Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 7043–7053

polymer

www.elsevier.com/locate/polymer

Synthesis and characterisation of uniform bisester tetra-amide segments

J. Krijgsman[1], D. Husken, R.J. Gaymans*

Laboratory of Polymer Technology, Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Received 13 November 2002; received in revised form 7 March 2003; accepted 24 July 2003

Abstract

The synthesis and characterisation of a new type of high melting and fast crystallising amide units that can be used for copolymerisation have been studied. These bisester tetra-amide or TxTxT-dimethyl segments (T is a terephthalic unit and x = $(CH_2)_n$ ($n = 2-8$)) can be synthesised in a two-step reaction. These segments are based on two-and-a-half repeating units of nylon-x,T. The structure of the products was confirmed by NMR. The melting temperature and enthalpy of xTx-diamine and TxTxT-dimethyl and -diphenyl were determined by DSC. The melting temperature increases with decreasing length of x. For odd x the melting temperature is lower. The melting temperature and enthalpy of the products decrease with decreasing purity.

Keywords: Uniform; Tetra-amide; Nylon-6,T

1. Introduction

Segmented or multi-block copolymers often consist of alternating crystallisable and amorphous segments. The high melting crystalline phase gives the material dimensional stability, heat stability and solvent resistance. If the crystallisable segment has a regular structure and a uniform length than the crystallisation of the segment is faster and more complete and the properties of the copolymer are better [1–4]. Thus far the only uniform amide segments that have been described are di-amides [5–13]. A higher melting temperature can be obtained, when tetra-amide segments are formed during polymerisation by extending bisester di-amide units with a diol [13–16]. These extended di-amide segments have a higher melting temperature because the lamellar thickness is higher [17]. However, the melting temperature is broad due to a distribution in the segment lengths.

A new type of uniform amide segment that is a bisester tetra-amide segment has been developed. This tetra-amide segment can form four hydrogen bonds as compared to the di-amide segments that can only form two. The lamellar thickness of a tetra-amide segment is higher than that of a di-amide segment and as a result the melting temperature is expected to be higher than that of the corresponding di-amide units [17].

Bisester tetra-amides can be synthesised from aliphatic, alicyclic or aromatic diamines and diacids or derivatives of diacids. In particular bisester tetra-amides TxTxT-dimethyl (Fig. 1) based on a terephthalic diacid (T) and an aliphatic diamine (x = $(CH_2)_n$ with $n = 2-8$) were studied. T6T6T-dimethyl, for example, is based on two-and-a-half repeating unit of nylon-6,T (poly(hexamethylene terephthalamide)).

The bisester tetra-amides can be synthesised quite easily in two steps. For example in the case of T6T6T-dimethyl, first 6T6-diamine (di-(4-aminohexyl)terephthalamide) is made from dimethyl terephthalate (DMT) and 1,6-hexanediamine. The synthesis of 6T6-diamine is derived from the synthesis of 4T4-diamine (di-(4-aminobutyl)terephthalamide, DABT) [5]. Then 6T6-diamine is reacted with methyl phenyl terephthalate (MPT) to obtain the corresponding bisester tetra-amide.

In this article the synthesis and characterisation of different bisester tetra-amide segments (TxTxT-dimethyl or TxTxT-diphenyl) and precursors thereof (xTx-diamine) are described. The structure, purity and melting behaviour of these segments were analysed using NMR and DSC. The bisester tetra-amides were studied by IR and WAXD as well.

---

* Corresponding author.
E-mail addresses: j.krijgsman@kema.nl (J. Krijgsman), r.j.gaymans@ct.utwente.nl (R.J. Gaymans).

[1] Present address: KEMA Nederland B.V., Arnhem, The Netherlands. Tel.: +31-263-563-531; fax: +31-263-563-531

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00681-5

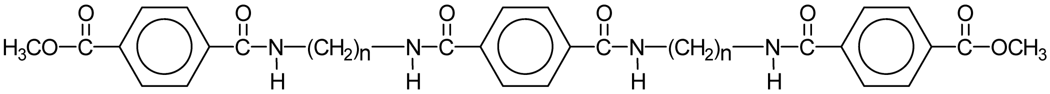

Fig. 1. Structure of TxTxT-dimethyl (x = $(CH_2)_n$ with $n = 2$–8).

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), 1,2-ethanediamine, 1,3-propanediamine, 1,4-butanediamine, 1,6-hexamethylenediamine (HMDA), 1,7-heptanediamine, 1,8-octanediamine, terephthaloylchloride (TCl), triethylamine, phenol, n-butyl acetate, diethyl ether and *N*-methyl-2-pyrrolidone (NMP) were purchased from Merck. Methyl-(4-chlorocarbonyl) benzoate (MCCB) was obtained from Dalian (no. 2 Organic Chemical Works P.R.O.C.). All chemicals were used as received.

2.2. Synthesis of methyl phenyl terephthalate (MPT)

A mixture of phenol (150 g, 1.6 mol) and triethylamine (73 g, 0.7 mol) was heated to 60 °C in a 500 ml flask equipped with magnetic stirrer, condenser, calcium chloride tube and nitrogen inlet. Then MCCB (100 g, 0.5 mol), previously dissolved in 200 ml NMP, was added dropwise. After 3 h the product was precipitated in 2 l of warm water (70 °C). The precipitate was separated using a glass filter and washed twice with 50/50 water/ethanol (50 °C). The product was subsequently dried in a vacuum oven at 50 °C. The yield was 93%. The purity as determined by ^{1}H NMR was $>98\%$ and the product had a melting temperature of 114 °C and a melting enthalpy of 135 J/g [^{1}H NMR: OCH_3, s, 3.91 ppm; OC_6H_5 (*ortho*), d, 6.97 ppm; OC_6H_5 (*para*), t, 7.14 ppm; OC_6H_5 (*meta*), t, 7.25 ppm; $-C_6H_4-CO-CH_3$, d, 8.05 ppm; $-C_6H_4-CO-C_6H_5$, d, 8.16 ppm].

2.3. Synthesis of diphenyl terephthalate (DPT)

A mixture of TCl (100 g, 0.5 mol) and phenol (140 g, 1.5 mol) was heated to 50 °C in a 500 ml flask equipped with magnetic stirrer, condenser, nitrogen inlet and HCl outlet. The HCl that was formed was lead through a NaOH solution (40 g, 1.0 mol in 1 l water). After 1 h the reaction mixture was partly solidified. After 3 h the product was washed with 2 l of warm water (70 °C). The product was separated with a glass filter and washed twice with warm ethanol (50 °C). The product was subsequently dried in a vacuum oven at 50 °C. The yield was 91%. The purity as determined by ^{1}H NMR was $>99\%$ and the product had a melting temperature of 206 °C and a melting enthalpy of 155 J/g [^{1}H NMR: OC_6H_5 (*ortho*), d, 7.25 ppm; OC_6H_5 (*para*), t, 7.41 ppm; OC_6H_5 (*meta*), t, 7.50 ppm; $OC-C_6H_4-CO$, s, 8.50 ppm].

2.4. Synthesis of di-(6-aminohexyl)terephthalamide (DAHT or 6T6-diamine) [5]

A mixture of DMT (39 g, 0.20 mol) and HMDA (139 g, 1.2 mol) was heated to 120 °C in a 1 l stirred round bottomed flask with nitrogen inlet and a reflux condenser. At 80 °C a clear solution was formed and methanol started boiling off. When a temperature of 120 °C was reached, precipitation had started. After 4 h at 120 °C 500 ml toluene was added to the thick suspension and the mixture was allowed to cool to 100 °C under stirring. The product was collected by filtration with a glass filter and washed twice with hot toluene (80 °C). Finally the product was washed with diethyl ether and dried at room temperature.

The product that contained some $6(T6)_n$-diamine (with $n \geq 2$) and other impurities, was recrystallised from n-butyl acetate at 110 °C (15 g/l).

2.4.1. Synthesis of other xTx-diamine segments

Other xTx-diamine segments were prepared according to the method for the synthesis of 6T6-diamine. The amine/ester ratio and the reaction time and temperature were changed for some reactions. Also the recrystallisation step was modified for some of the xTx-diamine segments (Table 1).

2.5. Synthesis of T6T6T-dimethyl

A mixture of 6T6-diamine (7.24 g, 0.02 mol) and MPT (20.5 g 0.08 mol) was dissolved in 400 ml NMP in a 1 l

Table 1
Reaction conditions for the synthesis of different xTx-diamine segments

	Excess amine [mol]	Temperature [°C]	Time [hours]	Yield [%]	Recrystallisation (n-butyl acetate) [g/l]
2T2-Diamine	5	60	5	83	50
3T3-Diamine	3	80	4	96	50
4T4-Diamine	3	100	4	77	20
6T6-Diamine	5	120	4	94	15
7T7-Diamine	5	100	4	81	10
8T8-Diamine	3	120	4	76	10

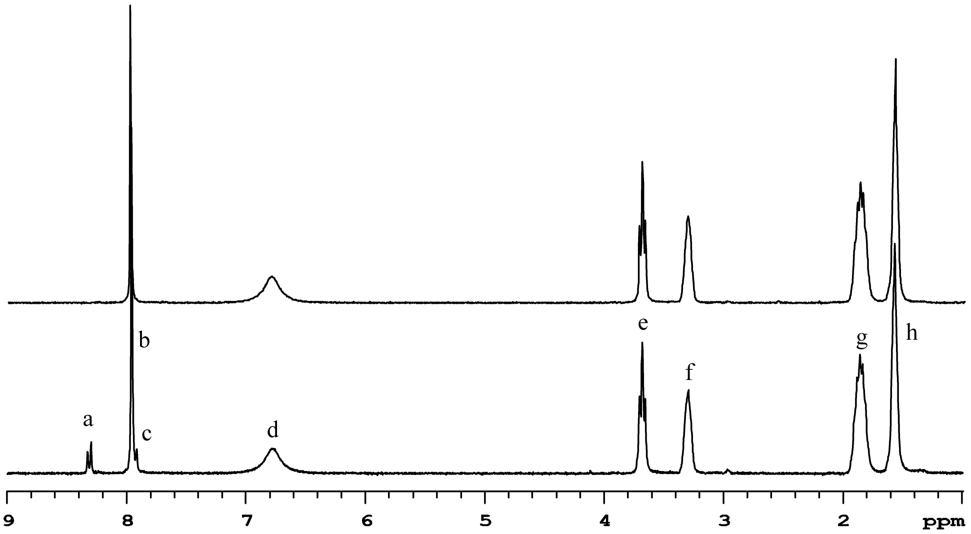

Fig. 2. 6T6-diamine before (lower curve) and after recrystallisation (upper curve).

stirred round bottomed flask with nitrogen inlet and a reflux condenser. The mixture was warmed to 120 °C and kept at that temperature for 16 h. After cooling, the precipitated product was collected by filtration using a glass filter and washed with NMP, warm toluene (70 °C) and warm acetone (50 °C). The product was dried in a vacuum oven at 50 °C.

2.5.1. Synthesis of other TxTxT-dimethyl segments

Other TxTxT-dimethyl segments were prepared according to the procedure for the synthesis of T6T6T-dimethyl using 0.02 mol of different xTx-diamines.

2.6. Synthesis of T6T6T-diphenyl

A mixture of 6T6-diamine (7.24 g, 0.02 mol) and DPT (38 g, 0.12 mol) was dissolved in 400 ml NMP in a 1 l stirred round bottomed flask with nitrogen inlet and a reflux condenser. The mixture was warmed to 120 °C and kept at that temperature for 16 h. After cooling, the precipitated product was collected by filtration using a glass filter and washed with NMP, warm toluene (70 °C) and warm acetone (50 °C). The product was dried in a vacuum oven at 50 °C.

The product that contained some $T(6T6T)_n$-diphenyl (with $n \geq 2$) as well, was recrystallised from NMP (120 °C, 40 g/l). The product was dried in a vacuum oven at 50 °C.

2.7. NMR

^1H NMR spectra were recorded on a Bruker spectrometer at 300 MHz. Deuterated trifluoro acetic acid (D-TFA) was used as a solvent.

2.8. DSC

DSC spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried samples of 3–7 mg were heated to 340 °C at a rate of 20 °C/min. The peak temperature of the melting peak of the first heating scan was taken as the melting temperature, the peak area was used to calculate the melting enthalpy.

2.9. WAXD

X-ray diffraction data of different TxTxT-dimethyl were collected with a Philips PW3710 based X'Pert-1 diffractometer in Bragg–Brentano geometry, using a Θ compensating divergence slit (12.5 mm length). Powder diffraction data collection was performed at room temperature, using a low-background spinning (1 r/s) specimen holder. Cu $K_{\alpha 1}$ radiation of 1.54056 Å was obtained, using a curved graphite monochomator. The data were collected in a range of $2\Theta = 4$–$60°$.

2.10. IR

FTIR data were obtained using a Bio-Rad Model FTS-60 spectrometer with a resolution of 4 cm^{-1}. Samples were prepared by pressing tablets of dry KBr that was milled together with some sample.

3. Results and discussion

3.1. Introduction

The synthesis and characterisation by NMR and DSC of 6T6-diamine, T6T6T-diphenyl and T6T6T-dimethyl will be described in detail. The results for other xTx-diamine and TxTxT-dimethyl segments will be given more briefly. The purity of the different products was calculated from the ^1H NMR spectra. The melting endotherms of the different segments as measured by DSC give an indication of the purity as well. A pure product has a high melting

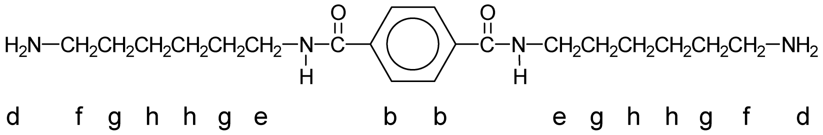

Fig. 3. Peak assignment of protons of 6T6-diamine.

temperature, a high heat of fusion (ΔH_m) and a sharp melting peak. It was not possible to measure the purity by GPC as the segments are not soluble in common GPC solvents.

3.2. 6T6-diamine

The melt reaction between dimethyl terephthalate and 1,6-hexamethylenediamine to synthesise 6T6-diamine was fast. Before the reaction temperature of 120 °C was reached, precipitation had caused solidification of the reaction mixture. The yield of this reaction was 94%. The product was a white powder. The product that was obtained in this melt reaction had a low purity (70–80%). It was not possible to calculate the theoretical Flory distribution of the product, as the reactivities of the second amine and second ester groups are different than that of their first groups [18]. After recrystallisation from boiling n-butyl acetate the purity was >97%. The yield of the recrystallisation step was 48%.

3.2.1. NMR

In Fig. 2 the ^{1}H NMR spectra of 6T6-diamine before and after recrystallisation are given. The peak assignments are given in Fig. 3 and in Table 2 the integrals and peak assignments for the product after synthesis and the product and residue after recrystallisation are given.

The integrals of the peaks of the product after recrystallisation correspond well with the theoretical number of protons. The NMR spectrum of this product contains no peaks of side products. Therefore it can be concluded that 6T6-diamine with a very high purity is obtained after recrystallisation.

The product directly after synthesis contains some side products. Peak a and c (two doublets) in the spectrum of the product are from a side product. The structure of this side product is not known. Next to this side product, also further reacted 6T6-diamine, for example 6T6T6-diamine and 6T6T6T6-diamine, will be present. The purity of the product directly after synthesis is approximately 70–80%. By recrystallisation of the product after synthesis from boiling n-butyl acetate 6T6-diamine of high purity can be obtained. The side product (peak a and c) and all further reacted 6T6-diamine do not dissolve in boiling n-butyl acetate and can be found in the residue after recrystallisation.

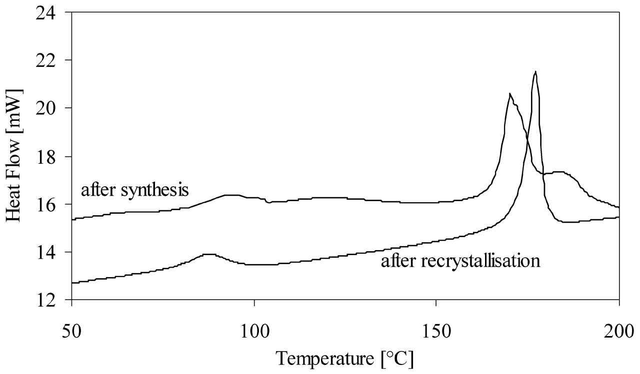

Fig. 4. First heating scan of 6T6-diamine after synthesis and after recrystallisation.

The uniformity of 6T6-diamine after recrystallisation can be calculated when several assumptions are made. In the first place it is assumed that no products with a lower molecular weight than 6T6-diamine are present, as these compounds will be removed from the product mixture during the washing steps. Secondly it is assumed that the only other products present are $6(T6)_n$. No products like 6T6T are present, otherwise a peak originating from the methyl ester endgroup on the terephthalic side (4.1 ppm) should be visible in the spectrum and this is not the case. The side product (peak a and c) remains in the residue during recrystallisation. A last assumption that is made, is that after recrystallisation only 6T6T6-diamine will be present next to the product 6T6-diamine, because further reacted 6T6-diamine such as 6T6T6T6-diamine is not likely to dissolve in n-butyl acetate.

Based on these assumptions the uniformity of the recrystallised product can be calculated by Equation (1). The ratio between the CH_2 group next to the amide bond (peak e) and the CH_2 group that is coupled to the NH_2 endgroup (peak f) is used to calculate the uniformity. For the product 6T6-diamine this ratio is 1:1, for 6T6T6-diamine the ratio amide-side/amine-side = 2:1.

$$\text{purity 6T6} - \text{diamine} = (2 - e/f)100\% \qquad [\%] \qquad (1)$$

Based on Equation (1) it can be concluded that the product after recrystallisation has a purity of >99%, and thus contains only up to 1% of the further reacted 6T6T6-diamine.

3.2.2. DSC

With DSC the melting endotherms of 6T6-diamine before and after recrystallisation were measured. In Fig. 4 the first heating scans of 6T6-diamine before and after recrystallisation are compared. In Table 3 the peak temperature of the melting peak and the heat of fusion of 6T6-diamine are given.

The DSC heating curve of recrystallised 6T6-diamine

Table 2
Chemical shifts δ and peak assignment of protons of 6T6-diamine

Peak	δ [ppm]	Type	Theoretical protons	Integral after synthesis	Integral after recrystallisation (product)	Integral after recrystallisation (residue)	Description
a	8.37	Doublet	*x*	0.58	0	1.36	Terephthalic *H*, impurity
b	7.98	Singlet	4	3.79	4.01	3.64	Terephthalic *H*
c	7.96	Doublet	*x*	0.58	0	1.36	Terephthalic *H*, impurity
d	6.8	Singlet	4	3.64	3.42	3.52	NH_2 Endgroups
e	3.69	Triplet	4	4.29	4.01	5.16	1st CH_2 HMDA, amide side
f	3.31	Singlet	4	4.00	4.00	4.00	6th CH_2 HMDA, amine side
g	1.86	Singlet	8	8.41	8.03	9.36	2th and 5th CH_2 HMDA
h	1.58	Singlet	8	8.43	8.05	9.16	3th and 4th CH_2 HMDA

shows a sharp melting peak with a peak temperature of 178 °C and a melting enthalpy of 130 J/g. The product after synthesis shows a double melting transition. The presence of further reacted products ($6(T6)_n$ with $n \geq 2$) and side products next to 6T6-diamine disturb the regular packing of 6T6-diamine and thus lowers the enthalpy and the melting point. Further reacted $(6(T6)_n$ has a higher melting temperature because the lamellar thickness is higher [17].

At 80–100 °C there is a broad peak that is possibly due to a transition in the crystalline structure of the 6T6-diamine. This phenomenon is well known polyamides, for example nylon-6,6 [19,20].

3.2.3. Other xTx-diamine segments

The other xTx-diamine segments could be prepared easily in a fast melt reaction according to the same method as for 6T6-diamine. The yield and purity of the products before and after recrystallisation and the melting temperatures and enthalpies of the recrystallised products are given in Table 3.

All xTx-diamine segments can be obtained with a high yield between 77 and 96%. The purity of the products after synthesis is above 67% and seems to increase with increasing length of the diamine.

Recrystallisation of xTx-diamines with $n = 6–8$ from n-butyl acetate gives the highest yields. Recrystallisation of the other xTx-diamines from n-butyl acetate was possible, but with lower yields. The use of other recrystallisation solvents may further improve the yields of these xTx-diamines.

With DSC it was shown that the xTx-diamine segments after synthesis all show multiple melting transitions. After recrystallisation all xTx-diamines have a high purity and show a sharp melting peak. The melting temperature increases with decreasing length of x for even x. For odd numbers of x the melting temperature is lower because these segments are less ordered. The melting enthalpy of 2T2-diamine and 3T3-diamine is very high. Probably degradation starts upon melting.

3.3. T6T6T-diphenyl

T6T6T-diphenyl was synthesised from diphenyl terephthalate (DPT) and 6T6-diamine using NMP as a solvent. During the reaction at 120 °C a part of the product precipitated and more product precipitated on cooling. The yield of this reaction was 90%. The product was a white powder. Despite the large excess of DPT used, the product had a low purity or uniformity. DPT can react at both ends and therefore further reacted products, such as T6T6T6T6T-diphenyl, can be formed easily. After recrystallisation from hot NMP the uniformity was excellent. The yield of the recrystallisation step was 53%.

3.3.1. NMR

In Fig. 5 the ^{1}H NMR spectrum of T6T6T-diphenyl after recrystallisation is given. The peak assignments are given in Fig. 6 and in Table 4 the integrals and peak assignments for the product after synthesis and for the product and residue after recrystallisation are given.

Table 3
Properties of different xTx-diamine, compared to 6T6-diamine

Amine		After synthesis		After recrystallisation			
$[(CH_2)_n]$ $n =$	T_m [°C]	Yield [%]	Purity [%]	Yield[a] [%]	Purity [%]	T_m [°C]	ΔH_m [J/g]
2	10	83	67	6	99	234	400
3	−22	96	78	8	98	209	300
4	27	77	68	11	96	210	150
6	39	94	71	48	99	178	130
7	28	81	79	64	96	168	100
8	53	90	93	43	98	173	130

[a] Yield of the recrystallisation step.

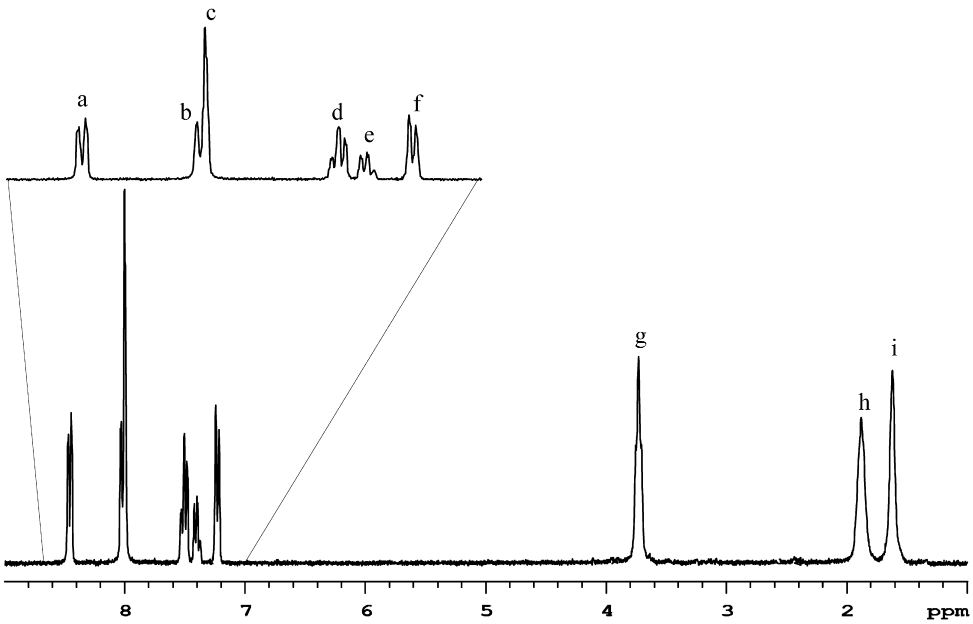

Fig. 5. ^{1} NMR spectrum of T6T6T-diphenyl.

The purity or uniformity of T6T6T-diphenyl can be calculated by comparing the integrals of the peaks of the aromatic protons of the ester–amide and amide–amide terephthalic groups. In this calculation it is assumed that there are no products with a lower molecular weight as these products are expected to be soluble in NMP. This assumption can be made because T6T6T-diphenyl itself is soluble in NMP when it is heated to at least 60 °C. Products with a lower molecular weight are therefore probably soluble in NMP at room temperature. Another assumption is that all products are endcapped by a terephthalic group. This assumption was made because in the spectrum of T6T6T-diphenyl no peaks of the amine endgroup (6.8 ppm) and the CH_2 group next to the amine endgroup (3.3 ppm) of 6T6-diamine can be found.

In pure T6T6T-diphenyl the ratio between the integral of peak a and peak b and c together is 1:2. For the hexa-amide T6T6T6T this ratio is 1:3 and for the octa-amide T6T6T6T6T 1:4. When the reaction is performed using 6T6-diamine of high purity it is expected that the product will only consist of tetra-amide and a little octa-amide.

$$\text{purity T6T6T} - \text{diphenyl} = (4 - (b + c)/a)/2 \times 100\% \quad [\%] \tag{2}$$

The purity of the T6T6T-diphenyl after recrystallisation as calculated by Equation (2) is 99%. So the product consists for 99% of T6T6T-diphenyl and only 1% of the octa-amide.

3.3.2. DSC

With DSC the melting endotherms of T6T6T-diphenyl of different purities were measured. In Fig. 7 the melting endotherms for T6T6T-diphenyl before and after recrystallisation (product and residue) are compared. In Table 5 the peak temperature of the melting peak and the heat of melting are given for T6T6T-diphenyl of different purities.

The yield of the reaction decreases when 6T6-diamine of a lower purity is used to synthesise T6T6T-diphenyl. As a result of the lower purity of the 6T6-diamine used, the purity of the T6T6T-diphenyl after synthesis also decreases. The purity of both products could be improved to >97% by recrystallisation from NMP. The melting temperature of T6T6T-diphenyl is 316 °C and the melting enthalpy is 129 J/g. The melting temperature and the heat of melting decrease with decreasing purity of the product. The presence of longer products than T6T6T-diphenyl disturb the regular packing of T6T6T-diphenyl and thus lower the enthalpy and the melting point. The residue after recrystallisation shows a melting transition with two peaks.

3.4. T6T6T-dimethyl

The excess of MPT that was used for the synthesis of T6T6T-dimethyl was smaller than that of DPT for the synthesis of T6T6T-diphenyl. The phenyl ester side of MPT will react better with the amine endgroup of 6T6-diamine than the methyl ester side. Therefore it is less likely that in

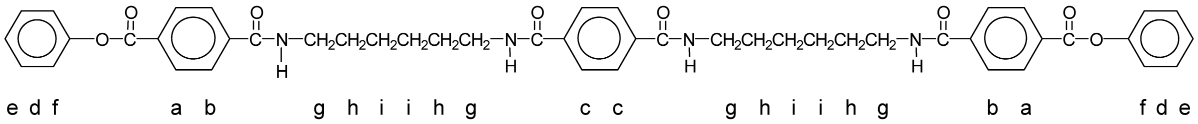

Fig. 6. Peak assignment of protons of T6T6T-diphenyl.

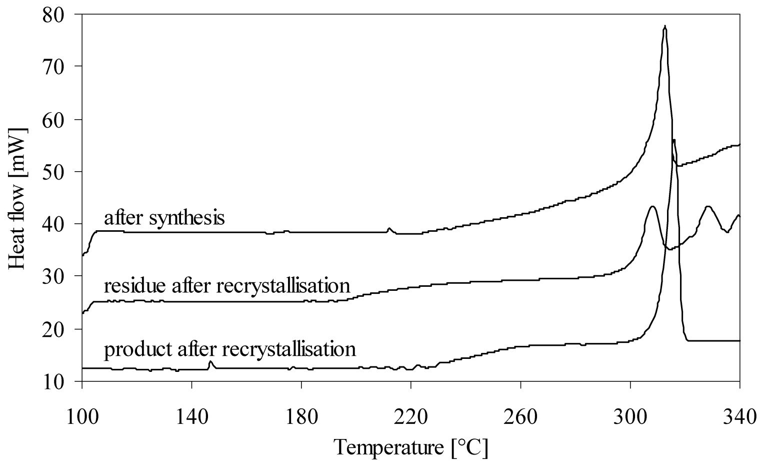

Fig. 7. First heating scan of T6T6T-diphenyl before and after recrystallisation (product and residue).

this reaction a lot of further reacted products will be created. When the reaction was carried out using 6T6-diamine of high purity (recrystallised) no further recrystallisation step was required. The yield of the reaction was 85%. The product was a white powder.

3.4.1. NMR

The molecular structure of the product T6T6T-dimethyl was verified by ^{1}H NMR in D-TFA. The ^{1}H NMR spectrum is given in Fig. 8. The peak assignments are given in Fig. 9 and in Table 6 the integrals and peak assignments for the product after synthesis are given.

The aromatic region of Fig. 8 shows a few very small peaks next to peak a–c. In Fig. 10 the aromatic region of Fig. 8 is enlarged to compare the positions of these small peaks with that of T6T6T-diphenyl. It is clear that there is an exact overlap. So the product that is obtained after reaction of 6T6-diamine with MPT contains a little T6T6T-diphenyl next to T6T6T-dimethyl. This is a result of the fact that MPT is able to react at the methyl ester side as well, although at a very low rate compared to the phenyl ester side.

The purity or uniformity of T6T6T-dimethyl can be calculated in the same way as for T6T6T-diphenyl by comparing the integrals of the peaks of the aromatic protons of the ester–amide and amide–amide terephthalic groups. The same assumptions as for T6T6T-diphenyl are applicable for T6T6T-dimethyl.

The amount of T6T6T-diphenyl present can be calculated from the ratio between the terephthalic phenyl ester–amide peak and the terephthalic methyl ester–amide peak according to Equation (3). It was calculated that the product T6T6T-dimethyl contains 3% of T6T6T-diphenyl.

$$\text{percentage T6T6T} - \text{diphenyl} = (a'/(a + a'))100\% \quad [\%] \tag{3}$$

In pure T6T6T-dimethyl the ratio between the integral of peak a, peak b and c together is 1:2. For the hexa-amide T6T6T6T this ratio is 1:3 and for the octa-amide T6T6T6T6T 1:4. When the reaction is performed using 6T6-diamine of high purity it is expected that the product will consist of tetra-amide and a little octa-amide. The presence of T6T6T-diphenyl next to T6T6T-dimethyl is not harmful to the purity of the product, because this side product will give the same structure in a polymer after a polycondensation reaction. So the peaks resulting from the

Table 4
Chemical shifts δ and assignment of protons of T6T6T-diphenyl

Peak	δ [ppm]	Type	Theoretical protons	Integral product after synthesis	Integral product after recrystallisation	Integral residue after recrystallisation	Description[a]
a	8.46	Doublet	4	4.00	4.00	4.00	Terephthalic *H*, EA, ester side
b	8.01	Doublet	4	4.00[b]	4.00[b]	4.00[b]	Terephthalic *H*, EA, amide side
c	7.99	Singlet	4	5.18[b]	4.02[b]	8.15[b]	Terephthalic *H*, AA
d	7.50	Multiplet	4	4.03	4.04	4.04	Phenyl ester endgroup *H* 3 and 5
e	7.40	Triplet	2	2.01	2.01	2.02	Phenyl ester endgroup *H* 4
f	7.23	Doublet	4	4.08	4.02	4.06	Phenyl ester endgroup *H* 2 and 6
g	3.73	Triplet	8	9.15	8.10	12.23	1st and 6th CH_2 HMDA
h	1.88	Singlet	8	9.20	8.28	12.36	2nd and 5th CH_2 HMDA
I	1.61	Singlet	8	9.17	8.26	12.40	3rd and 4th CH_2 HMDA

[a] EA = ester–amide substituted terephthalic group, AA = amide–amide substituted terephthalic group, HMDA = hexamethylenediamine.

[b] The sum of the integrals of peak b and c was 9.18, peak c was calculated by assuming peak a = peak b.

Table 5
Properties of T6T6T-diphenyl before and after recrystallisation synthesised from 6T6-diamine of high and low purity

Purity 6T6-diamine [%]	Product	Yield [%]	Purity [%]	T_m (peak) [°C]	ΔH_m [J/g]
98	After synthesis	90	89	312	123
	After recrystallisation	53	99	316	129
71	After synthesis	83	70	308	105
	After recrystallisation	28	97	316	128

Table 6
Chemical shifts δ and assignment of protons of T6T6T-dimethyl

Peak	δ [ppm]	Type	Theoretical protons	Integral	Description
a	8.27	Doublet	4	4.00	Terephthalic *H*, methyl ester–amide, ester side
a'	8.46	Doublet	4^{b}	0.12	Terephthalic *H*, phenyl ester–amide, ester side
b	7.98	Singlet	4	4.16^{a}	Terephthalic *H*, amide–amide
c	7.94	Doublet	4	4.00^{a}	Terephthalic *H*, methyl ester–amide, amide side
c'	8.01	Doublet	4^{b}	0.12^{a}	Terephthalic *H*, phenyl ester–amide, amide side
q	7.50	Multiplet	4^{b}	0.12	Phenyl ester endgroup *H* 3 and 5
q	7.40	Triplet	2^{b}	0.06	Phenyl ester endgroup *H* 4
q	7.23	Doublet	4^{b}	0.12	Phenyl ester endgroup *H* 2 and 6
d	4.14	Singlet	6	5.96	Methyl ester endgroup CH_3
e	3.72	Triplet	8	8.36	1st and 6th CH_2 HMDA
f	1.87	Singlet	8	8.52	2nd and 5th CH_2 HMDA
g	1.60	Singlet	8	8.50	3rd and 4th CH_2 HMDA

[a] The sum of the integrals of peak b, c and c' was 8.28, the integral of peak b was calculated by assuming peak c = peak a and peak c' = peak a'.

[b] Protons of phenyl ester endgroups of T6T6T-diphenyl.

Table 7
Properties of T6T6T-dimethyl synthesised from 6T6-diamine of high and lower purities

Purity 6T6-diamine [%]	Yield [%]	Purity [%]	T_m (peak) [°C]	ΔH_m [J/g]
98	85	99	303	152
85	79	88	298	144
77	70	83	295	142
71	64	76	291	138

Table 8
Properties of different TxTxT-dimethyl segments

TxTxT-dimethyl	Yield [%]	Purity [%]	T_m [°C]	ΔH_m [J/g]
T2T2T	74	97	$>340^{a}$	–
T3T3T	43	97	307	128
T4T4T	71	97	$>340^{a}$	–
T6T6T	85	99	303	152
T7T7T	69	96	262	99
T8T8T	73	93	268	163

[a] 340 °C is the maximum temperature for the DSC apparatus used.

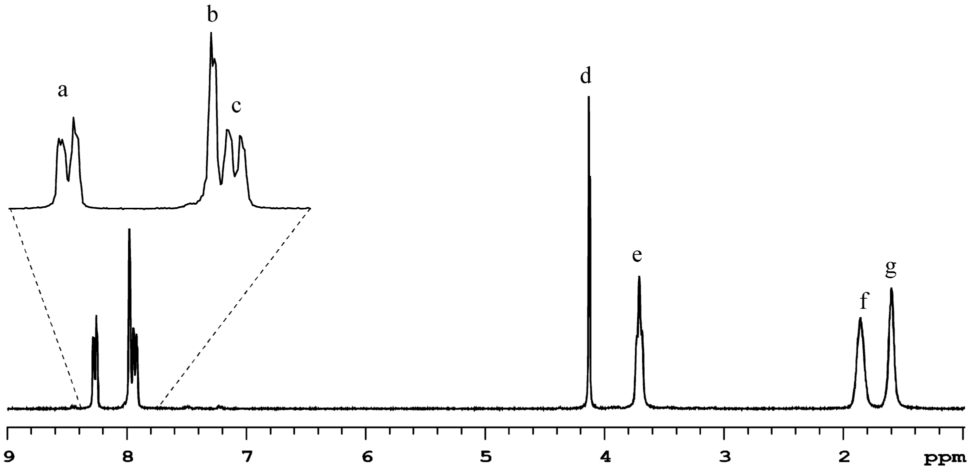

Fig. 8. ^{1}H NMR spectrum of T6T6T-dimethyl.

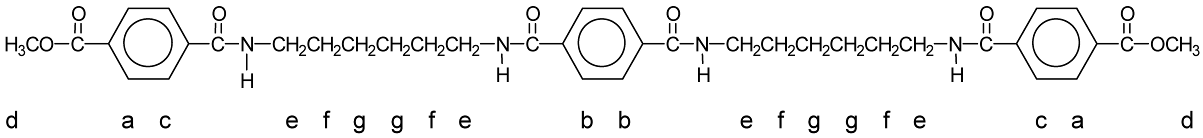

Fig. 9. Peak assignment of protons of T6T6T-dimethyl.

terephthalic phenyl ester–amide, can be added to that of the terephthalic methyl ester–amide and the purity of T6T6T-dimethyl can be calculated with Equation 4.

$$\text{purity T6T6T} - \text{dimethyl} = (4 - (\mathrm{b} + \mathrm{c} + \mathrm{c}')/(\mathrm{a} + \mathrm{a}'))/2 \times 100\% \qquad [\%] \tag{4}$$

The purity of the T6T6T-dimethyl after synthesis as calculated by Equation (4) is 99%. So the product consists for 99% of T6T6T-dimethyl (including 3% T6T6T-diphenyl) and only 1% of the octa-amide.

3.4.2. DSC

The melting endotherms of T6T6T-dimethyl of different purities were measured with DSC. In Fig. 11 the melting endotherms for T6T6T-dimethyl of high and low purity are compared. In Table 7 the peak temperature of the melting peak and the heat of fusion are given for T6T6T-dimethyl segments of different purities.

The yield of the reaction decreases when 6T6-diamine of a lower purity is used to synthesise T6T6T-dimethyl. The purity of the T6T6T-dimethyl decreases with decreasing purity of the 6T6-diamine used. The melting temperature and the heat of melting decrease with decreasing purity of the product.

Pure T6T6T-dimethyl has a melting temperature of 303 °C and a melting enthalpy of 152 J/g. The melting temperature of T6T6T-dimethyl is in between that of T6T-dimethyl (232–235 °C) [7,8], and that of nylon-6,T (371 °C) [21]. The melting temperature of T6T6T-dimethyl is 13°C lower than that of T6T6T-diphenyl, due to decreased stiffness of the endgroups. If desired, the melting temperature of the T6T6T segment can be further decreased by using more flexible endgroups, such as ethyl or butyl. For example, the melting temperature of T6T-dimethyl is 232 °C and that of T6T-dibutyl is 187 °C [7].

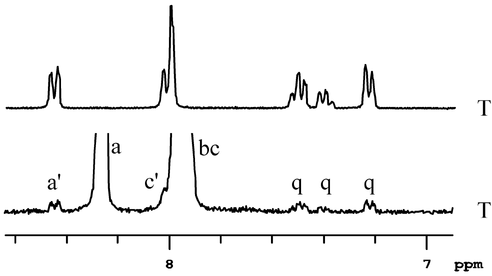

Fig. 10. Comparison of the aromatic region of T6T6T-dimethyl and T6T6T-diphenyl.

3.4.3. Other TxTxT-dimethyl segments

The yield and purity of the other TxTxT-dimethyl segments and the melting temperatures and enthalpies are given in Table 8. All TxTxT-dimethyl could be prepared from recrystallised xTx-diamine with high yield and purity. No recrystallisation step was required as for T6T6T-diphenyl. The melting temperature of TxTxT-dimethyl decreases with increasing amine length for even *n*. The melting temperature of T2T2T-dimethyl and T4T4T-dimethyl could not be determined because these were above 340 °C. The melting temperature and heat of crystallisation of TxTxT with odd *n* (x = $(CH_2)_n$) is lower because these segments are less ordered.

3.5. WAXD

With wide angle X-ray diffraction the diffraction patterns of the different purified TxTxT-dimethyl segments were measured (Fig. 12). The WAXD diagrams in Fig. 12 are typical for crystalline substances of low molecular weight and comparable to di-amide segments such as T4T-dimethyl [16]. The different TxTxT-dimethyl segments show a broad spectrum of peaks, indicating the presence of different crystalline structures. It can be noted that the large peak at $2\Theta = 6–8°$ shifts to lower values with increasing length of the diamine in the tetra-amide, indicating an increasing lamellar thickness in the chain direction. T7T7T-dimethyl deviates from this trend and has this peak at a lower value indicating higher lamellar thickness. This is a result of the odd number of CH_2 groups between the terephthalic groups, which decreases the crystalline order. The other main peaks at $2\Theta = 15–30°$ do not show such a shift. These peaks may be attributed to the lateral crystal sizes. These sizes are expected to be comparable for different TxTxT-dimethyl

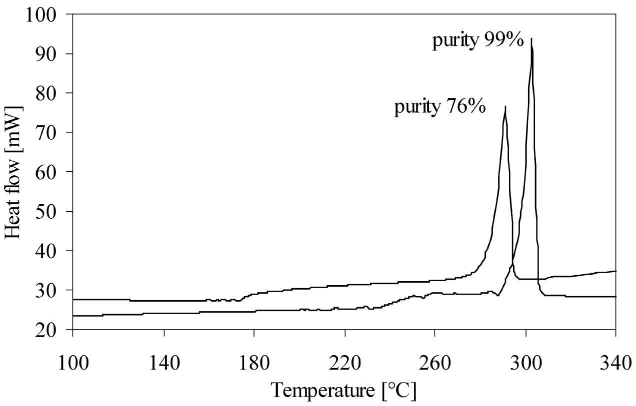

Fig. 11. First heating scan of T6T6T-dimethyl of low and high purity.

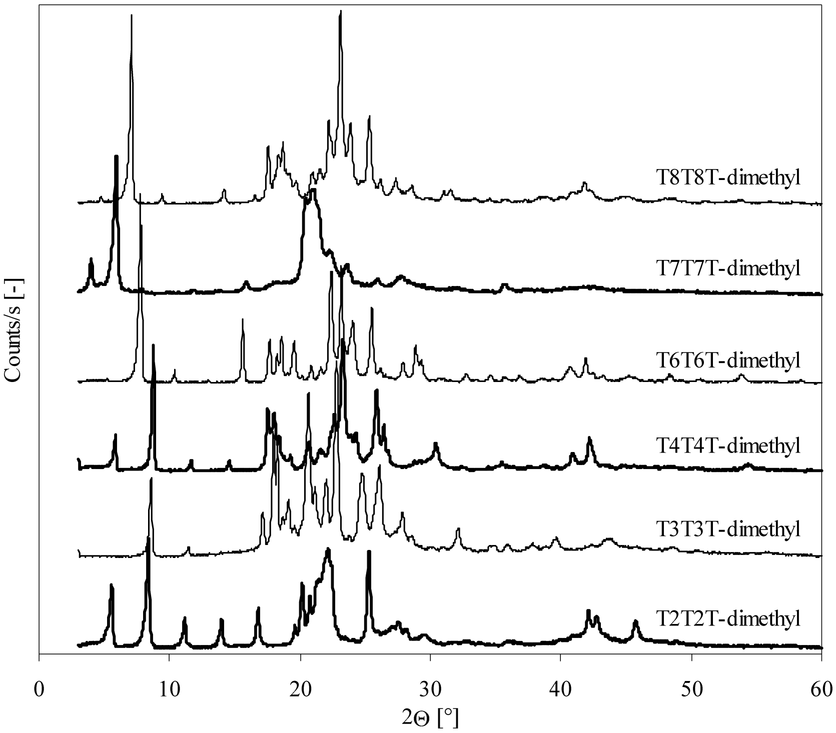

Fig. 12. WAXD spectrum of different TxTxT-dimethyl segments of high purity.

segments. In each sample, crystallites of different sizes are present. Only T2T2T-dimethyl and T7T7T-dimethyl show one broad peak instead of a spectrum of many sharp peaks.

3.6. IR

With IR spectroscopy the formation of amide and ester groups can be observed. In Fig. 13 the IR spectra of 6T6-diamine and T6T6T-dimethyl are compared. Both 6T6-diamine and T6T6T-dimethyl show the amide carbonyl band at 1628 cm^{-1}. T6T6T-dimethyl shows an ester carbonyl band at 1721 cm^{-1} next to this amide carbonyl band. T6T6T-dimethyl also shows a peak of the CH_3 methyl ester endgroup at 1112 cm^{-1}. The fact that 6T6-diamine does not show a peak at 1721 and 1112 cm^{-1} confirms the assumption that 6T6-diamine does not contain any DMT that has reacted at only one side, such as 6T or 6T6T.

4. Conclusions

Bisester tetra-amide TxTxT-dimethyl segments with $x = (CH_2)_n$ and $n = 2-8$ can be synthesised in a two-step reaction. The first step is the synthesis of xTx-diamine in the

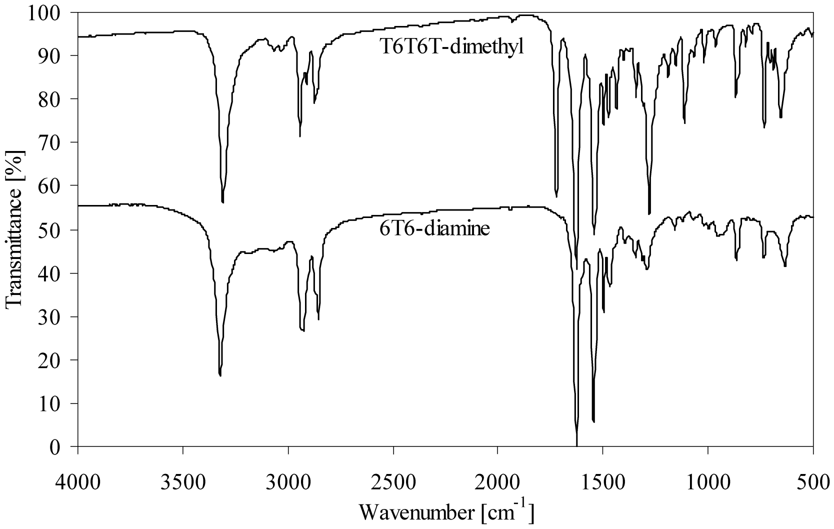

Fig. 13. IR spectrum of 6T6-diamine and T6T6T-dimethyl; the spectrum of 6T6-diamine is shifted by 40% on the y-axis.

melt, followed by recrystallisation to improve the purity. TxTxT-dimethyl can then be prepared in a reaction of xTx-diamine with methyl phenyl terephthalate in solution. The structure of the products could be confirmed by NMR. The purity of the tetra-amide product depends on the purity of the xTx-diamine used. The product xTx-diamine does not contain any side products such as xT or xTxT.

The melting temperature and enthalpy of xTx-diamine and TxTxT-dimethyl and -diphenyl were determined by DSC. The melting temperature increases with decreasing length of x. For odd x the melting temperature is lower. The melting temperature and enthalpy of the products decrease with decreasing purity.

Acknowledgements

This work was financially supported by the Dutch Polymer Institute (DPI, Eindhoven, The Netherlands).

References

[1] Harrell LL. Macromolecules 1969;2(6):607.

[2] Ng HN, Allegrazza AE, Seymour RW, Cooper SL. Polymer 1973;14:255.

[3] Eisenbach CD, Baumgartner M, Gunter G. In: Lal J, Mark JE, editors. Advances in elastomer and rubber elasticity, proceedings symposium, vol. 51. New York: Plenum Press; 1985.

[4] Miller JA, Shaow BL, Hwang KKS, Wu KS, Gibson PE, Cooper SL. Macromolecules 1985;18(1):32.

[5] Gaymans RJ, Aalto S, Maurer FHJ. J Polym Sci, Part A: Polym Chem 1989;27:423.

[6] Williams JLR, Laakso TM, Dunham KR, Borden DG, VandenBerghe J, VanAllan JA, Reynolds DD. J Org Chem 1960;25:817.

[7] Cicero i L., Di Gregotio F., Platone E., US 1,365,952, 1970.

[8] Cognigni F., Mariano A., US 4,614,815, 1986.

[9] Brisson J, Brisse F. Macromolecules 1986;19:2632.

[10] Niesten MCEJ, Feijen J, Gaymans RJ. Polymer 2000;41(24):8487.

[11] Serrano PJM, Van Bennekom ACM, Gaymans RJ. Polymer 1998; 39(23):5773.

[12] Bouma K, Lohmeijer JHGM, Gaymans RJ. Polymer 2000;41(8):2719.

[13] Sorta E, Della Fortuna G. Polymer 1980;21:728.

[14] Niesten MCEJ, Bosch H, Gaymans RJ. J Appl Polym Sci 2001; 81(7):1605.

[15] Perego G, Cesart M, Della Fortuna G. J Appl Polym Sci 1984;29: 1141.

[16] Guang L, Gaymans RJ. Polymer 1997;38(19):4891.

[17] Hoffman JD, Weeks JJ. J Res Nail Bur Stand A 1962;66:13.

[18] Sekiquchi H, Coutin B. In: Kricheldorf HR, editor. Handbook of polymer synthesis, part A. New York: Marcel Dekker; 1992. Chapter 14.

[19] Todoki M, Kawaguchi T. J Polym Sci, Polym Phys Ed 1977;15:1067.

[20] Hirschinger J, Miura H, Gardner KH, English AD. Macromolecules 1990;23:2153.

[21] Morgan PW, Kwolek SL. Macromolecules 1975;8:104.