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Lyotropic Para-Linked Aromatic Poly(amic ethyl ester)s

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Summary: The synthesis, characterization and application of lyotropic precursor polymers for polyimides, poly(amic ethyl ester)s (PAE) are presented. By the use of non-coplanar and para-linked monomers, rigid-rod PAEs are synthesized in a typical polycondensation reaction yielding liquid crystalline solutions at concentrations of 30-40 wt% in NMP at 100 °C. These lyotropic solutions permit for the first time the fabrication of orientation PAE layers by shear which are thermally converted to the corresponding polyimide. The bulk orientation in the thin films is characterized by spectroscopic methods. In addition the lyotropic solution is spun into fibers in a dry-jet wet spinning process. The obtained fiber orientation is characterized by tensile tests and wide angle X-ray scattering.

Keywords: nanolayers, orientation, polyimides, solution properties, structure-property relations

Introduction

The macroscopic orientation of polyimides and their precursor polymers in bulk and at the surface is important for a technical as well as an academic interest. In the course of our research we are investigating the development of intrinsically anisotropic precursor systems, their orientation and application possibilities.

Since several years poly(amic ethyl ester)s (PAE) are used increasingly instead of poly(amic acid)s (PAA) as precursors for polyimides.[1-4] PAEs have improved solubility, better resistance to hydrolytic degradation, yield high molecular weight products, but require higher and broader imidization temperatures. For technical applications based on PMDA, such as insulating layers in computer chips, only the meta isomer is employed since the good solubility of the resulting precursor polymer permits the preparation of concentrated solutions. PAEs based on the para isomer only should exhibit similar behavior as it is well established for lyotropic para-linked polyaramides.[5-7] As shown in Scheme 1 the incorporation of flexible elements such as meta or oxygen links results in flexible precursor systems. In contrast the usage of para links in

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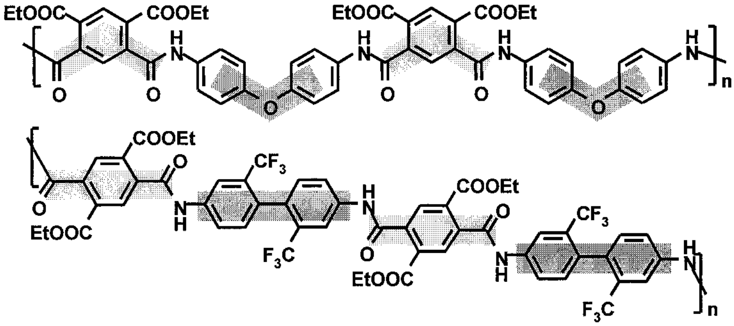
combination with linear non-coplanar diamines results in an extended rod-like precursor polymer. For PAAs no lyotropic phases have been found for PMDA/4,4'-ODA up to 30wt% solvent content which was attributed to the existence of the para and meta isomer within the PAA backbone. Indications of lyotropic behavior was described for the first time in the PAA of PMDA/4,4'-MDA. At room temperature this system turns opaque over 15wt% solid content in NMP and shows at 20wt% spherulitic crystals.[8] A few years ago we reported[9] the first para-linked aromatic PAE that exhibits a lyotropic liquid crystalline phase. By use of THF as cosolvent in combination with NMP, at 35-55wt% in NMP lyotropic solutions were observed after evaporation of the volatile cosolvent.[10]



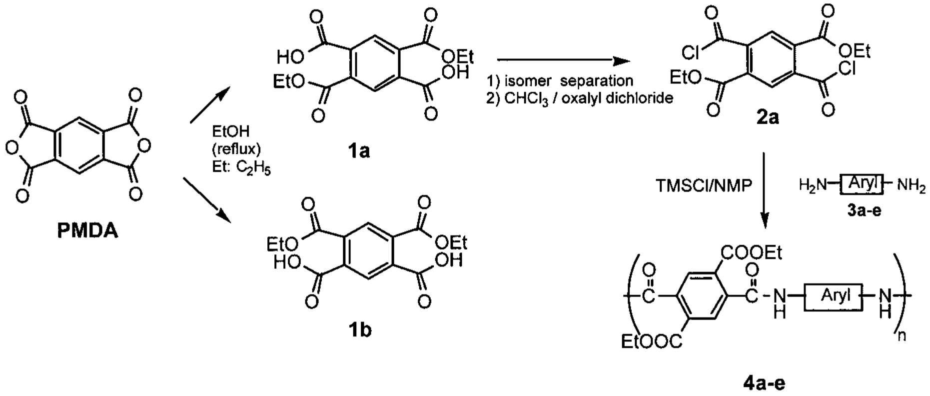
Scheme 1. Chain conformations of a flexible PAE (top) with meta-linked amid units and kinked, flexible diamines compared to an extended PAE (bottom) with para-linked amid units and rod-like non-coplanar diamines.

Polyimides are commonly used as orientation layers in nematic liquid crystal displays (LCD). The planar alignment of the LC director is achieved by rubbing (buffing) the polyimide layer.[11] The mechanism of the orientating effect is still subject of many investigations. Most polyimides used for orientation layers possess a more or less flexible structure. The development of lyotropic rigid-rod PAEs permits for the first time the investigation of PAE and polyimide layers obtained additionally by orientation methods such as shear. This opens up also a method of preparing PI orientation layers without a separate buffing processing step. Furthermore structure-property relationships comparing rod-like (para) to flexible (meta) PAEs can be developed.

Another area of utilizing the orientation development in PAE and/or PI is the processing into fibers and subsequent drawing. The spinning of lyotropic solutions of polyaramids into fibers and their orientation was thoroughly investigated for the commercialization of Kevlar® fibers.[5] In the case of para-linked PAEs the high aspect ratios of fibers can be advantageously used to induce orientation by i) starting with nematic lyotropic solutions and ii) drawing the obtained fibers before and during imidization.

Synthesis of Para-linked Poly(amic ethyl ester)s

All PAEs were synthesized according to literature procedures[1-4, 9] as shown in Scheme 2. PMDA was refluxed in excess ethanol to form an isomeric mixture of para (**1a**) and meta (**1b**) isomers. The key step of separating the isomers[4] is based on the lower solubility of **1a** which can be isolated and purified by a series of extraction and recrystallization to 96% (^{1}H-NMR). **1a** can be easily converted to the acid dichloride **2a** with excess oxalyl chloride in chloroform. The polycondensation to the PAEs was performed in anhydrous NMP at 5wt% polymer concentration as described in ref. [9] An in-situ activation of the diamine **3** was achieved by adding molar amounts of chlorotrimethylsilane (TMSCl). The acid dichloride **2a** was added to this mixture and after 4 h the PAEs **4a-e** were precipitated in water, extracted with acetone and dried, yielding almost quantitative conversions.

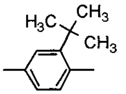
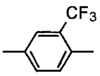
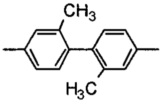
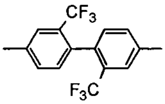
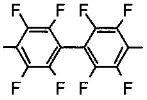


Scheme 2. Synthesis of para-linked rigid-rod PAEs **4a-e**.

Solution Properties and Lyotropic Behavior

All synthesized PAEs form isotropic solutions up to 20wt% and are completely soluble in NMP without the addition of inorganic salts such as LiCl. The inherent viscosities in NMP at 30°C are listed in Table 1 and range between 0.30-1.88 dl/g. The GPC (gel permeation chromatography) in DMAc/LiCl at 70°C revealed number average molecular weights in the range of 30000-50000 g/mol except **4e**. However, the calibration with polystyrene standards results in too high values since polyaramids are considerably more rigid. The low inherent viscosity/molecular weight of the polymer **4e** seems to be the consequence of the high degree of fluorination and the reduced reactivity of the diamine. For the formation and examination of lyotropic systems the polymers **4a-e** were dissolved in NMP at 10wt% without a co-solvent and then concentrated by evaporation at 100°C. The final concentration was determined gravimetrically. All PAEs turned opaque above 30wt% and in some cases liquid crystalline behavior at elevated temperatures or under strong shear was found.

Table 1. Molecular weight characterization of PAEs **4a-e** by viscosimetry and GPC

PAE 4	**a**	**b**	**c**	**d**	**e**
–[Ar]–:					
η_{inh}[a] **[dl/g]**	1.00	1.02	1.88	1.86 (para) 0.66 (meta)	0.30
M_n (GPC)[b]	29000	34000	39000	47000 (para) 49000 (meta)	18000
PD[c]	2.2	2.1	2.5	2.7 (para) 2.1 (meta)	1.9

a) In NMP at 30°C and 0.5 g/dl.
b) In DMAc/0.05M LiCl at 70°C, polystyrene calibration
c) Polydispersity (M_w/M_n)

Rod-like aromatic polyamides and consequently the ones investigated in this study have the strong tendency to form gels. Table 2 summarizes the temperature ranges for the melting of the PAE-gels either to an isotropic (iso) or a lyotropic (lyo) solution. The observation under a polarized light microscopy is possible up to 140°C before major solvent evaporation occurs and imidization progresses. In most cases for concentrations below 30wt% the birefringent gels melt to an isotropic non-birefringent solution. However at higher concentrations around 40wt% the gels melt into a liquid crystalline solution. After annealing a typical nematic Schlieren texture is observed. The transition of the gel state to the isotropic or lyotropic solution is not sharp but extended over a wide temperature range of 20-30°C and coexistence of a gel and isotropic, or gel and lyotropic biphase is observed (Fig. 1).

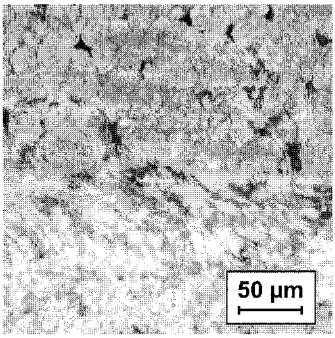


Fig. 1. Spherulitic gel (top) and lyotropic (bottom) domains coexisting in PAE **4d** at 40wt% in NMP at the transition of gel to lyotropic solution (70°C).

Table 2. Temperature ranges in °C of the melting of **4a-e** either to an isotropic (iso) or a lyotropic (lyo) solution determined at a polarization light microscope up to 140°C.

	Concentration/wt%				
4	10	20	30	40	50
a	iso	80-95⇨iso	90-110⇨iso	**105-125⇨lyo**	gel[a]
b	iso	iso	30-50⇨iso	gel[a, b]	gel[a, b]
c	50-80⇨iso	80-110⇨iso	**100-120⇨lyo**	**110-130⇨lyo**	**120-140⇨lyo**
d	iso	iso	60-80⇨iso	**50-80⇨lyo**	**60-100⇨lyo**
e	iso	iso	gel[a, c]	gel[a, c]	gel[a, c]

a) No melting of the gel up to 140°C.
b) After strong shearing a lyotropic phase was observed which gels again within minutes.
c) After strong shearing a lyotropic phase was observed which is stable for months.

For **4d** which contains a non-coplanar 2,2'-di(trifluoromethyl)biphenylene diamine unit the gel formation was first observed at 30wt%. The gel melts between 60 and 80°C into an isotropic solution. At 40 and 50wt% above the gel melting temperature in the range of 50-80°C and 60-100°C, respectively, a lyotropic solution with a typical nematic texture was found. A hypothesis to explain the unusual gelation behavior of the solutions of **4b** and **4e** could be the substitution position of the fluorine atoms at the diamine unit. In both cases it seems to be possible that under shear the fluorine atoms form predominately *intra*molecular hydrogen bonds with the N-H-groups of the adjacent amid linkage, thus supporting the formation of a lyotropic solution. Whereas from isotropic solutions and without shearing a substantial fraction of *inter*molecular hydrogen bridges is formed between the polymer chains resulting in macroscopic gelation. In conclusion, it is evident that the capability of para-linked aromatic PAEs to form stable lyotropic solutions is depending on the particular diamine used. The critical concentration for lyotropism for such polymers is in the range of 30 to 40wt%. The lyotropic phase of **4d** was characterized in great detail by polarization microscopy, DSC, temperature dependent X-ray diffraction, and FT-IR spectropscopy, the results are summarized in ref.[15] Here only a comparison of the surface morphology by SEM is depicted in Figure 2. The meta-linked PAE **4d** forms an isotropic solution and the dried gel shows no distinct surface morphology (Fig. 2, a). However the para-linked **4d** forms a lyotropic solution and here the dried gel forms a distinct 'ground beef' morphology and worm-like structural features are visible (Fig. 2, b).

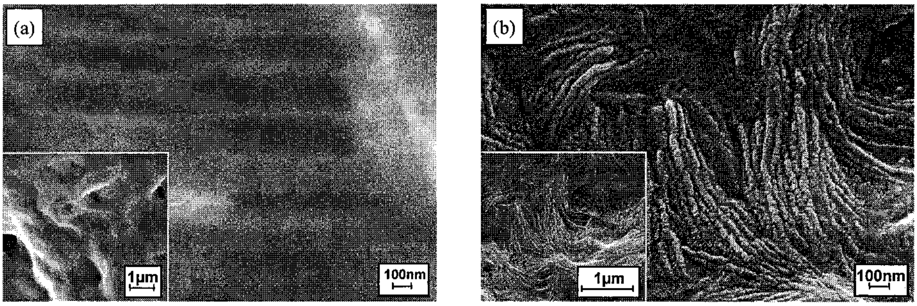


Fig. 2. Scanning electron microscopy images obtained of dried gels of PAE **4d** at a concentration of 50wt%. (a): meta-**4d**,(b): para-**4d.**

Orientation of PAEs in Thin Films by Shear

One objective of the conducted research is to compare the orientation behavior of PAE layers originated from lyotropic para-**4d** solutions with layers obtained from isotropic solutions, e. g. the meta isomer of **4d** or commercial isotropic PI kits[12] for the preparation of orientation layers. For layer preparation the PAE are concentrated up to 50wt% in NMP and heated into the lyotropic phase around 100°C. Then the lyotropic solution was sheared onto a cleaned glass substrate with a doctor blade constructed of a bundle of parallel glass rods which were pressed on the glass substrate while moving with 25 mm/s. This technique permits the fabrication of highly oriented PAE thin films in a thickness range of 20 to 60 nm with high reproducibility. The thus obtained PAE layers were dried at 100°C, characterized, and thermally converted to the PI.

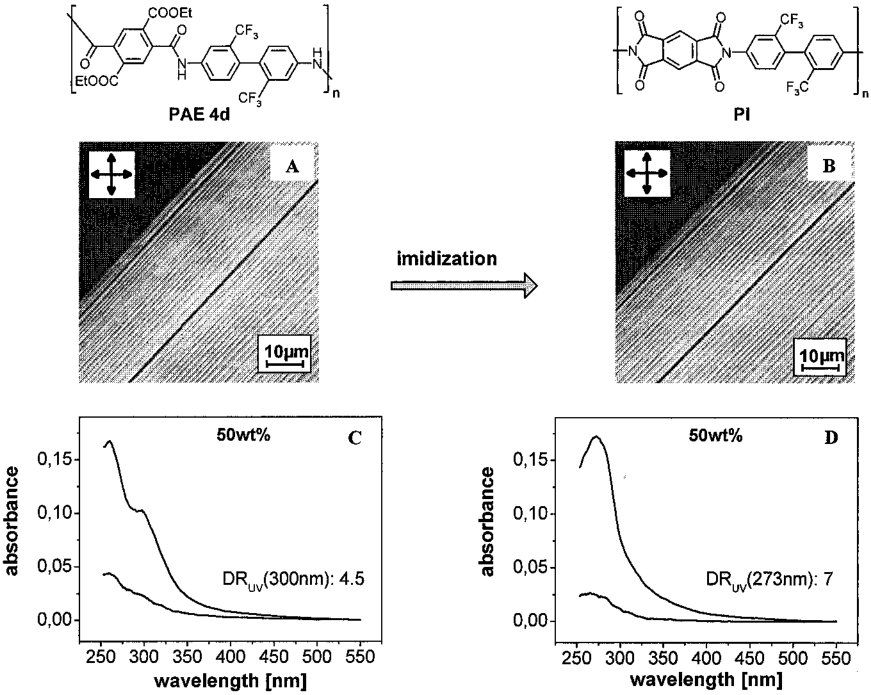


Fig. 3. Polarized light microscopy of para-**4d** (A) and the corresponding imidized structure (B). The layers were characterized by polarized UV/Vis spectroscopy (C, D). The resulting dichroic ratios are plotted in the graphs.

To characterize the obtained orientation the layers were investigated with polarizing techniques, such as light microscopy, FT-IR and UV/Vis spectroscopy.[13] Figure 3 shows the polarized light micrograph of the layer prepared with this shearing technique using the lyotropic solution of para-**4d**. The shearing (and orientation) axis of the layer is rotated at 45° since complete extinction is observed at 0 and 90°. No differences are visible after imidization. Polarized UV/Vis spectroscopic measurements (Figure 4) show that the orientation is fully preserved and the dichroic ratio, as indicator for orientation, is increased after imidization. In the polarization micrographs shown in Figure 3 the layers show striations in shearing direction. These striations where further characterized by a mechanical scanning profiler and SEM (Figure 4 and 5).

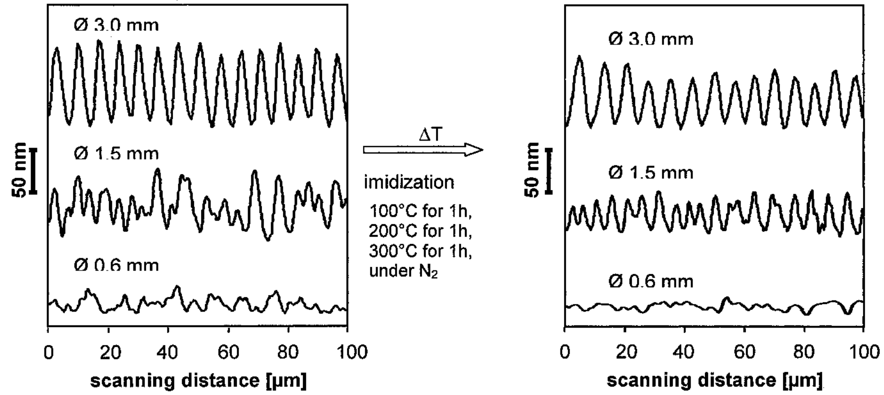


Fig. 4. Mechanical scanned surface profiles of para-**4d** orientation layers prepared by the shearing technique using glass rods with different diameters before (left) and after imidization (right).

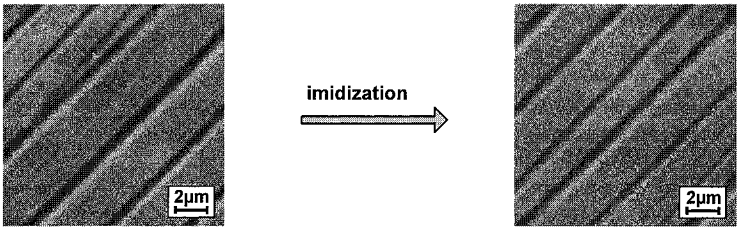


Fig. 5. Scanning electron microscopy (SEM) of oriented layers prepared by shearing with 3 mm glass rods. Left: precursor polymer para-**4d**; right: after imidization (1h at 100°C, 1h at 200°C, 1h at 300°C, 10 K/min; under nitrogen). The darker diagonal lines represent the raised profile.

The distance between the maxima of the striations is around 2 µm. The film shows no dewetting and completely covers the glass slide. The average film thickness below the profile is around 25 nm and the profile height is in the range of 40 nm.

Fiber Spinning from Lyotropic Solutions

PAE monofilaments of para-**4d** were spun from a 40 wt% lyotropic solution in NMP in a dry jet-wet spinning process.[14] At this time no air gap was used and spinning rates were low i. e. 3m/min. In preliminary spinning experiments several coagulation solvents and spinning conditions were tested (Fig. 6) and mechanical fiber properties were evaluated as function thereof.

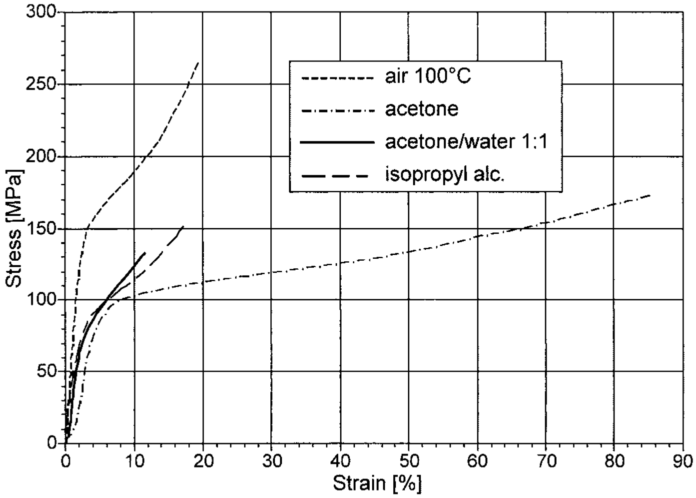


Fig. 6. Stress-strain curves for para-**4d** fibers coagulated in different solvents.

Water is not suitable and fibers with extremely poor mechanical properties are obtained. Acetone yields fibers with lower modulus but very high elongation probably due to a plasticizing effect. An acetone/water 1:1 mixture reduces the elongation dramatically, even at lower water contents. Dry spinning results in fibers with high tenacities and a twofold increase in modulus. Figure 7 shows SEM micrographs of an acetone coagulated PAE fiber. The fiber surface is smooth and unstructured, the fracture surface shows no fibrillation and a very porous morphology is revealed. Based on these results spinning was first attempted as dry spinning. However the spinning set-up available which is optimized for dry-jet wet-spinning did not yield sufficient amounts of continuous fibers. Therefore acetone was used as coagulation medium and in a continuous spinning homogenous fibers with sufficient wet-strength were obtained. Also the fibers could be drawn during spinning in the acetone bath with draw ratios of 2-3. Table 3 lists the obtained mechanical properties of fibers spun from para-**4d** at 100°C and 40wt% with acetone as coagulation bath. All samples have been dried at 50°C in vacuum for 24h before testing. The fibers just coagulated in acetone show high elasticity and thus the highest elongation. Drawing at 100°C in a continuous process with 2.5 cm/sec in air does not change the fiber properties dramatically thus all solvent was removed during drying. Successive heat treatment at 200°C toughens the fiber shown by the increased modulus, tenacity and decreased elongation. This indicates a progressing imidization. After the last treatment process at 300°C the imidization is more complete, modulus and tenacity increased again, the elongation is dramatically decreased indicating an embrittlement of the material. The fiber which was directly drawn in acetone shows prior to any heat treatment high mechanical performance, however accompanied with a low elongation which impede further drawing steps.

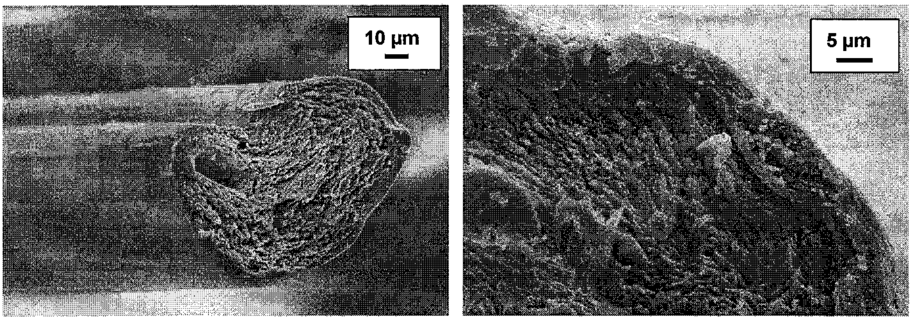


Fig. 7. Fracture surface of a para-**4d** fiber coagulated as-spun in acetone. The left micrograph shows a detailed view of the layered skin-core morphology of the fiber.

Table 3. Mechanical properties of para-**4d** fibers spun in a dry-jet wet-spinning process at 100°C. Data are the average of eight single measurements.

Fiber sample	**(1)**	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**
Process	as spun and coagulated in acetone	sample (1) drawn at 100°C	sample (2) drawn at 200°C	sample (3) drawn at 300°C	drawn in acetone during spinning	sample (5) imidized
cross-head speed [mm/min]	4	4	4	2	2	1
Fiber diameter [μm]	96±8	96±7	84±9	81±9	59±3	54±2
Modulus E [GPa]	6.4±1	6.21±0.7	10.62±2.1	15.8±2.9	23.3±1.8	37.5±5
Tenacity [MPa]	212±37	203±30	286±67	307±51	539±62	547±136
Elongation at break [%]	23.8±2.6	26.0±4.1	13.1±2.9	3.4±0.6	3.4±0.2	1.7±0.4

In Figure 8 the WAXS fiber patterns of sample (1), left, and (5), center, and (6), right, are depicted. The intrinsically much higher orientation of sample (5) is evident by sharper equatorial reflexes whereas the increased meridional reflexes indicate also a better alignment of the polymer chains in fiber axis. This orientation is further improved during imidization in fiber (6). To study the improvement of orientation during drawing more experiments with the imidized fiber are in progress.

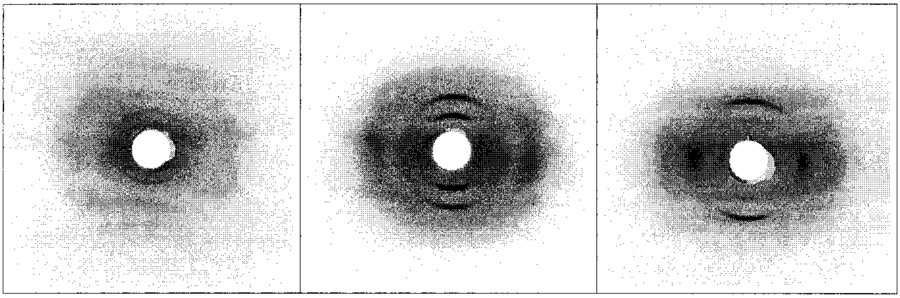


Fig. 8. Wide-angle X-ray diffraction pattern of para-**4d** fibers coagulated in acetone (1) (left) and the same polymer coagulated and drawn in acetone (5) (center). Fiber (5) was finally imidized, forming fiber (6) (right).

Experimental

The synthesis, detailed analytical and mesomorphic characterization of PAEs **4a-e** is published in ref.[15] The orientation of the lyotropic solution of **4d** was performed on oxygen plasma etched glass slides with a DACA Instr. Tribotrak machine. A pressure of 1 MPa at a moving speed of 25 mm/sec at 100°C was used. Polarized optical microscopy was performed on a Leitz Laborlux 12-Pol equipped with a Mettler FP 82 hot stage. UV/Vis spectra were recorded on quartz glass slides on a Hitachi U-3000 spectrophotometer with Glan-Thompson polarizers. Layer thickness and profile were scanned with a Dektak 3030 Step Profiler. Fiber spinning experiments were conducted with a solution fiber spinning line similar to the equipment described in ref.[14] A 100 μm spinnerette was used. For heat setting experiments a custom built drawing rig was employed. With this frequency controlled equipment the fiber can be drawn at high reproducibility. Imidization was performed on a metal spool at 100°C for 1h, 200°C for 1h and 300°C for 1h with a ramping time of 10K/min. Fibers were tested according to ASTM D3379 in an Instron 5565 universal tester equipped with a 10N load cell. The complete fiber spinning process and fiber characterization will be published elsewhere.[16] SEM micrographs were recorded on a LEON 1530 scanning electron microscope after sputtering with Pd/Pt. WAXS diffraction pattern were obtained on a Seifert Isoflex 3000 (CuKα at 1.5kW) equipped with a fiber set-up in a Laue camera.

Conclusions

Lyotropic precursor solutions for polyimides based on para-linked aromatic poly(amic ethyl ester)s were prepared and characterized. Lyotropic nematic phases in NMP were observed at concentrations above 40 to 50wt%. Then the lyotropic solutions were sheared on a substrate and oriented layers in the thickness range of 20-40 nm were obtained. This technique permits the fabrication of bulk orientation layers without a separate buffing/rubbing step. The UV/Vis measurements resulted in dichroic ratios of 4.5 for the PAE orientation layer and an increase to 7 for the imidized layer. Furthermore the lyotropic solutions were spun into fibers in a dry-jet wet-spinning process. The mechanical properties of the fibers were investigated as function of processing conditions and thus the fiber orientation. By drawing in acetone a fiber with three times higher modulus and doubled tenacity was obtained.

Acknowledgement

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[1] M. Konieczny, H. Xu, R. Battaglia, S. L. Wunder, W. Volksen, *Polymer* ***38***, 2969 (1997).
[2] W. Volksen, D. Y. Yoon, J.L. Hedrick, D. Hofer, *Mat. Res. Soc. Symp. Proc.* ***227***, 23 (1991).
[3] W. Volksen, D.Y. Yoon, J.L. Hedrick, *IEEE Trans. of Comp., Hybrids, and Manuf. Techn.* ***15***, 107 (1992).
[4] W. Volksen, *Adv. Polym. Sci.* ***117***, 111 (1994).
[5] H. H. Yang, *Kevlar aramid fiber*, J. Wiley & Sons, Chichester, 1993.
[6] W. Hatke, H.-W. Schmidt, *Makromol. Chem. Phys.* ***195***, 3579 (1994).
[7] W. Hatke, H.-W. Schmidt , W. Heitz, *J. Polym. Sci. Polym. Chem.* ***29***, 1387 (1991).
[8] W. T. Whang, S. C. Wu, *J. Polym. Sci. Part A*, ***26***, 2749 (1988).
[9] K. H. Becker, H.-W. Schmidt, *Macromolecules* ***25***, 6784 (1992).
[10] K. H. Becker, H.-W. Schmidt, *ACS Polymer Preprints* ***35***(1), 349 (1994).
[11] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suszuki, S. Morokowa, *Jpn. J. Appl. Phys.* ***33***, L1323 (1994); C.L.H. Delvin, S.D. Glab, S. Chiang, T.P. Russell, *J. Appl. Polym. Sci.* ***80***, 1470 (2001).
[12] Merck Liquicoat® PI-Kit ZLI-2650
[13] C. Neuber, R. Giesa, H.-W. Schmidt, *Adv. Materials*, submitted.
[14] G. C. Rutledge, U. W. Suter, C. D. Papaspyrides, *Macromolecules* ***24***, 1934 (1991).
[15] C. Neuber, R. Giesa, H.-W. Schmidt, *Macromol. Chem. Phys.* ***203***, 598 (2002).
[16] C. Neuber, R. Giesa, H.-W. Schmidt, *J. Appl. Polym. Sci.* (2003), to be published.