more reliable values for the purity of the T4T dimethyl. Only a minor impurity consisting of longer amide blocks already leads to a drastic drop in the melting enthalpy and the melting temperature. Also the presence of small amounts of low molecular weight products (e.g. cyclic products) which do not contain amide–amide triads and thus can not be detected by n.m.r., were detectable with d.s.c. The n.m.r. results would wrongly imply that the product was pure (e.g. T4T-5 and T4T-9).

So a combination of n.m.r. and d.s.c. analyses gave the best results. We consider the product to be sufficiently

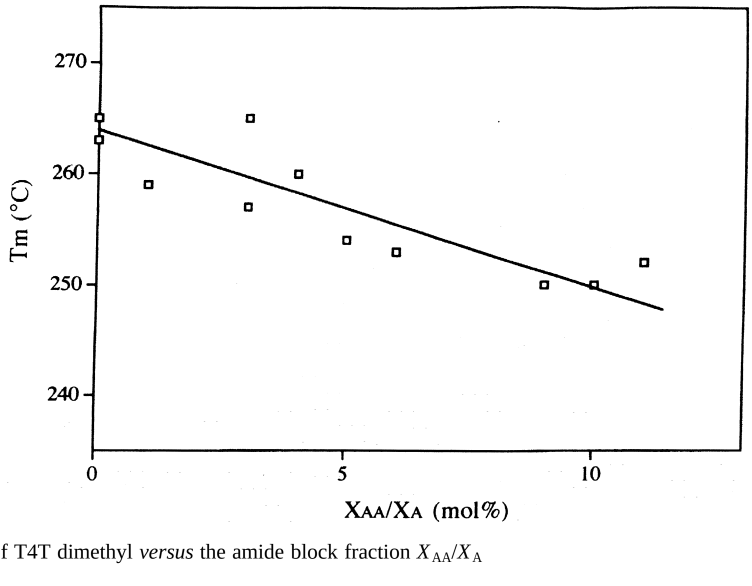


Figure 6 Melting temperature of T4T dimethyl *versus* the amide block fraction X_{AA}/X_A

pure for polymerization if the $X_{\mathrm{AA}}/X_{\mathrm{A}}$ value is less than 2%, the melting enthalpy is higher than 158 J/g and the melting temperature is 264–265°C. The ΔH_m value measured for purified T4T dimethyl (176 J/g) was higher than the value calculated with the Van Krevelen method (155 J/g)[21].

CONCLUSIONS

In this study it was shown that pure T4T dimethyl could be obtained by reaction of 1,4-butanediamine and dimethyl terephthalate. A methanol/toluene mixture was used as reaction medium. Important in this reaction was the partial solubility of the T4 intermediate and the poor solubility of T4T dimethyl. Dropwise adding of the BDA increased the DMT/BDA ratio, leading to a higher purity of the product. By changing the concentration of the solvents, the purity of the products was changed. Lowering the methanol concentration resulted in products with a higher purity. Replacing the methanol by butanol, which allowed higher reaction temperatures, did not increase the yield and purity. Reaction in a non-polar solvent (*m*-xylene) gave a pure product, but in a low yield.

Methanol was necessary for the reaction to take place, but probably only in the first step of the reaction. Reducing the methanol content in a later stage of the reaction increased the purity of the T4T dimethyl while the yield was still high. The best way to obtain pure T4T dimethyl was by using a small amount of methanol and distilling off the methanol during the reaction.

The catalyst $LiOCH_3$ was necessary to obtain a high yield. The yield was very susceptible to a fresh catalyst and a dry reaction system.

The T4T dimethyl could be further purified by recrystallization from hot NMP. The purified product still contained a small amount of lithium residues (20–30 ppm).

The T4T dimethyl showed two endothermic transitions. The first peak at 160–175°C was attributed to a transition in the crystalline structure. The triclinic cell structure transforms into a pseudo hexagonal one. The purified product had a melting temperature of 265°C and a melting enthalpy of more than 176 J/g. The melting temperature decreased with increasing amide block fraction.

ACKNOWLEDGEMENTS

This work was financially supported by Dow Benelux NV, Terneuzen, The Netherlands.

REFERENCES

1. Aharoni, S. M., *Macromolecules*, 1988, **21**, 1941.
2. Carothers, W. H., US Patent 2.071,250, DuPont de Nemours, USA, 1931.
3. Goodman, I. and Sheahan, R. J., *Eur. Polym. J.*, 1990, **26**, 1081.
4. Goodman, I. and Rodriguez, M. T., *Macromol. Chem. Phys.*, 1994, **195**, 1075.
5. Williams, J. L. R., Laakso, T. M. and Contois, L., *Eur. J. Polym. Sci.*, 1962, **61**, 353.
6. Williams, J. L. R., Laakso, T. M., Dunham, K. R., Borden, D. G., Van Den Berghe, J., Van Allan, J. A. and Reynolds, D. D., *J. Org. Chem.*, 1960, **25**, 817.
7. Goodman, I. and Starmer, D. A., *Eur. Polym. J.*, 1991, **27**, 515.
8. Manzini, G., Creszenci, V., Ciana, A., Ciceri, L., Della Fortuna, G. and Zotteri, L., *Eur. Polym. J.*, 1973, **9**, 941.
9. Ciceri, L., Di Gregorio, F. and Platone, E., GB Patent 1 365 952, Snam Progetti S.p.a., Milan, 1971.
10. Gaymans, R. J. and de Haan, J. L., *Polymer*, 1993, **34**, 436011.
11. Van Bennekom, A. C. M. and Gaymans, R. J, *Polymer*, 1996, **37**, 5439.
12. Matthijssen, J.-J., Segmented block copolymers with uniform crystalline blocks, a high melting temperature and a high glass transition temperature. Twaio report, University of Twente, 1993.
13. Challis, B. C. and Butler, A. R., *The Chemistry of the Amino Group*, Chap. 6. Interscience Publishers, London, 1968.
14. Cognigni, F. and Mariano, A., DE Patent 30 29 970 A1, Anic. S.p.a., Italy, 1981.
15. Tonelli, A. E., *NMR Spectroscopy and Polymer Microstructure: The Confirmational Connection*. AT and T Bell Laboratories, Murray, NJ, 1989.
16. Todoki, M. and Kawaguchi, T., *J. Polym. Sci. Phys. Ed.*, 1977, **15**, 1067.
17. Hirschinger, J., Miura, H., Gardner, K. H. and English, A. D., *Macromolecules*, 1990, **23**, 2153.
18. Brill, R., *J. für die Praktische Chemie N.F.*, 1942, **161**, 49.
19. Ramesh, C., Keller, A. and Eltink, S., *J. Polymer*, 1994, **35**, 2843.
20. Ramesh, C., Keller, A. and Eltink, S., *J. Polymer*, 1994, **35**, 2483.
21. Van Krevelen, D. W., *Properties of Polymers*, Chap. 6. Elsevier, Amsterdam, 1989.