ELSEVIER

Polymer 41 (2000) 3531–3539

polymer

New polyamides with long alkane segments: nylon 6.24 and 6.34

M. Ehrenstein, S. Dellsperger, C. Kocher, N. Stutzmann, C. Weder, P. Smith*

Department of Materials, Institute of Polymers, ETH Zürich, CH-8092 Zürich, Switzerland

Received 2 June 1999; received in revised form 16 August 1999; accepted 19 August 1999

Abstract

A series of new amphiphilic, semi-crystalline polyamides based on hexamethylenediamine and long alkane carboxylic diacids has been synthesized and characterized, here exemplified by polyamide 6.24 (PA-6.24) and polyamide 6.34 (PA-6.34). The polymers were produced by melt polycondensation, which yielded materials of weight-average molecular weights in the range of 30,000–35,000 g/mol. The thermal properties of the polyamides were investigated by various thermo-analytical methods. PA-6.24 and PA-6.34 exhibit relatively high melting temperatures of 189 and 177°C, respectively. Both materials display rather poor solubility in solvents that are used for common polyamides, but by contrast, dissolve in, e.g. ethanesulfonic acid. PA-6.34 was found to aggregate in dilute methanesulfonic acid solutions and form thermo-reversible gels in H_2SO_4, which we attribute to its amphiphilic character. The latter enabled the use of PA-6.34 as a "compatibilizer" for blends of polyolefins and polyamides. Finally, the Young's moduli of isotropic films of PA-6.24 and PA-6.34 were determined to be 1.3 and 0.7 GPa, respectively, representing a stiffness that is intermediate between that of common polyamides and polyethylene.

Keywords: Polyamides; Hexamethylenediamine; Long alkane carboxylic diacids

---

1. Introduction

Linear aliphatic polyamides, commonly known as nylons,[1] occupy a prominent position in the realm of polymers. Nylons are semi-crystalline polymers that usually exhibit a relatively high modulus, toughness and strength, low creep and good temperature resistance that allow widespread use of this family of polymers as fibers and engineering thermoplastics [1,2]. The attractive matrix of properties of polyamides originates in strong hydrogen bonds, which are formed by the amide groups [3]. Since their discovery by Carothers in 1934 [4,5], many nylons have been investigated, a number of which have been commercialized during the past 50 years [2]. Relatively little effort has been made to explore and exploit nylons that comprise long aliphatic segments (>dodecane). The incorporation of such aliphatic segments into polyamides potentially might lead to a class of amphiphilic polyamides that in certain aspects could bridge the gap between polyamides and polyolefins. Due to their anticipated amphiphilic character, these materials might find applications as coatings, compatibilizers between, e.g. nylons and polyolefins, as well as partially hydrophobic high-temperature engineering polymers.

A literature review yielded several reports that describe AABB nylons that comprise long aliphatic segments [1,6–9]. The most important group of these polyamides contains carboxylic diacids, which are derived from unsaturated fatty acids like oleic, eladic and linoleic acids [8]. Due to their origin these diacids are usually branched and rather ill-defined. Nevertheless, these polyamides occupy a relevant commercial niche in the area of adhesives, inks and coatings. Also copolymers of these diacids with caprolactam, hexatriacontanediamine and nonadioic acid have been described, presumably for use as high-impact-strength polyamides [7]. For zinc-chloride-resistant materials, another class of polyamide copolymers was synthesized [6], which contain a fraction of long aliphatic dicarboxylic acids or long aliphatic diamines. However, the latter polyamides were poorly defined copolymers, which comprised only small fractions of long aliphatic diacids. As a matter of fact, attempts to prepare homopolymers of the first-mentioned monomers were reported to have failed [6]. Careful studies of medium long chain nylons (up to nylon 6.18) were carried out by Jones et al. [9]. Unfortunately, no synthetic details and molecular characterization data were presented on this material that was referred to be a research sample of I.C.I.

In the case of n-nylons, to our knowledge, the highest

---

* Corresponding author.

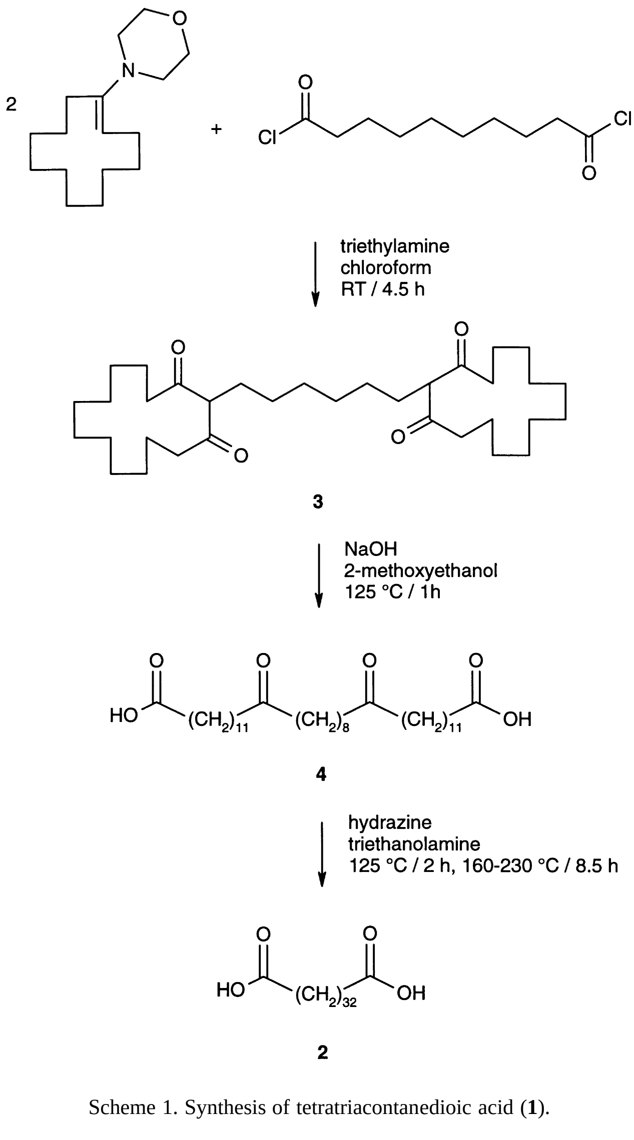
[1] As it is common practice, nylon is here used as a synonym for AABB polyamides as well as AB polyamides; the latter are also referred to as n-nylons.

PII: S0032-3861(99)00590-X

Nomenclature

PA-6.24	Poly(iminohexamethylene-iminotetracosanoyl)
PA-6.34	Poly(iminohexamethylene-iminotetratriacontanoyl)
1	Tetracosanedioic acid
2	Tetratriacontanedioic acid
3	2,2-Hexamethylene-bis-(cyclotetradecane-dione-(1,3))
4	13,22-Dioxo-tetratriacontanedioic acid

investigated homologue is 22-nylon [10]. The latter was reported to exhibit a melting point of around 145°C, and thus lacks the temperature-resistance of common nylons. In order to prevent the formation of materials of a low melting temperature, we elected to incorporate extended aliphatic segments into AABB nylons, because these polymers usually exhibit higher melting points than their corresponding AB nylons [2].



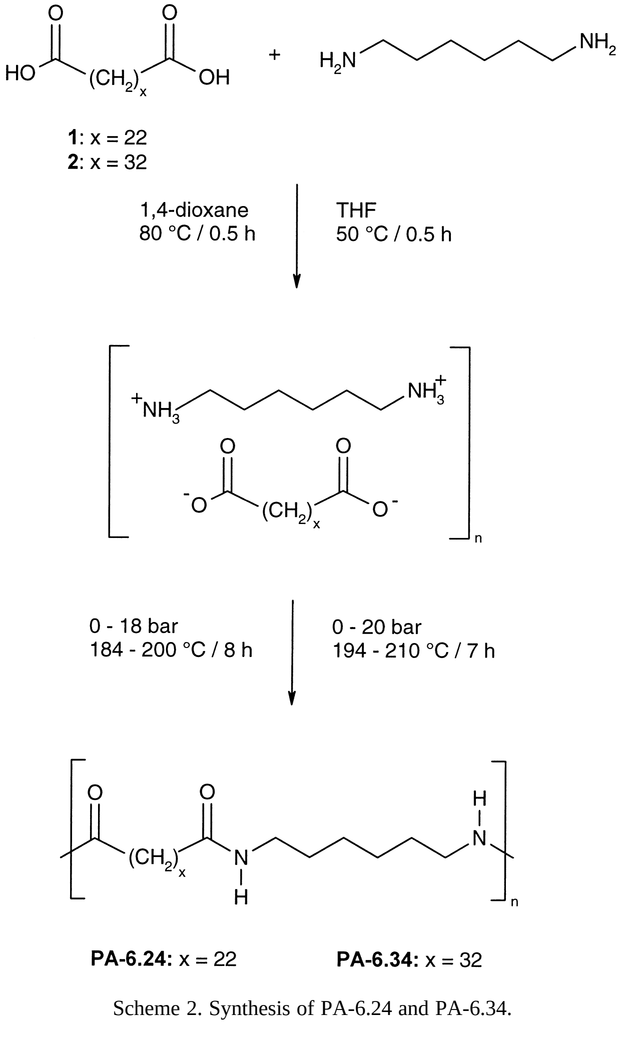
Scheme 1. Synthesis of tetratriacontanedioic acid (**1**).

In this paper, we describe the synthesis and certain properties of PA-6.24 and PA-6.34 as examples of a series of nylons comprising long aliphatic segments. We demonstrate that incorporation of the latter indeed leads to polyamides of amphiphilic nature, which potentially makes the new materials attractive for a number of applications that range from compatibilizers to high strength fibers [11].

2. Results and discussion

2.1. Monomer synthesis

Tetracosanedioic acid (**1**), which was employed for the synthesis of PA-6.24, represents—to the best of our knowledge—the longest, commercially available linear aliphatic diacid. In order to make polyamides with even longer aliphatic segments accessible, tetratriacontanedioic acid (**2**) was synthesized in this work. A variety of methods has been developed in the past for the preparation of extended diacids, such as the Kolbe electrolysis of alkanoic



Scheme 2. Synthesis of PA-6.24 and PA-6.34.

Table 1
Solubility of PA-6.24 and PA-6.34 in various liquids. Key: (−) insoluble, (+) soluble, (G) forms gel

Solvent	PA-6.6		PA-6.24		PA-6.34	
	25°C	50°C	25°C	50°C	25°C	50°C
Toluene	−	−	−	−	−	−
Chloroform	−	−	−	−	−	−
NMP	−	−	−	−	−	−
DMSO	−	−	−	−	−	−
m-Cresol	+	+	−	+	−	+
Formic acid	+	+	−	−	−	−
Sulfuric acid	+	+	+	+	G[a]	G[a]
Methanesulfonic acid	+	+	+	+	+	+
Ethanesulfonic acid	+	+	+	+	+	+

[a] Soluble at 80°C.

acids [12,13], the oxidation of cycloalkanols and natural alkenes [14], microbial conversion of alkanes [15,16] and others [17,18]. Tetratriacontanedioic acid (**2**) previously has been prepared in moderate yield (∼13%) by electrochemical coupling of hexadecane dicarboxylic acid monoethylester [13], and in higher yield (46%) by the enamine-coupling route, originally proposed by Hünig et al. [19]. Because of the significantly higher yield, we followed the latter route in the present work (Scheme 1). The key step is the "chain-extending" cycloadditon of a diketene (which is formed in situ from sebacoyl chloride) with two equivalents of 1-morpholino-cyclododecene. This addition is followed by a ring-opening reaction of 2,2-hexamethylene-bis-(cyclotetradecanedione-(1,3)) (**3**) with sodium hydroxide. Both keto-functions of the resulting 13,22-dioxo-tetratriacontanedioic acid (**4**) were reduced with a Wolff–Kishner reduction with hydrazine. The final overall yield was 44% and is in good agreement with previously published results [19].

2.2. Synthesis of polymers

PA-6.24 and PA-6.34 were synthesized by the standard melt-polycondensation of hexamethylenediamine and the appropriate dicarboxylic diacid, as shown in Scheme 2. In order to prepare high-molecular weight polymers, we first produced the hexamethylenediamine salts of the dicarboxylic diacids and thoroughly purified the latter by recrystallization from THF or a (1:5 v/v) mixture of dioxane and toluene. Subsequently, these salts were polymerized in an autoclave, which allowed for careful control of pressure, as well as temperature during the reaction. Routine application of high pressure (nitrogen) prevented evaporation of hexamethylenediamine at the early stages of the polycondensation. Also, a small excess of the latter was added to the diamine salts of the dicarboxylic diacids to compensate for any losses. Typical reaction times were in the range of 7–8 h. The resulting PA-6.24 and PA-6.34 were characterized to satisfaction by ^{1}H-NMR and ^{13}C-NMR spectroscopy, and elemental analysis.

Table 2
Viscosity of PA-6.24 and PA-6.34 in various sulfonic acids

Polyamide	$\bar{M}_w$ [a]	η_{inh} [b] (MSA), dl/g	η_{inh} [b](ESA), dl/g
PA-6.24, this work	35 000	0.72	0.92
PA-6.34, this work	30 000	0.09	0.85

[a] Determined by light scattering in MSA.
[b] At *RT*, $c = 0.5$ g/dl.

2.3. Solution characterization of PA-6.24 and PA-6.34

The solubility in a wide range of solvents of the new polymers was evaluated through visual and optical microscopic examinations. For this purpose, approximately 20 mg of polymer was added under vigorous stirring to 1 ml of selected solvents. The results are summarized in Table 1 together with data obtained with common PA-6.6 (Solutia, Vydyne 21). Methanesulfonic acid (MSA) and ethanesulfonic acid (ESA) proved to be good room-temperature solvents for PA-6.24 and the latter for PA-6.34. Classical solvents for common nylons such as *m*-cresol and sulfuric acid, on the other hand, did not dissolve the present polymers at ambient temperature. Despite the fact that a substantial aliphatic segment is present in the repeat unit of both PA-6.24 and PA-6.34, common organic solvents such as chloroform did not dissolve these polymers, at ambient temperature and at elevated temperatures. Also, notorious H-bond-breaking organic solvents such as 1-methyl-2-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO) did not dissolve PA-6.24 and PA-6.34. A most remarkable and interesting phase behavior was observed for PA-6.34 in sulfuric acid. At elevated temperatures, i.e. above 80°C, PA-6.34 dissolved in this acid yielding viscous solutions. Upon cooling, clear (thermo-reversible) gels formed. We ascribe the thermo-reversible gelation to the melting and reformation of "crystals" comprising the long aliphatic segment present in the novel polyamide. This view is consistent with the fact that the temperature at which the present polyamide dissolved is in the vicinity of the melting temperature of the long alkane that constitutes it (72–75°C for $C_{34}H_{70}$).

In order to obtain an indication of the molecular weight of the newly synthesized nylons, the inherent viscosities of PA-6.24 and PA-6.34 were measured at a polymer concentration of 0.5 g/dl at 25°C in MSA and ESA. The results are summarized in Table 2. The viscosities measured in ESA (PA-6.24, 0.92 dl/g; PA-6.34, 0.85 dl/g) are indicative of the polymeric character of both polyamides. However, an unexpectedly low value of PA-6.34 was observed in MSA (0.09 dl/g). In order to investigate the origin of this deviating behavior in more detail, static light-scattering experiments were carried out on PA-6.24 and PA-6.34. These investigations revealed weight-average molecular weights ($\bar{M}_w$) of 35 000 for PA-6.24 and 30 000 (both ±5,000) for PA-6.34; both in MSA. In addition,

Table 3
Selected properties of PA-6.24 and PA-6.34 in comparison with those of PA-6.6 and PA-12 Ref. [2]

Property	PA-6.6[a]	PA-6.24	PA-6.34	PA-12[a]
Melting temperature (DSC)	264°C	189°C	177°C	180°C
Solid transition (DSC)	48°C	54°C	88°C[b]	42°C
Solid transition (DMTA)	80°C	58°C	57°C[b]	62°C
Water content (TGA, 50% rel. humidity)	2.5%	1.0%	0.4%	0.8%

[a] See Ref. [2].

[b] Solid transitions of a melt-pressed film.

light-scattering measurements of PA-6.34 in MSA revealed a relative small radius of gyration of 260 ± 80 Å in comparison to PA-6.24 in MSA, which showed a radius of gyration of 350 ± 80 Å. The value of PA-6.34 is indicative of a small end-to-end distance, which suggests the formation of aggregates of PA-6.34 in MSA. This result appears to explain the unusual low viscosity of this system. Unfortunately, fluorescence of ESA prevented comparable experiments in this solvent.

2.4. Thermal properties

Thermal characteristics of the present polyamides were investigated using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA) at heating rates of 10 or 20°C/min. The results, together with data for PA-6.6 and PA-12 are summarized in Table 3. TGA experiments showed that for both polymers, PA-6.24 and PA-6.34, decomposition sets in at around 400 and 420°C in, respectively, air and under nitrogen atmosphere. DSC thermograms of PA-6.24 and PA-6.34, recorded at 10°C/min on samples that were once-molten and cooled, displayed well-defined melting temperatures at 189 and 177°C (see Fig. 1), respectively. These values, not surprisingly, are slightly below the melting temperature reported for nylon 6.18 (i.e. 192°C) [9]. In addition, the DSC traces of carefully dried (16 h, 100°C, vacuum) PA-6.24 showed a glass transition temperature (T_g) around 54°C; i.e. in the standard range of the α-relaxation of common nylons [2]. In the case of a melt-pressed film of PA-6.34 an unexpected high transition was observed at 88°C. In order to investigate the thermal behavior of PA-6.34 in some more detail, we performed quenching and annealing experiments. In the former, PA-6.34 was first molten at 205°C for 15 min under inert atmosphere, and subsequently rapidly cooled down by immersing the sample in liquid nitrogen. Annealing experiments were conducted in the DSC, in which the samples were tempered at 100°C for 60 h under nitrogen atmosphere. Heating of quenched material was accompanied by a significant recrystallization as can be seen from the DSC heating scan of this sample (Fig. 2); the latter appears to indicate a relatively low rate of crystallization of PA-6.34. This observation is not unexpected in view of the very large crystalline unit cell of this polymer and the extensive molecular motion required to form the proper register. DMTA measurements indicated a clear transition at 58°C for PA-6.24, which is in good agreement with the T_g found with DSC. For the melt-pressed sample of PA-6.34, a transition at 57°C was distinguished, which is lower than the values observed in DSC experiments, but is located in the range of T_gs of common nylons.

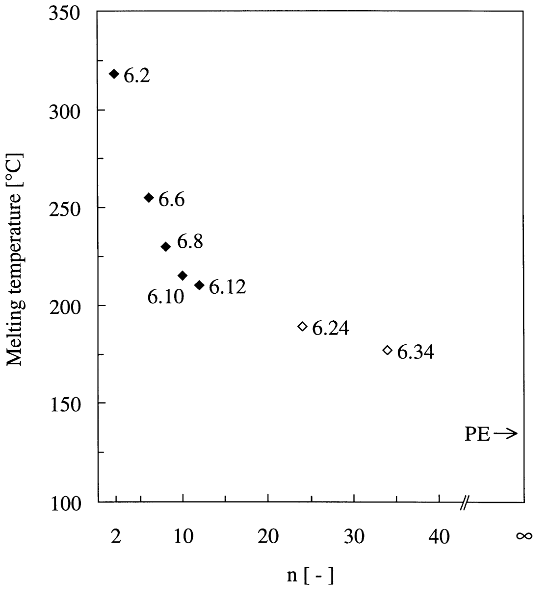


Fig. 1. Melting temperatures of polyamide series PA-6.n: (◆) Refs. [2,24]; (◇) this work.

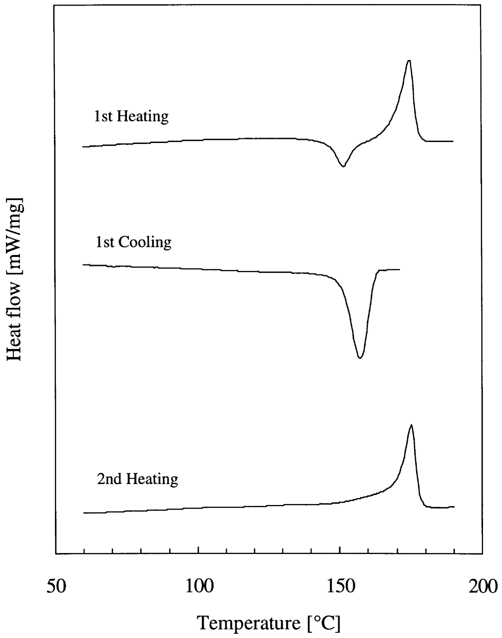


Fig. 2. Differential scanning calorimetry thermograms of PA-6.34. The sample was quenched from the melt by immersion in liquid nitrogen prior to the first heating scan; heating and cooling rates 10°C/min.

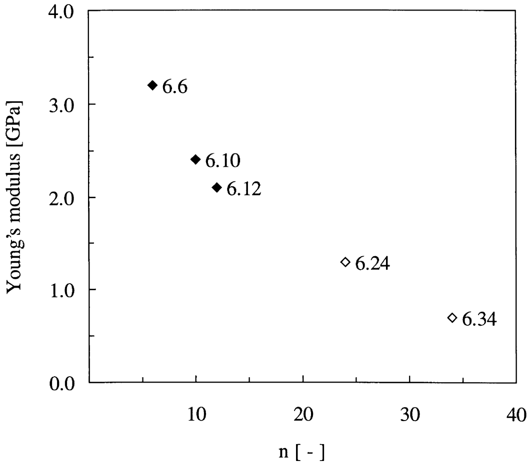


Fig. 3. Young's moduli of melt-crystallized, isotropic, dried samples of polyamides PA-6.n at room temperature: (◆) Ref. [2]; (◇) this work.

2.5. Mechanical properties

Dry, melt-pressed polyamide films were prepared and their mechanical properties were investigated by standard tensile tests at different temperatures (Experimental Section). The Young's moduli of melt-crystallized, isotropic samples at room temperature were found to be 1.3 GPa for PA-6.24 and 0.7 GPa for PA-6.34; the tensile strengths were 33 and 21 MPa, respectively. In comparison with common nylons, these values initially seem to be rather low. However, illustrated in Figs. 3 and 4, which compare the mechanical properties of the series polyamides 6.*n* (of comparable molecular weight), the characteristics of PA-6.24 and PA-6.34 follow the expected trend, both with respect to mechanical and thermal properties—and indeed in that sense fill the gap between standard polyamides and polyethylene.

PA-6.34 films were oriented by tensile deformation at a temperature of 150°C, to a maximum draw ratio of up to 5.3 (Fig. 5). This value is comparable to that observed for standard nylons [20], and is indicative of the reasonable molecular weight of the present materials [21]. The Young's modulus of a five times drawn film was determined to be 3.7 GPa.

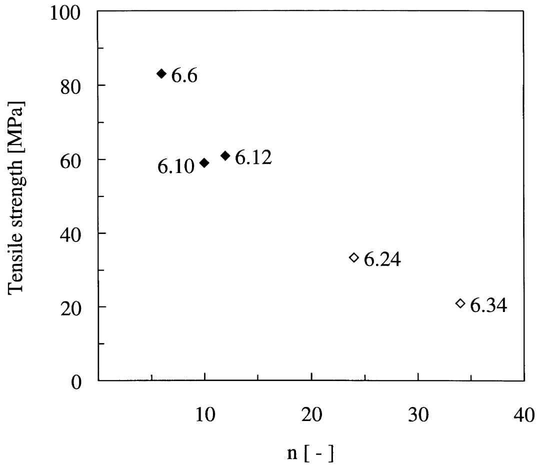


Fig. 4. Tensile strengths of melt-crystallized, isotropic, dried samples of polyamides PA-6.n at room temperature: (◆) Ref. [2]; (◇) this work.

2.6. Wide-angle X-ray diffraction

X-ray diffractograms of PA-6.34 showed two prominent reflections (Fig. 6a), indicative of a significant degree of crystallinity of this material. The X-ray pattern of the oriented PA-6.34 samples unambiguously show the uniaxial orientation of the drawn films (Fig. 6b). Detailed analysis of the crystal structure of this polymer will be published elsewhere.

2.7. Compatibilizing properties

The (poly-)amphiphilic nature of PA-6.34 could make this material a potential candidate for application as "compatibilizer" in blends of, for example, polyolefins and nylons. The latter have recently attracted significant interest [22], not the least because of recycling of carpet waste. In initial experiments, two different polymer blends were prepared and examined, comprising PA-6, and polyethylene and isotactic polypropylene, respectively. The blends contained equal weight-fractions of the hydrophilic PA-6 and the hydrophobic polymer, and 5% w/w PA-6.34 (based on overall weight). The blends were produced in a mini-twin-screw extruder (see Experimental Section for details). Light-microscopy photomicrographs of the different blends are shown in Fig. 7, together with the respective reference experiments (no added PA-6.34). As is evident from these micrographs, the addition of PA-6.34 to both blend systems investigated here dramatically decreased the size of the PA-6 and polyolefin domains.

3. Conclusions

We presented the (melt-polycondensation) synthesis and characterization of PA-6.24 and PA-6.34. The weight-average molecular weights of these new polymers were in the range 30,000–35,000. The thermal and mechanical properties of PA-6.24 and PA-6.34 were found to be in between those of common polyamides and polyethylene. PA-6.34 displayed a most interesting thermo-reversible gelation behavior in sulfuric acid, which offers the possibility of new fiber spinning processes. We also demonstrated the potentially useful "compatitilizing" property of PA-6.34 in, e.g. blends of PA-6 and polyolefins. Current work is directed towards further characterization and exploration of the properties of the present polymers, the synthesis of polyamides containing even longer aliphatic segments, as well as of copolymers that could combine some of the advantages of common nylons and the new polyamides.

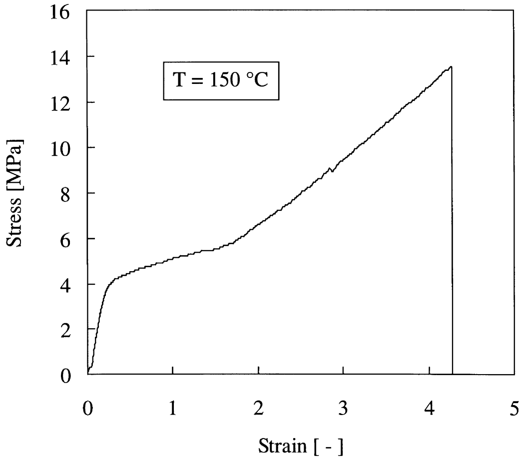


Fig. 5. Stress–strain curve at 150°C of a dried film of PA-6.34.

4. Experimental section

4.1. General methods

All reagents and solvents were purchased from Fluka, Aldrich and Merck, except tetracosanedioic acid (**1**), which was obtained from Across. Only analytical grade quality chemicals were used. DSC and TGA measurements were performed on a Netzsch DSC 200 and a TG 209 instrument, respectively. Melting points were determined by DSC measurements and taken as the peak values of endotherms. The DMTA measurements were carried out under nitrogen atmosphere on a DMTA 3e Rheometric Scientific instrument. ^{1}H-NMR and ^{13}C-NMR spectral data are expressed in ppm relative to an internal TMS standard and were obtained on various Bruker NMR spectrometers. All viscosity measurements were made at 25°C and a concentration of 0.5 g/dl using Ubbelohde capillaries from Schott (type 53020/II) in combination with a Schott AVS 410 viscometer. Elemental analyses and mass spectra were carried out by the Microanalysis and Mass Spectra Laboratories of the Department of Chemistry of ETH Zürich. X-ray measurements were performed on a Seifert ISO-Debeyflex 2002, using a Ni-filtered Cu-K$_{\alpha}$ as ray source (conditions: 12 and 24 h, 30 mA, 35 kV). All mechanical measurements were carried out on an Instron 4464 tensile tester equipped with a load cell of 10 N. The static light-scattering measurements were carried out with a Malvern 4700 PS/MW spectrometer, equipped with an argon ion laser (Coherent, Innova 200-10, wavelength $\lambda_0 = 488$ nm), a digital autocorrelator (Malvern 7032ES/136C), and a computer-controlled and stepping-motor driven variable-angle detection system. Light-scattering experiments were performed according to the procedures given elsewhere [23]. Unless otherwise stated, all polyamide samples were dried for at least 12 h at 80°C under vacuum (10 mbar) before they were used for any experiment.

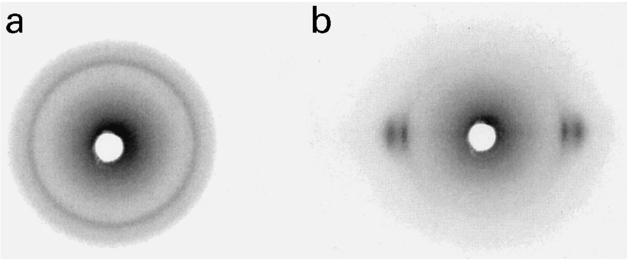


Fig. 6. Wide-angle X-ray diffraction patterns of PA-6.34: (a) isotropic; (b) drawn at 150°C to a draw-ratio (λ) of 5.3; drawing axis vertical.

4.2. Monomer synthesis

4.2.1. 2,2-Hexamethylene-bis(cyclotetradecanedione-(1,3)) (3)

Under argon atmosphere, a solution of 1-morpholino-1-cyclododecene (60.02 g, 238.7 mmol), triethylamine (35 ml) and chloroform (30 ml) was cooled to −6°C. A solution of sebacoyl chloride (21.29 g, 88.6 mmol) in chloroform (30 ml) was added over the course of 16 min dropwise to the stirred and cooled solution; the temperature of the reaction mixture was kept below 15°C. After the addition was completed, chloroform (20 ml) was added and the reaction mixture was stirred for 4.5 h at room temperature. The resulting suspension was subsequently homogenized by the addition of chloroform (460 ml). Hydrochloric acid (2.5 M, 250 ml) was added to the clear, yellow solution, and the mixture was stirred for 20 h. The two phases were separated and the aqueous layer was extracted with chloroform (2×150 ml). The combined organic phases were washed with diluted, aqueous HCl (3×500 ml), dried ($MgSO_4$), and evaporated in vacuo. The resulting off-white solid was extracted in boiling methanol for 1 h; the product was isolated by filtration at 35°C. The product was recrystallized from ethyl acetate (1200 ml), to yield pure 2,2-hexamethylene-bis-(cyclotetradecanedione-(1,3)) (**3**) as a white powder (23.7 g, 50.3%); m.p. 120.9 and 151.4°C. ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ 3.59 (t, $J = 7.23$ Hz, 2H), 2.50–2.36 (m, 8H), 1.80–1.75 (m, 4H), 1.72–1.64 (m, 4H), 1.62–1.55 (m, 4H), 1.40–1.13 (m, 36H). ^{13}C-NMR (125 MHz, $CDCl_3$; 300 K): δ 206.25 (*C*=O), 68.67 (O=C–*C*H–C=O), 39.67, 29.12, 27.98, 27.37, 26.33, 25.55, 25.36, 24.97, 21.03 (all aliphatic –CH_2–). Mass spectrum: *m*/*e* 530.3 (M^+ parent). Anal. Calcd for $C_{34}H_{58}O_4$: C, 76.93; H, 11.01; O, 12.06; Found: C, 77.04; H, 11.22; O, 11.86.

4.2.2. 13,22-Dioxo-tetratriacontanedioic acid (4)

2,2-Hexamethylene-bis-(cyclotetra-decanedione-(1,3)) (**3**) (23.7 g, 44.6 mmol) was dissolved in 2-methoxyethanol (250 ml) at 125°C, and a hot (115°C) solution of NaOH (11.9 g, 296.9 mmol) in 2-methoxyethanol (155 ml) was added quickly to the rapidly stirred solution. A white solid formed immediately, and stirring became difficult. After stirring for 1 h at 125°C, the reaction mixture was allowed

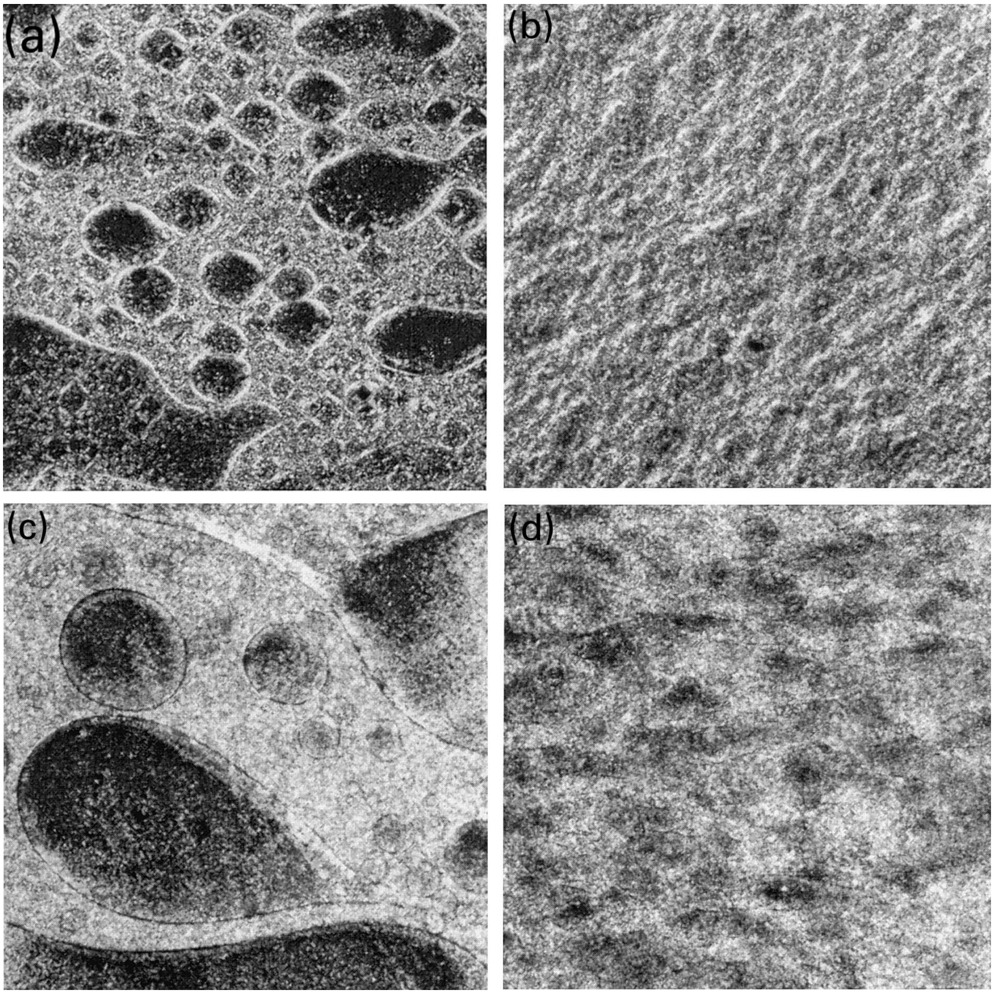


Fig. 7. Optical photomicrographs (phase contrast) of different polymer blends: (a) PA-6/PE (50/50% w/w); (b) PA-6/PE/PA-6.34 (47.5/47.5/5% w/w); (c) PA-6/i-PP (50/50% w/w); (d) PA-6/i-PP/PA-6.34 (47.5/47.5/5% w/w).

to cool to room temperature, the product was isolated by filtration and washed with 2-methoxyethanol and ethanol. Recrystallization from acetic acid (100%, 700 ml) yielded 13,22-dioxo-tetratriacontanedioic acid (**4**) (24.33 g, 96.2%) as a slightly pink powder; m.p. 146.1°C. ^{1}H-NMR (500 MHz, DMSO-d_6, 353 K): δ 2.36 (t, $J = 7.28$ Hz, 8H), 2.17 (t, $J = 7.36$ Hz, 4H), 1.54–1.45 (m, 12H), 1.29–1.19 (m, 36H). ^{13}C-NMR (125 MHz, DMSO-d_6; 353 K): δ 209.77 (CH_2–*C*O–CH_2), 173.68 (–CH_2–*C*OOH), 41.42, 41.40 (–*C*H_2–CO–*C*H_2–), 33.34 (–*C*H_2–COOH), 28.39, 28.34, 28.26, 28.17, 28.15, 28.12, 28.09, 24.07, 22.89, 22.85 (all aliphatic –*C*H_2–). Anal. Calcd for $C_{34}H_{62}O_6$: C, 72.04; H, 11.02; O, 16.93; Found: C, 72.29; H, 11.21; O, 16.66.

4.2.3. Tetratriacontanedioic acid (2)

Hydrazine monohydrate (100 ml) was added to a solution of 13,22-dioxo-tetratriacontanedioic acid (**4**) (24.12 g, 42.55 mmol) in triethanolamine (200 ml) and the reaction mixture was stirred for 2 h at 125°C. After cooling to 80°C, a hot solution of KOH (13.2 g, 235.2 mmol) in triethanolamine (70 ml) was added to the reaction mixture. The resulting solution was vigorously stirred, heated to 160°C and after stirring for 20 min at this temperature carefully heated to 230°C during 105 min. The solution was stirred at 230°C for 6.5 h and cooled to *RT* at which it solidified. Water (350 ml) was added, the mixture was heated to 100°C and the resulting suspension was filtered while hot. The resulting solid was first recrystallized from acetic acid (100%, 600 ml) and then from a mixture of 1,4-dioxane (4500 ml) and 12 M HCl (75 ml). Tetratriacontanedioic acid (**2**) was obtained as a white powder (21.10 g, 92%); m.p. 133.0°C. ^{1}H-NMR (300 MHz, DMSO-d_6, 353 K): δ 2.17 (t, $J = 7.30$ Hz, 4H), 1.54–1.47 (m, 4H), 1.37–1.24 (m, 58H). ^{13}C-NMR (125 MHz, DMSO-d_6; 353 K): δ173.61 (–*C*OOH), 33.36 (–*C*H_2–COOH), 28.51, 28.24, 28.15, 24.10 (all aliphatic –*C*H_2–). Anal. Calcd for $C_{34}H_{66}O_4$: C, 75.78; H, 12.34; O, 11.88; Found: C, 75.33; H, 12.53; O, 12.33.

4.3. Polymer synthesis

4.3.1. Polyamide 6.24

Tetracosanedioic acid (**1**) (2.17 g, 5.45 mmol) was dissolved in THF (110 ml) at 50°C and a solution of hexamethylenediamine (0.66 g, 5.65 mmol) in THF (15 ml) was added under vigorous stirring. The hexamethylenediamine-tetracosanedioic acid salt immediately precipitated. The mixture was stirred for another 30 min at 50°C, allowed to cool to room temperature, and the white product was collected by filtration. The hexamethylenediamine–tetracosanedioic acid salt was recrystallized from a mixture of ethanol (130 ml) and water (40 ml), and was obtained as a white powder (2.30 g, 86%); m.p. 161.4°C.

A glass tube was charged with hexamethylenediamine–tetracosanedioic acid salt (1.68 g, 3.42 mmol) and a slight excess of hexamethylenediamine (22 mg, 0.19 mmol) was added. The glass tube was snugly fitted into an autoclave. After the autoclave was evacuated and flushed with nitrogen and after this cycle had been repeated three times, a nitrogen pressure of 15 bar was applied. The reaction was subsequently started, by quickly raising the autoclave temperature to 194°C; an increase in pressure to about 20 bar was observed. After keeping the autoclave for 2 h at 194°C, the temperature was increased to 202°C. After 1.5 h under these conditions, the pressure was decreased *(10 bar)* and the autoclave was kept for 2 h. In a last step, a vacuum (<0.1 mbar) was established, the temperature was increased to 210°C and the reaction was continued for another 2 h. The autoclave was then cooled to room temperature. The resulting PA-6.24 was obtained as a white solid (1.29, 83%) and was pulverized in a freezing mill; m.p. 189.0°C. ^{1}H-NMR (300 MHz, phenol-d_6, 353 K): δ 3.17 (t, $J = 7.20$, 4H), 2.16 (t, $J = 7.60$, 4H), 1.64 (t, $J = 7.00$, 4H), 1.26–1.45 (m, 40H), 1.05–1.16 (m, 4H). ^{13}C-NMR (300 MHz, phenol-d_6, 300 K): δ 176.32 (–*C*ONH–), 40.13 (–CONH–*C*H$_2$–), 36.97 (–*C*H2–CONH–), 29.90, 29.83, 29.77, 29.61, 29.38, 29.24, 26.39, 26.11 (all aliphatic –*C*H$_2$–). Anal. Calcd for $C_{30}H_{58}N_2O_2$: C, 75.26; H, 12.21; N, 5.85; O, 6.68; Found: C, 75.06; H, 12.11; N, 5.89; O, 7.07.

4.3.2. Polyamide 6.34

Tetratriacontanedioic acid (**2**) (5.39 g, 10.00 mmol) was dissolved in 1,4-dioxane (400 ml) at 90°C and a solution of hexamethylenediamine (1.16 g, 10.00 mmol) in 1,4-dioxane (50 ml) was added under vigorous stirring. The hexamethylenediamine–tetratriacontanedioic acid salt immediately precipitated. The mixture was stirred for another 30 min at 100°C, allowed to cool to room temperature, and the white product was collected by filtration. The hexamethylenediamine–tetratriacontanedioic acid salt was recrystallized from a mixture of 1,4-dioxane (200 ml) and toluene (1000 ml), and was obtained as a white powder (5.44 g, 83%); m.p. 157.7°C.

A glass tube was charged with hexamethylenediamine–tetratriacontanedioic acid salt (5.25 g, 8.01 mmol) and a slight excess of hexamethylenediamine (19 mg, 0.16 mmol) was added. The glass tube was snugly fitted into an autoclave. After the autoclave was evacuated and flushed with nitrogen and this cycle had been repeated three times, a nitrogen pressure of 16 bar was applied. The reaction was subsequently started by quickly raising the autoclave temperature to 184°C; an increase in pressure to about 18 bar was observed. The temperature was gradually increased to 192°C over a period of 3.5 h. The pressure was then decreased and the polycondensation was continued at a pressure of 6 bar and temperature of 192°C for 2 h. Finally, a vacuum (<0.1 mbar) was established, the temperature was increased to 200°C and the reaction was continued for another 2.5 h. The autoclave was then cooled to room temperature. The resulting PA-6.34 was obtained as a white solid (4.21 g, 85%) and was pulverized in a freezing mill; m.p. 177.0°C. ^{1}H-NMR (300 MHz, phenol-d_6, 353 K): δ3.17 (t, $J = 7.20$, 4H), 2.16 (t, $J = 7.60$, 4H), 1.64 (t, $J = 7.00$, 4H), 1.21–1.50 (m, 60H), 1.06–1.18 (m, 4H). ^{13}C-NMR (300 MHz, phenol-d_6, 300 K): δ 176.31 (–*C*ONH–), 40.12 (–CONH–*C*H$_2$–), 36.97 (–*C*H2–CONH–), 29.89, 29.77, 29.62, 29.38, 29.24, 26.39, 26.11 (all aliphatic –*C*H$_2$–). Anal. Calcd for $C_{40}H_{78}N_2O_2$: C, 77.61; H, 12.70; N, 4.53; O, 5.17; Found: C, 77.61; H, 12.63; N, 4.68; O, 5.14.

4.4. Mechanical characterization

Polyamide film samples were produced by melt compression molding between two poly(tetrafluoroethylene) (PTFE) sheets of a thickness of 0.4 mm. PA-6.24 and PA-6.34 powders were filled into the mould, and heated at 205 and 195°C, respectively. After 5 min a force of 1.0 tons was applied for 2 min; subsequent quenching to ambient resulted in films of a thickness of about 80 μm. Mechanical tensile testing of the films was performed in a temperature range of 25 to 150°C and at a strain rate of 100%/min on dog-bone shaped samples (test area $= 12.7\ \text{mm} \times 2\ \text{mm}$). For this purpose a tensile tester (Instron 4464) equipped with a controlled atmosphere chamber was employed.

4.5. Blend preparation

A twin-screw mini-mixer (commercially available from DACA Instruments, Santa Barbara, CA) was used for all blending experiments. In order to prevent any degradation of the polymers, the entire process of feeding, mixing, and extrusion was carried out under a constant flow of nitrogen (5 l/min). The mixer was preheated to a temperature of 240°C before adding the polymers in the following order: polyethylene (DSM, $\bar{M}_w = 100\,000$) or isotactic polypropylene (Polysciences, $\bar{M}_w = 220\,000$), respectively, polyamide 6 (Polysciences, $\bar{M}_w = 35\,000$), and finally PA-6.34. All blends investigated comprised a 1:1 w/w ratio of the polyolefin and PA-6, and in the case of the compatibilized blends a total weight-fraction of 5% w/w of PA-6.34 was used. The mixer drive was set to 50 rpm for the filling process. The blends were extruded in recycling-mode for 10 min at a speed of 150 rpm. Before discharging, the speed of the mixer was reduced to 50 rpm.

4.6. Blend characterization

Thin films of a thickness of approximately 100 μm were prepared as described above, but pressed at a temperature of 240°C. A Leica DMRX light microscope in transmitted light mode was used for optical investigation of the polymer blend films.

Acknowledgements

We thank Solutia, Inc. for support of this work, Drs. J. H. Southern and D. H. Martin for many fruitful discussions and Prof. Peter Schurtenberger, ETH Zürich, for conducting the light-scattering studies. We also wish to acknowledge Dipl.-Ing. Gaby Riedel, University of Erlangen-Nürnberg, for carrying out DMTA measurements. Finally, we acknowledge the critical and useful comments of the reviewers.

References

[1] Welgos RJ. Encyclopedia of polymer science and engineering, 2. New York: Wiley, 1988. p. 11.
[2] Kohan MI. Nylon plastics handbook, Munich: Carl Hanser Verlag, 1995.
[3] Morgan PW. Condensation polymers, 10. New York: Wiley, 1965.
[4] Carothers WH. US Patent 2,130,948, 1938.
[5] Carothers WH, Graves GD. US Patent 2,163,584, 1939.
[6] Sims WM, Bliss AD. German Patent 2,225,515, 1972.
[7] Sims WM. German Patent 2,626,273, 1976.
[8] Johnson RW, Valdespino JM, Gordon RL, Miller GE, Kight RW. 2. Encyclopedia of polymer science and engineering, 11. New York: Wiley, 1988.
[9] Jones NA, Atkins EDT, Hill MJ, Cooper SJ, Franco L. Polymer 1997;38:2689.
[10] Dupont G, Champetier G, Cohen J, J.P P. Compt Rend Acad Sci France 1957;245:1542.
[11] Weenink WD. Nylon−sulfonic acid systems. PhD thesis, ETH Zürich, 1999.
[12] Signer R, Sprecher P. Helv Chim Acta 1947;30:1001.
[13] Fairweather DA. Proc R Soc Edinburgh 1925;45:4433.
[14] Ellis BA. Org Syn 1941;1:18 Coll Vol.
[15] Shiio I, Uchio R. Japanese Patent 51-6750.
[16] Hata S. Japanese Patent 48-26238.
[17] Seher A. Ann Chem 1954;589:222.
[18] Wagner RB, Zook HD. Synthetic organic chemistry, New York: Wiley, 1953.
[19] Hünig S, Buysch H-J. Chem Ber 1967;100:4017.
[20] Postema AR, Smith P, English AD. Polym Commun 1990;31:444.
[21] Smith P, Matheson RR, Irvine PA. Polym Commun 1984;25:294.
[22] Ohlsson B, Hassander H, Törnell B. Polymer 1998;39:4715.
[23] Grob MC, Schurtenberger P, Suter UW. Macromol Chem Phys 1995;196:1391.
[24] Brandrup J, Immergut EH. Polymer Handbook, 3. New York: Wiley, 1989.