

LYOTROPIC PARA-LINKED AROMATIC POLY(AMIC ETHYL ESTER)S AS PRECURSORS FOR RIGID ROD POLYIMIDS

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Introduction

Most polyimides [1] are difficult to process due to their insolubility and their decomposition before melting. Thus processing is performed in a two step procedure via a poly(amic acid), PAA, as precursor polymer. In addition, poly(amic ester)s, PAE, have been developed as superior precursor systems [2-4]. Compared to the PAAs, PAEs have improved solubilities, better resistance to hydrolytic degradation, yield high molecular weight products, but suffer from higher and broader imidization temperatures. In most cases only the meta isomer is employed since the resulting precursor polymer exhibits enhanced solubility which permits the use of concentrated solutions for processing compared to the para polymer. However, precursor polymers with para linkage might exhibit lyotropic behavior of soluble, rigid-rod polyaramides [5-7]. Also the spinning of lyotropic polyaramid solutions into fibers and their orientation by drawing was thoroughly investigated for the commercialization of Kevlar® fibers [5].

In the case of PAAs, lyotropic phases have been not found for PMDA/4,4'-ODA up to 25 wt% which was attributed to the lack of isomeric purity. In the same work lyotropic phases have been observed first in a system of PMDA/4,4'-MDA [8]. A few years ago we reported [9] that by use of THF as cosolvent in combination with NMP, at 35-55 wt% lyotropic solutions of **4a** [10] were observed after evaporation of the cosolvent.

Results

Synthesis

To investigate systematically the structure-property relationships of lyotropic PAE systems, a series of new rod-like para linked PAEs (Fig.1) was synthesized and characterized [11]. The mesomorphic behavior was investigated by optical polarization microscopy, DSC, X-ray diffraction and FTIR-spectroscopy. The orientation behavior of sheared lyotropic PAE films is topic of a separate contribution.

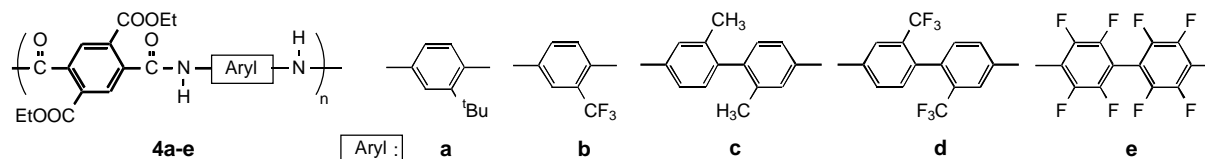


Figure 1: Chemical structures of rigid-rod poly(amic ethyl ester)s **4a-e**

Mesomorphic behavior

All synthesized PAEs are completely soluble in NMP without the addition of inorganic salts such as LiCl. For the formation and examination of lyotropic systems the polymers **4 a-e** are dissolved without a cosolvent in NMP at 10 wt% and then concentrated by evaporation at 100 °C. The final concentration was determined gravimetrically. All PAEs turned opaque above 30 wt% and exhibited liquid crystalline behavior, which was investigated by polarization microscopy (Table 1). No investigations above 140°C were performed at this point since progressive imidization changes the prepolymer structure. The listed temperature ranges show coexistence of a gel and shearable lyotropic phase with a typical nematic schlieren texture (not shown).

Table 1: Solution viscosities of **4a-e** and temperatur ranges [°C] of the melting of either to an isotropic (iso) or a lyotropic (lyo) solution determined under crossed polarizers up to 140 °C.

PAE	$\eta_{inh}^{a)}$ [dl/g]	Concentration [wt%]				
		10	20	30	40	50
4a	1.00	isotop	80-95→iso	90-110→iso	105-125→lyo	gel ^{b)}
4b	1.02	isotop	isotop	30-50→iso	gel ^{b), c)}	gel ^{b), c)}
4c	1.88	50-80→iso	80-110→iso	100-120→lyo	110-130→lyo	120-140→lyo
4d	1.86	isotop	isotop	60-80→iso	50-80→lyo	60-100→lyo
4e	0.30	isotop	isotop	gel ^{b), d)}	gel ^{b), d)}	gel ^{b), d)}

a) in NMP at 30 °C and 0.5 g/dl

b) no melting of the gel up to 140 °C

c) strong shear induced a metastable lyotropic phase

d) strong shear induced a stable lyotropic phase

Morphology

The surface morphology of a dried gel of 50 wt% **4d** is shown in Figure 2. The 100 nm scale bar indicates wormlike substructures (arrow) in the range of 30 nm. Analogous prepared samples of meta-PAEs exhibit a completely featureless morphology.

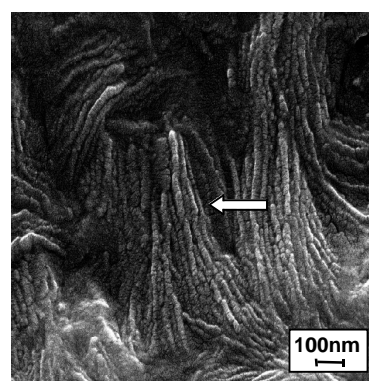


Figure 2: SEM of the dried gel (**4d** at 50 wt%)

Fiber spinning

PAE monofilaments of **4d** were spun from a 30 wt% lyotropic solution in NMP in a dry jet-wet spinning process. Several coagulation solvents and spinning conditions were tested (Fig. 3) and mechanical fiber properties were evaluated as function thereof. Water is unsuitable and fibers with extremely poor mechanical properties are obtained. Acetone yields fibers with lower modulus but very high elongation probably due to a plastizing effect. An acetone/water 1:1 mixture reduces the elongation dramatically, even at lower water contents (not shown). Dry spinning results in fibers with high tenacities and a twofold increase in modulus. Further spinning experiments, imidization of the fibers and characterization of the fiber orientation are in progress.

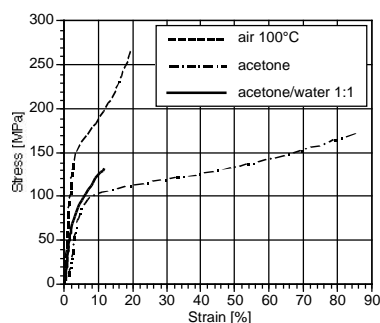


Figure 3: Stress-strain curves for PAE fibers coagulated in different solvents

Acknowledgement: This work was supported by the SFB 481, Projekt A6. We are indebted to C. Drummer (BIMF) for the SEM work.

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