Macromol. Symp. ***130,*** *91–102 (1998)*

SYNTHESIS AND CHARACTERIZATION OF ALIPHATIC POLY(ESTER-AMIDE)S CONTAINING SYMMETRICAL BISAMIDE BLOCKS

Henk R. Stapert, Pieter J. Dijkstra and Jan Feijen*

Department of Chemical Technology and Institute for Biomedical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Abstract:

A series of symmetrical diols were synthesised through ring-opening of lactones with different ring sizes by alkane diamines in moderate to good yields. Ring-opening of the dilactones glycolide and lactide with a diamine in equimolar amounts afforded symmetrical diols in quantitative yield.

Aliphatic poly(ester-amide)s were prepared by polycondensation of N,N'-bis(caproyl)butane diamide, dimethyl adipate and 1,4-butanediol. The structure of the diamide was retained in the polymer. The polymers synthesized are semi-crystalline materials that possess ordered structures in the solid phase over almost the entire copolymer range. Depending on thermal history and copolymer composition thermal analyses is in agreement with the presence of pseudo-hexagonal crystal structures below 75°C, a fast melting recrystallization at this temperature and a triclinic structure at higher temperatures.

INTRODUCTION

The introduction of hydrogen bonding in synthetic macromolecules is a method to induce molecular interaction and organisation (ref.1). The use of hydrogen bonds in material design has resulted in semi-crystalline polymers with high modules and high tensile strength (ref.2), in fast crystallising poly(ester-amide)s (ref.3) and also in thermoplastic elastomers with better defined (phase separated) crystalline and amorphous phases (ref.4). Liquid crystallinity in polymers is sometimes induced by hydrogen bonding (ref.5) even without the use of monomeric mesogens (ref.6). More-over the use of hydrogen bonds in supra molecular chemistry has recently led to new polymers based on macromolecular arrangement of hydrogen donor and acceptor groups of low molecular weight building blocks (ref.7). Materials based on these concepts generally also incorporate rigid aromatic moieties in the main or side chain of the polymer molecules. Highly regular and strictly alternating aliphatic or aliphatic-aromatic polyamides (ref.8) and poly(ester-amide)s (ref. 3,6,9) are examples of materials that show high order through hydrogen bonding.

The concept of structural organisation in polymeric materials through hydrogen bonding and incorporation of highly symmetrical (ref. 10) or rigid segments may well be used in the development of novel biodegradable polymers for biomedical or environmental use. Aliphatic

CCC 1022-1360/98/$ 10.00

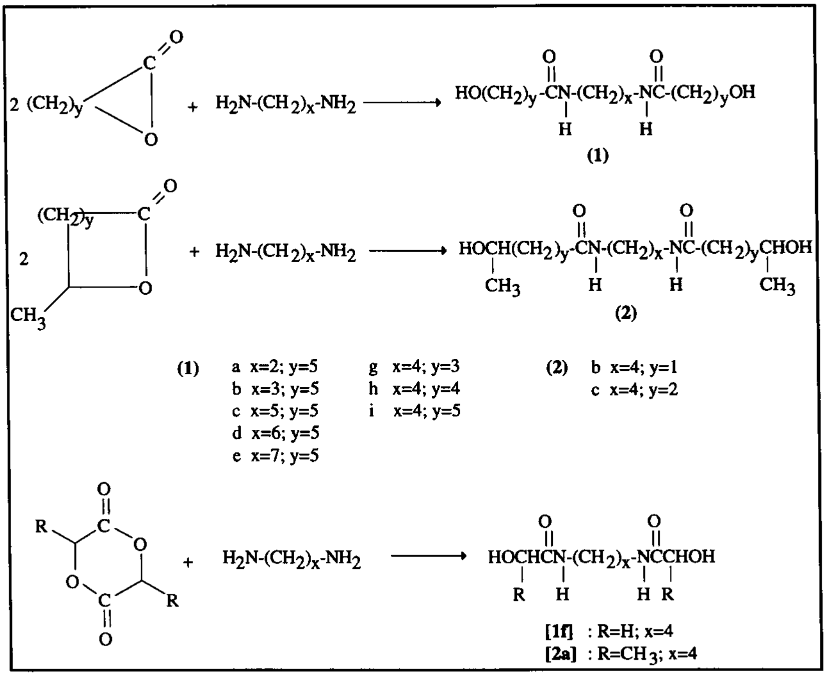
polyesters, such as poly(ε-caprolactone) (ref.11) and poly(butylene adipate) (ref.11) are known to be biodegradable, highly crystalline but lack the physical and/or mechanical properties necessary for broad use. Synthetic aliphatic polyamides are generally not biodegradable (ref.12) but have favourable crystallisation properties, are thermally stable up to high temperature and have high moduli and tensile strength. The combination of the favourable properties of both classes of materials may lead to materials that combine good end-use properties, processing properties and biodegradability. To improve properties of aliphatic polyesters by following the concepts outlined above we have incorporated short and symmetrical, uniform amide monomers through polycondensation. We therefore have designed and developed a class of aliphatic poly(ester-amide)s based on symmetrical diamide-diol monomers and have studied their potential for environmental use. In this article we describe the synthesis and characterisation of the diamide-diol monomers and the aliphatic poly(ester-amide)s based on (the symmetrical diamide-diol) N,N'-bis(caproyl)butane diamide.

RESULTS AND DISCUSSION

Synthesis of monomers

The N,N'-bis(caproyl)alkane diamides **1a-e** were synthesised in moderate to good yields through a ring-opening reaction of ε-caprolactone using α,ω-alkane diamines. In a similar way several diol monomers were prepared starting from 1,4–butanediamines and lactones with different ring sizes (Scheme 1). The ^{1}H-NMR spectrum of the crude products revealed the presence of oligomeric products. Besides the expected methylene protons next to the amide carbonyl at δ 2.05 a signal was present at δ 2.28 belonging to methylene protons next to an ester carbonyl group. Also an additional signal was present at δ 3.98 which belongs to the methylene protons next to an oxygen acyl group. Obviously the experimental conditions allowed the successive oligomerization through the formed hydroxyl end groups even in the absence of catalysts. Purification of the monomers was established by recrystallization from acetonitril water mixtures or from methanol water mixtures (25:1, v:v) for compounds **1a-i** or from THF for **2a-c**. Monomers **1** and **2** are soluble in water but increasing the number of methylene units in the diamine or lactone decreases its water solubility. All monomers are soluble in dipolar aprotic solvents like DMSO and are insoluble in solvents like chloroform and toluene. A representative ^{1}H-NMR spectrum of the monomers prepared is given in Fig. 1 for the compound **1i**. The amide and hydroxyl protons were found at δ 7.74 and δ 4.34 and are characteristic for these bisamide diols. No signals of methylene protons next to an ester carbonyl were present in the purified monomers. In the ^{13}C-NMR spectrum only one carbonyl carbon atom was present at δ 178.0. These spectroscopic data reveal the absence of oligomers. The high purity of the monomers was also confirmed by elemental analysis and HPLC (data not shown). It was not possible to prepare a bisamide diol monomer from propiolactone and

1,4-diaminobutane and therefore no data are given for this compound. Monomers in which y=1 were prepared by reaction of a diamine with the dilactone glycolide. Surprisingly almost no oligomerization occurred and using an equimolar ratio of the compounds afforded the product **1f** in almost quantitative yield. The formed hydroxyl group is less reactive than the amine group still present after the ring-opening of the glycolide in the first step. This free amine group reacts with the ester functional group with the formation of the product. In a similar way diamines react with lactide to give bis(amide)-diols like **2a** with secondary hydroxyl groups in quantitative yield. Because these diols are not reactive in the polycondensation reactions, under the reaction conditions used and as described in the next section, these will not be discussed here further.



(1)
a x=2; y=5
b x=3; y=5
c x=5; y=5
d x=6; y=5
e x=7; y=5
g x=4; y=3
h x=4; y=4
i x=4; y=5

(2)
b x=4; y=1
c x=4; y=2

[1f] : R=H; x=4
[2a] : R=CH3; x=4

Scheme 1. Ringopening of lactones by primairy aliphatic diamines

The melting temperatures of monomers **1a-i** are presented in Fig. 2a. The odd-even effect observed for compounds **1a-e** is characteristic for these bisamides and has been observed in many structurally resembling compounds (ref.13). Although the differences in melting temperatures are small for the monomers **1f-i** a reversed odd-even effect is observed. This effect may be due to structurally favourable conformations of the hydroxyl groups in monomers prepared from lactones comprising an odd number of methylene groups in the ring.

Interestingly the odd-even effect in **1a-e** is also observed in the undercooling data for these

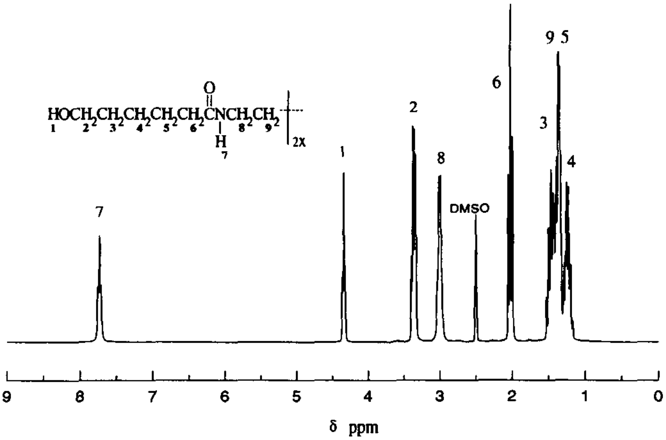


Fig.1. ^{1}H-NMR spectrum of the monomer **1i**.

monomers (Fig. 2b). Monomers with relatively high melting temperatures show a fast crystallisation from the melt. Contrary, this effect is not observed for **1f-i** and fast crystallisation only is observed when y≥3.

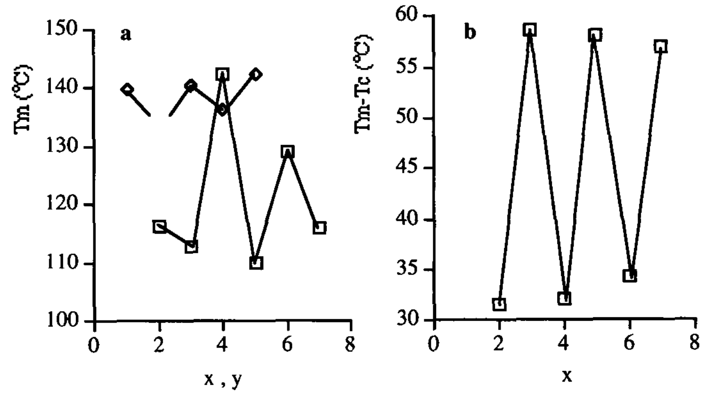
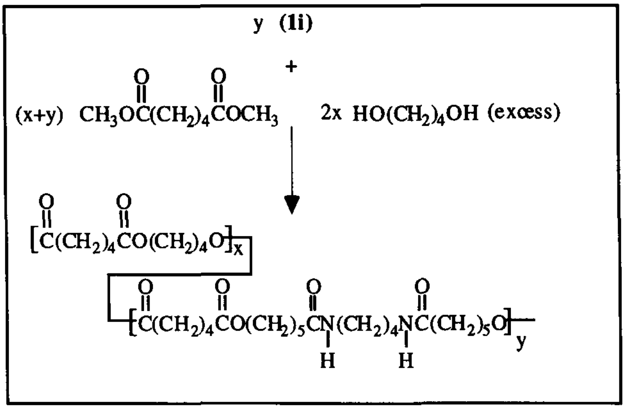


Fig.2. Melting points (a) and undercooling (b) of biamide diol monomers as a function of the number of methylene groups. □ **(1)a-e**; ◇ **(1)f-i**.

Synthesis of polymers

Based on the melting temperatures and crystallisation rate of the monomers prepared the monomer N,N'-bis(caproyl)butane diamide **1i** (m.p: 140 °C) was selected for the polycondensation with adipic acid in order to prepare aliphatic poly(ester-amide)s. The polymerisation of (**1i**) and adipic acid or dimethyl adipate was carried out at 170 °C and at low pressure in the presence of $Ti(OBu)_4$ as a catalyst (10^{-2} mbar). The alternating polymer (Scheme 2, x=0) could only be obtained as a low molecular weight material. This is most likely due to the low reactivity of the end groups and the difficult retainment of a 1:1 stoeichiometry during the condensation reaction. Attempts to retain equimolar amounts of adipic acid or dimethyl adipate and the monomer **1i** in the condensation reaction were unsuccessful. Deactivation of the $Ti(OBu)_4$ catalyst through co-ordination to the amide groups and free acid groups may also have a negative effect on the polymerisation rate. Moreover, polycondensations carried out at higher temperatures lead to decomposition and strong colouring of the polymer. Polymerization reactions carried out with monomer **1i**, 1,4-butanediol and dimethyl adipate yielded polymers with molecular weights up to 50.000 (Table 1, x:y 50:50). These molecular weights are comparable or higher than those of poly(butylene adipate) prepared from dimethyl adipate and 1,4-butane diol applying the same polycondensation conditions. Solution casted films ($CHCl_3$) prepared from these synthesised materials had good mechanical strength. Decreasing the amount of 1,4-butanediol and dimethyl adipate resulted in poly(ester-amide)s having low molecular weights (x:y = 25:75)



Scheme 2. Polycondensation reaction

The ^1H-NMR spectrum of a polymer prepared from **1i**, 1,4-butanediol and dimethyl adipate in a molar ratio x:y = 75:25 is presented in Fig.3. The structure of the monomer is preserved in the polymer. The ^1H-NMR spectra were also used to estimate the molecular weights of the polymers with the assumption that polymer chains are terminated with hydroxyl groups. Values were calculated from the signals of the end groups at δ 3.6 and the signal of the methylene groups next to the ester bond at δ 4.5. In case of polymers having a bisamide monomer content up to 50mol%, molecular weights could also be determined from GPC measurements. The molecular weights as determined with the two methods appeared to resemble each other. The molecular weight distributions (Mw/Mn) were in all cases around two. In Table 1 the molecular weight, melting and glass transition temperatures have been presented.

Table 1. *Thermal properties and molecular weights of poly(esteramide)s*

polymer (mol %) x:y	Tm^a) (°C)	ΔHm (J/g)	Tg (°C)	Mw (g/mole)
100:0	61	49	-58	20.500
89:11	75	4	-56	21.900
75:25	111	4	-49	48.000
50:50	130	48	-31	14.000
25:75	140	53	-31	4.000 b)
0:100	145	58	-11	5.000 b)

a) upper disordering temperature; b) Mn, NMR-endgroup analysis

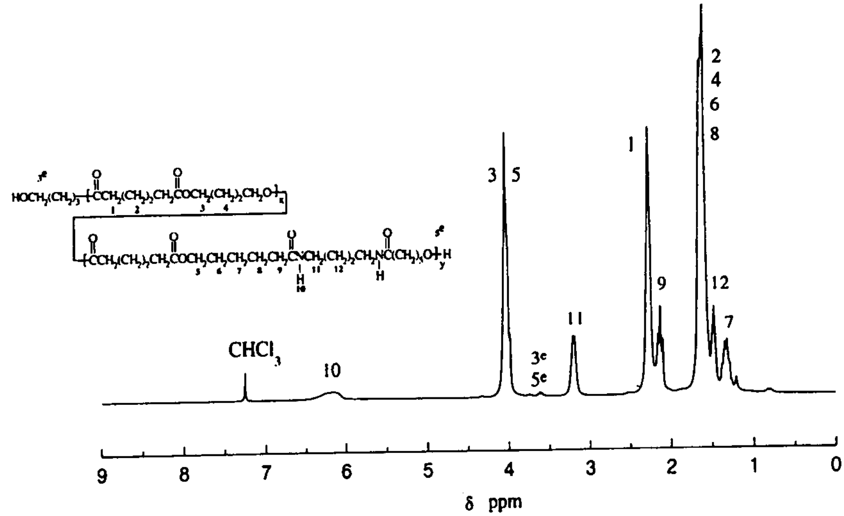


Fig. 3. ^{1}H-NMR spectrum of polymer (x:y = 75:25) based on **1i**.

Thermal properties

The poly(ester-amide)s displayed an interesting phase behaviour. DSC second heating curves of the polymers (20 °C/min, Fig. 4) revealed a subsequent melting recrystallization transition around 75 °C and a second melting transition at higher temperatures. The latter transition decreased (both Tm and ΔHm) with decreasing bisamide monomer content of polymers and was ascribed to the melting of a 'triclinic' crystal structure. The former transition could be due to the melting of a lower ordered structure (pseudo-hexagonal) and direct recrystallization in the higher ordered 'triclinic' structure. This transition was almost independent of the copolymer composition.

DSC first cooling curves (20 °C/min, Fig. 4) revealed one or two first order transitions, depending on the copolymer composition. Cooling (< 40 °C/min) of polymers with $y>45$mol% showed a crystallisation transition above 75 °C which was dependent on the cooling rate and a (often smaller) transition between 65 and 75 °C, almost independent of cooling rates. When higher cooling rates were applied only one transition just below 75 °C occurred which did not change using higher cooling rates. This transition was present in polymers with y between 11 mol% and 100 mol%, and was also slightly dependent on the copolymer composition. The transition resembles a monotropic phase transition as recently described by Heberer (ref.14).

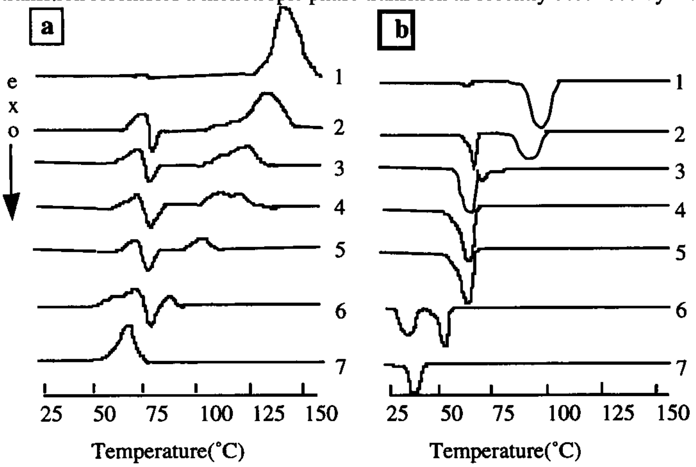


Fig.4 DSC second heating curves (a) and first cooling curves (b) of copolymers (all rates 20 °C/min). 1: $y = 75$ mol%; 2: $y = 50$ mol%; 3: $y = 45$ mol%; 4: $y = 31$ mol%; 5: $y = 21$ mol%; 6: $y = 11$ mol%; 7: $y = 6$ mol%

When less than 11 mol% amide monomer was incorporated a new crystallisation transition occurred at lower temperatures, which was ascribed to crystallisation of the butylene adipate blocks.

Furthermore, polarisation microscopy revealed a biphasic melt containing birefringent structures which resemble the batonnets structure known for smectic A or C type liquid crystalline polymers (ref. 6). The amount of birefringence was dependent on the amount of bisamide block used. No complete isotropization was observed up to the polymer decomposition temperature. These preliminary results indicate that the ester-amide moieties segregate, causing the polymer to stretch and to form very thin lamellar morphologies probably stabilised by hydrogen bonds (highly ordered smectic phase). Further work is currently underway to test this hypothesis and the results will be published separately.

EXPERIMENTAL PART

Methods:

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 operating at 250 MHz (^1H) or 62.5 MHz (^{13}C). Molecular weights were determined by integration of the ^1H NMR spectra. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions (M_w/M_n). A Waters 6000A GPC apparatus equipped with three Waters μStyragel (500, 10^3, 10^4, 10^5 Å pore diameter) columns was used, combined with a H502 viscometer detector (Viscotek Corp.) for determination of absolute values of molecular weights. Polymers were dissolved in chloroform (1.0 wt.-%) and elution was performed at 25 °C at a flow rate of 1.6 mL/min using $CHCl_3$ as eluent.

Thermal analysis of polymers was carried out with a Perkin-Elmer DSC7 differential scanning calorimeter calibrated with pure indium. In a standard run the polymers were heated from - 80 °C to 175 °C at a heating rate of 20 °C/min, annealed for 1 minute and cooled (-20 °C/min) to -80 °C, whereafter a second heating curve was recorded.

Monomer synthesis: typical procedure for N,N'-bis(caproyl)butane diamide (**1**). To a solution of 8.35 g (0.949 mol) 1,4-butane diamine in a mixture of 25 ml of THF and 5 ml of water a solution of 21.66 g (0.19 mole) of ε-caprolactone in 25 ml of THF was added at room temperature. The resulting solution was refluxed for 16 h. The solvent was evaporated under reduced pressure and the crude pale yellow oil obtained was dissolved in 150 ml of methanol or acetonitril. The pH of the solution was adjusted to 11.5 with the addition of the required amount of 1M NaOH. The mixture was subsequently mixed with 500 ml of THF whereupon the product crystallised. The product was filtered off and dried.

N,N'-1,2-ethanediyl-bis[6-hydroxy-hexanamide](**1a**): Yield: 46%, m.p. 116-117 °C.**^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.33 (bs, 2H), $HOC\underline{H}_2CH_2$: δ=3.37 (t,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.48 (p, 4H), $HOCH_2CH_2C\underline{H}_2$: δ=1.25 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.42 (p, 4H), $C\underline{H}_2C(O)N(H)$: δ=2.05 (t, 4H), $C(O)N(\underline{H})$: δ=7.81 (b, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.08 (bs, 4H); **^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.61 , $HOCH_2\underline{C}H_2$: δ=35.50, $HOCH_2CH_2\underline{C}H_2$: δ=25.14, $\underline{C}H_2CH_2C(O)$: δ=25.19, $\underline{C}H_2C(O)N(H)$: δ=32.26, $\underline{C}(O)N(H)$: δ=172.33, $N(H)\underline{C}H_2CH_2$: δ=38.34; **Elemental analysis**: Calc. C: 58.29%, N: 9.72%, H: 9.79%; Found: C: 57.77±0.09%, N: 9.54±0.06%, H: 9.88±0.04%; H_2O: 0.05±0.01%.

N,N'-1,3-propanediyl-bis[6-hydroxy-hexanamide](**1b**): Yield: 40%, m.p. 113 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.39 (bs, 2H), $HOC\underline{H}_2CH_2$: δ=3.38 (t,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.48 (p, 4H), $HOCH_2CH_2C\underline{H}_2$: δ=1.27 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.45 (p, 4H), $C\underline{H}_2C(O)N(H)$: δ=2.05 (t, 4H), $C(O)N(\underline{H})$: δ=7.77 (bs, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.04 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.4-1.5 (2H); **^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.60 , $HOCH_2\underline{C}H_2$: δ=35.51, $HOCH_2CH_2\underline{C}H_2$: δ=25.20, $\underline{C}H_2CH_2C(O)$: δ=25.24, $\underline{C}H_2C(O)N(H)$: δ=32.27, $\underline{C}(O)N(H)$: δ=172.06, $N(H)\underline{C}H_2CH_2$: δ=36.22 , $N(H)CH_2\underline{C}H_2$: δ=29.32; **Elemental analysis**: Calc. C: 59.56%, N: 9.27%, H: 10.00%; Found: C: 53.39±0.05%, N: 7.93±0.11%, H: 9.10±0.06%; H_2O: 1.09±0.01 %.

N,N'-1,5-pentanediyl-bis[6-hydroxy-hexanamide](**1c**): Yield: 19%, m.p. 115-116 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.39 (bs, 2H), $HOC\underline{H}_2CH_2$: δ=3.39 (t,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.48 (p, 4H), $HOCH_2CH_2C\underline{H}_2$: δ=1.28 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.4-1.5 (p, 4H), $C\underline{H}_2C(O)N(H)$: δ=2.05 (t, 4H), $C(O)N(\underline{H})$: δ=7.75 (bs, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.00 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.4-1.5 (4H), $N(H)CH_2CH_2C\underline{H}_2$: δ=1.4-1.5 (2H); **^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.60 , $HOCH_2\underline{C}H_2$: δ=35.48, $HOCH_2CH_2\underline{C}H_2$: δ=25.21, $\underline{C}H_2CH_2C(O)$: δ=25.26, $\underline{C}H_2C(O)N(H)$: δ=32.25, $\underline{C}(O)N(H)$: δ=171.92, $N(H)\underline{C}H_2CH_2$: δ=38.26 , $N(H)CH_2\underline{C}H_2$: δ=28.82, $N(H)CH_2CH_2\underline{C}H2$: δ=23.77; **Elemental analysis**: Calc. C: 61.77%, N: 8.48%, H: 10.38%; Found: C: 58.48±0.20%, N: 7.74±0.09%, H: 9.91±0.05%; H_2O: 0.68±0.05 %.

N,N'-1,6-hexandiyl-bis[6-hydroxy-hexanamide](**1d**): Yield: 60% MeOH/H_2O, 85% Acetonitril, m.p.129 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.35 (bs, 2H), $HOC\underline{H}_2CH_2$: δ=3.36 (t,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.48 (p, 4H), $HOCH_2CH_2C\underline{H}_2$: δ=1.2-1.3 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.4-1.5 (p, 4H), $C\underline{H}_2C(O)N(H)$: δ=2.05 (t, 4H), $C(O)N(\underline{H})$: δ=7.74 (bs, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.00 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.3-1.5 (4H), $N(H)CH_2CH_2C\underline{H}_2$: δ=1.2-1.3 (2H); **^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.57 , $HOCH_2\underline{C}H_2$: δ=35.37, $HOCH_2CH_2\underline{C}H_2$: δ=25.13, $\underline{C}H_2CH_2C(O)$: δ=25.81, $\underline{C}H_2C(O)N(H)$: δ=32.63, $\underline{C}(O)N(H)$: δ=173.32, $N(H)\underline{C}H_2CH_2$: δ=37.7 , $N(H)CH_2\underline{C}H_2$: δ=28.64, $N(H)CH_2CH_2\underline{C}H2$: δ=24.81; **Elemental analysis**: Calc. C: 62.74%, N: 8.13%, H: 10.54%; Found: C: 62.33±0.16%, N: 7.81±0.04%, H: 10.62±0.05%; H_2O: 0.11±0.01 %.

N,N'-1,7-heptanediyl-bis[6-hydroxy-hexanamide](**1e**): Yield: 21% MeOH/H_2O, m.p.120 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.35 (bs, 2H), $HOC\underline{H}_2CH_2$: δ=3.38 (t,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.48 (p, 4H), $HOCH_2CH_2C\underline{H}_2$: δ=1.2-1.3 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.3-1.5 (p, 4H), $C\underline{H}_2C(O)N(H)$: δ=2.03 (t, 4H), $C(O)N(\underline{H})$: δ=7.74 (bs, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.03 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.2-1.4 (4H), $N(H)CH_2CH_2C\underline{H}_2$: δ=1.2-1.4 (4H); $N(H)CH_2CH_2CH_2C\underline{H}_2$: δ=1.2-1.4 (2H).**^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.61 , $HOCH_2\underline{C}H_2$: δ=35.49, $HOCH_2CH_2\underline{C}H_2$: δ=25.19, $\underline{C}H_2CH_2C(O)$: δ=25.28, $\underline{C}H_2C(O)N(H)$: δ=32.27, $\underline{C}(O)N(H)$: δ=171.87, $N(H)\underline{C}H_2CH_2$: δ=38.31 , $N(H)CH_2\underline{C}H_2$: δ=29.10, $N(H)CH_2CH_2\underline{C}H2$: δ=26.35, $N(H)CH_2CH_2CH_2\underline{C}H_2$: δ=28.43; **Elemental analysis**: Calc. C: 63.64%, N: 7.82%, H: 10.69%; Found: C: 62.66±0.07%, N: 7.71±0.05%, H: 10.78±0.09%; H_2O: 0.05±0.01 %.

N,N'-1,4-butanediyl-bis[2-hydroxy-ethanamide](**1f**): Yield: 99%, m.p.140 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.45 (bs, 2H), $HOC\underline{H}_2C(O)$: δ=3.80 (s,4H), $C(O)N(\underline{H})$: δ=7.73 (bt, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.09 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.40 (t,4H).**^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2C(O)$: δ=60.40 , $\underline{C}(O)N(H)$: δ=171.56, $N(H)\underline{C}H_2CH_2$: δ=37.70 , $N(H)CH_2\underline{C}H_2$: δ=26.73; **Elemental analysis**: Calc. C: 47.03%, N: 13.72%, H: 7.90%; Found: C: 46.09±0.07%, N: 13.32±0.04%, H: 7.93±0.02%; H_2O: 0.37±0.05 %.

N,N'-1,2-butanediyl-bis[4-hydroxy-butanamide](**1g**): Yield: 65%, m.p.140 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.45 (t, 2H), $HOC\underline{H}_2CH_2$: δ=3.37 (m,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.62 (p, 4H), $CH_2C\underline{H}_2C(O)$: δ=2.08 (t, 4H), $C(O)N(\underline{H})$: δ=7.78 (bt, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.02 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.35 (bs,4H).**^{13}C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.32, $HOCH_2\underline{C}H_2$: δ=28.66, $HOCH_2CH_2\underline{C}H_2$: δ=32.13, $\underline{C}(O)N(H)$: δ=171.98, $N(H)\underline{C}H_2CH_2$: δ=38.12 , $N(H)CH_2\underline{C}H_2$: δ=26.63; **Elemental analysis**: Calc. C: 55.35%, N: 10.76%, H: 9.30%; Found: C: 55.38±0.02%, N: 10.74±0.01%, H: 9.43±0.01%; H_2O: 0 %.

N,N'-1,4-butanediyl-bis[5-hydroxy-pentanamide](**1h**): Yield: 70%, m.p. 136-137 °C. **^{1}H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.35 (bs, 2H), $HOC\underline{H}_2CH_2$: δ=3.39 (dt,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.63 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.4 (4H), $CH_2C\underline{H}_2C(O)$: δ=2.02 (t, 4H), $C(O)N(\underline{H})$: δ=7.70 (bs, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.02 (dt, 4H),

$N(H)CH_2C\underline{H}_2$: δ=1.3-1.4 (4H).^{13}**C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.42, $HOCH_2\underline{C}H_2$: δ=35.24, $HOCH_2CH_2\underline{C}H_2$: δ=21.93, $CH_2C(O)$: δ=32.06, $\underline{C}(O)N(H)$: δ=171.97, $N(H)\underline{C}H_2CH_2$: δ=38.09 , $N(H)CH_2\underline{C}H_2$: δ=26.66; **Elemental analysis**: Calc. C: 58.29%, N: 9.72%, H: 9.79%; Found: C: 57.52±0.02%, N: 9.46±0.01%, H: 9.83±0.01%; H_2O: 0 %.

N,N'-1,4-butanediyl-bis[6-hydroxy-hexanamide](**1i**):Yield: 71% (MeOH/H_2O); 83% (Acetonitril), m.p. 140 °C. ^{1}**H-NMR** (DMSO-d_6): $\underline{H}OCH_2$: δ=4.34 (b, 2H), $HOC\underline{H}_2CH_2$: δ=3.4 (dt,4H), $HOCH_2C\underline{H}_2CH_2$: δ=1.55 (p, 4H), $HOCH_2CH_2C\underline{H}_2$: δ=1.23 (p, 4H), $C\underline{H}_2CH_2C(O)$: δ=1.3-1.4 (p, 4H), $C\underline{H}_2C(O)N(H)$: δ=2.02 (t, 4H), $C(O)N(\underline{H})$: δ=7.74 (b, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.02 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.3-1.4 (4H); ^{13}**C-NMR** (DMSO-d_6): $HO\underline{C}H_2$: δ=60.60 , $HOCH_2\underline{C}H_2$: δ=35.48, $HOCH_2CH_2\underline{C}H_2$: δ=25.21, $\underline{C}H_2CH_2C(O)$: δ=25.25, $\underline{C}H_2C(O)N(H)$: δ=32.25, $\underline{C}(O)N(H)$: δ=171.92, $N(H)\underline{C}H_2CH_2$: δ=38.08 , $N(H)CH_2\underline{C}H_2$: δ=26.66; **Elemental analysis**: Calc. C: 60.71%, N: 8.86%, H: 10.20%; Found: C: 58.87±0.23%, N: 8.44±0.02%, H: 10.13±0.03%; H_2O: 0.11±0.04 %.

N,N'-1,4-butanediyl-bis[2-hydroxy-2-methyl-ethanamide](**2a**): Yield: 99,5% (THF), m.p. 89-90 °C. ^{1}**H-NMR** (DMSO-d_6): $\underline{H}OCH(CH_3)C(O)$: δ=5.42 (d, 2H), $HOC\underline{H}(CH_3)C(O)$: δ=3.93 (p, 2H), $HOCH(C\underline{H}_3)C(O)$: δ=1.21 (d, 6H), $C(O)N(\underline{H})$: δ=7.67 (t, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.05 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.40 (t, 4H).^{13}**C-NMR** (DMSO-d_6): $HO\underline{C}H(CH_3)C(O)$: δ=67.22, $HOCH(\underline{C}H_3)C(O)$: δ=21.08, $\underline{C}(O)N(H)$: δ=174.29, $N(H)\underline{C}H_2CH_2$: δ=37.81, $N(H)CH_2\underline{C}H_2$: δ=26.61; **Elemental analysis**: Calc. C: 51.69%, N: 12.06%, H: 8.68%; Found: C: 51.78±0.11%, N: 11.88±0.03%, H: 8.88±0.03%; H_2O: 0.17±0.02 %.

N,N'-1,4-butanediyl-bis[3-hydroxy-3-methyl-propanamide](**2b**): Yield: 99% (THF), m.p. 99-100 °C. ^{1}**H-NMR** (DMSO-d_6): $\underline{H}OCH(CH_3)C(O)$: δ=4.7 (bs, 2H), $HOC\underline{H}(CH_3)C(O)$: δ=3.98 (p, 2H), $HOCH(C\underline{H}_3)C(O)$: δ=1.05 (d, 6H), $HOCH(CH_3)C\underline{H}_2C(O)$: δ=2.14 (dq, 4H), $C(O)N(\underline{H})$: δ=7.78 (bt, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.03 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.38 (bs, 4H).^{13}**C-NMR** (DMSO-d_6): $HO\underline{C}H(CH_3)C(O)$: δ=63.76, $HOCH(\underline{C}H_3)C(O)$: δ=23.31, $HOCH(CH_3)\underline{C}H_2C(O)$: δ=45.28, $\underline{C}(O)N(H)$: δ=170.51, $N(H)\underline{C}H_2CH_2$: δ=38.03, $N(H)CH_2\underline{C}H_2$: δ=26.57; **Elemental analysis**: Calc. C: 55.35%, N: 10.76%, H: 9.30%; Found: C: 53.57±0.09%, N: 10.63±0.04%, H: 9.25±0.08%; H_2O: 2.56±0.17 %.

N,N'-1,4-butanediyl-bis[4-hydroxy-4-methyl-butanamide]((**2c**): Yield: 99% (THF), m.p. 113 °C. ^{1}**H-NMR** (DMSO-d_6): $\underline{H}OCH(CH_3)C(O)$: δ=4.50 (s, 2H), $HOC\underline{H}(CH_3)CH_2$: δ=3.60 (q, 2H), $HOCH(C\underline{H}_3)CH_2$: δ=1.05 (d, 6H), $CH(CH_3)C\underline{H}_2$: δ=1.55(q, 4H), $CH_2C\underline{H}_2C(O)$: δ=2.06 (q, 4H), $C(O)N(\underline{H})$: δ=7.82 (bt, 2H), $N(H)C\underline{H}_2CH_2$: δ=3.05 (dt, 4H), $N(H)CH_2C\underline{H}_2$: δ=1.35 (bs, 4H).^{13}**C-NMR** (DMSO-d_6): $HO\underline{C}H(CH_3)C(O)$: δ=65.45, $HOCH(\underline{C}H_3)C(O)$: δ=23.43, $HOCH(CH_3)\underline{C}H_2$: δ=32.03, $CH_2C\underline{H}_2C(O)$: δ=34.84 $\underline{C}(O)N(H)$: δ=172.20, $N(H)\underline{C}H_2CH_2$: δ=38.14, $N(H)CH_2\underline{C}H_2$: δ=26.63; **Elemental analysis**: Calc. C: 58.29%, N: 9.72%, H: 9.79%; Found: C: 57.69±0.17%, N: 9.56±0.06%, H: 9.85±0.06%; H_2O: 0.05±0.01 %.

Polymer synthesis; typical procedure for 3 gram poly(ester-amide) (x:y = 75:25 %) containing 12.5 mole% bis amide monomer **1i** in the feed. To a mixture of 2,0 g adipic acid dimethyl ester, 1,6 g butane diol and 0,92 g **1i** 90 µl of a $Ti(OBu)_4$ solution (0,05g/ml in toluene) was added. The mixture was heated to 175 °C and the methanol formed was distilled off during 1 to 2 hours. Under reduced pressure(5 mbar) the temperature was raised to 190 °C whereafter the pressure was further reduced to 0.1 mbar. The excess diol was distilled during 10 h period. The pale yellow viscous melt was cooled and characterised.

CONCLUSIONS

It is shown that well defined block copolymers can be made from structurally well defined short diamide blocks, aliphatic diesters and diols. Rapid crystallisation of the copoly(ester amide)s was observed over a very broad range of the copolymer composition. The copoly(ester amide)s showed both an isotropic and a very stable LC-phase, presumably a smectic A or C type, in the melt. This is believed to be a first observation of a liquid crystalline phase in aliphatic poly(ester amide)s (without use of monomeric mesogens).

REFERENCES

1. a) Carothers, W.H., US Patent 2.071,250, **1931**, DuPont de Nemours, USA; b) Dreyfuss,P., Keller,A., *J. Macromol. Sci. -Phys.*,**1970**, *B4(4)*, 811-836, ; c) Brill,R., *Makromol. Chem.*,**1956**, *18*, 294; d) Magill,J.H., *J. Pol. Sci.: Part A-2*, **1966**, vol. 4, 243-265; e) Hinrichsen,G. *Die Makromol. Chem.*, **1973**, *166*, 291-306. And references cited therein.

2.a) Kricheldorf,H.R., Kaschig,J., *J. Eur. Polym.*,**1978**, *14*, 923; b) Williams,J.L.R., Laakso,T.M., Contois,L.E., *J.Polym. Sci.*,**1962**, *61*, 353.

3. a) Garcia,D., Starkweather,H., *J.Polym. Sci. Polym. Phys. Ed.*, **1985**, *32*, 537; b) Ramesh,C., Keller,A. Eltink,S.J.E.A., *Polymer*, **1994**, *35*, 5293. And references cited therein.

4. a) Harrell Jr.,L.L., *Macromolecules*, **1969**, *2*, 607, ; b) Ng,H.N., Allegrezza,A.E., Seymour,R.W. and Cooper,S.L. *Polymer*, **1973**, *14*, 255.

5.a) Beginn,U. Latterman,G. *ACS Polymer Preprints*, **1995**, 70; b) Han,H., Roychowdhury,S., Bhowmik,P.K., *ACS Polymer Preprints*, **1995**, 126; c) Han,H., Molla,A. H., Bhowmik,P.K., *ACS Polymer Preprints*, **1995**, 332; d) Bhowmik,P.K., Wang,X., Han,H. , Sarker,A. M., *ACS Polymer Preprints*, **1995**, 324.

6. a) Aharoni,S.M., Macromolecules, **1988**, *21*, 1941; b) Aharoni, S.M., Correale, S.T. Hammond,W.B., Hatfield,F.R. and Murthy, N.S., Macromolecules, **1989**, *22*, 1137; c) Hatfield, F.R., Aharoni,S.M., Macromolecules, **1989**, *22*, 3807; d) Murthy,N.S., Aharoni,S.M., Macromolecules, **1992**, *25*, 1177.

7. a) Lehn,J.-M. Angew. Chem., **1988**, *100*, 91; b) Fouquey,C., Lehn,J.-M. , Levelut,A.-M., Adv. Mater. **1990**, *2*, 254.

8. J. Zimmerman, "Polyamides", in: *Encyclopedia of Polymer Science and Engineering*, **1988**, vol. 11, Wiley, New York, 315.

9. Goodman, I, Sheahan, R.J., *Eur. Polym. J.*, **1990**, *26*, 10, 1081.

10. C.D. Eisenbach, E. Stadler, Macromol. Chem. Phys., **1995**, *196*, 833

11. a) Tokiwa,Y, Suzuki,T, Takeda,K, *Agric. Biol. Chem.*, **1988**, *52(8)*, 1937. b) e.g. Albertsson,A.-C. and Karlsson,S., in: *Comprehensive Polymer Science*, Allen,G,

Bevington,J.C., Eds., first suppl. (Volume Eds. Aggarwal,S.L., Russo,S.), Pergamon Press, Oxford, **1992**, Chapt. 13, p.285. And references cited therein.

12. e.g. Huang S.J., in: *Comprehensive Polymer Science*, Allen,G, Bevington,J.C., Eds., Vol. 6 (Volume Eds. Eastmond, G.C., Ledwith, A., Russo,S., Sigwalt,P.), Pergamon Press, Oxford, **1989**, Chapt. 21, p.597. And references cited therein.
13. e.g. Solomons, T.W.G. Organic Chemistry, **1988**, John Wiley & Sons, New York.
14. Heberer,D, Keller,A, Percec,V., *J. Pol. Sci.:Part B: Pol. Physics*, **1995**, 33, 1877.