

# Microphase separation in semifluorinated polyesters

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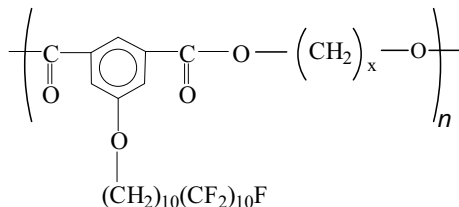
**Abstract.** Temperature-resolved scattering measurements (SAXS and WAXS) combined with other methods giving thermal behaviour information (DSC, Broadband Dielectric Spectroscopy) were used to get detailed information about the structural changes induced by increasing flexibility of polyesters with semifluorinated side chains and an alternating backbone of isophthalic acid and alkane diols. Intra- and intermolecular microphase separation gives rise to a layered structure with alternating sub-layers of semifluorinated side chains and polyester backbones according to the molecular model reported in [1]. This structure is accompanied by hexagonal and cubic structures in low molecular weight SF-polymers.

## Introduction

The occurrence of self-organisation in semifluorinated polymer segments composed of an alkyl chain and a perfluoroalkyl chain connected by a covalent bond is well known. The thermodynamic immiscibility of such chains, together with the regular structure of both chains is a strong driving force to form highly ordered solid state structures. Thus, structural investigations of semifluorinated compounds have been widely reported. However, in a variety of investigations both the chemical structure of the polymer backbone, the number of C atoms in the alkyl and perfluoroalkyl part and finally, also the methods of synthesis and preparation of the samples differed largely. A general conclusion about the influence of the flexibility of the polymer backbone and the length of the side chain on the solid phase structure formed cannot be derived unambiguously. Therefore, the effects of the flexibility of the polymer backbone on the self-organisation behaviour were examined. Oxydecyl perfluorodecyl side chains, long enough to undergo microphase separation, were selected as subject (cf. Formula 1). The polymeric backbone with systematic altered flexibility was a polyester because this main chain offers the opportunity to change the stiffness in a systematic manner. Systematic changes of the synthesis conditions lead to different molecular weights of the polymers corresponding to the lengths of the polymer backbones, which have caused further investigations concerning these parameters as reason for structural peculiarities.

## Experimental

**Synthesis:** The semifluorinated isophthalic acid IPA-H10F10 was synthesized as already reported [2] and polycondensed in the melt with following reaction conditions: 260 °C / 3 h /  $1.33 \times 10^2$  Pa [2]. Samples were isorefractive with PFP/CHCl<sub>3</sub>, thus only solution viscosities  $\eta_{inh} \sim 0.38$  dL/g (in PFP/ CHCl<sub>3</sub>: 50/50 v/v, 25 °C) could be measured (polyesters without side chain had  $M_n \sim 9.3$  kDa and  $M_w \sim 18$  kDa), low molecular samples had  $\eta_{inh} \sim 0.08$  dL/g.



**Formula 1.** General structure of the polyesters **IPA-H10F10 – Hx**

(Hx = alkane diol: - O – R – O – ;

R: (CH<sub>2</sub>)<sub>x</sub>; x = 2 ... 10).

**DSC:** DSC-7 (Perkin Elmer), scan rates: 20 K/min.

**Temperature-dependent SAXS/WAXS:** Soft Condensed Matter Beamline A2 (HASYLAB at DESY Hamburg), SR wavelength: 0.15 nm, linear detectors, heating/cooling rates: 3 K/min.

**Broadband Dielectric Spectroscopy:** High Resolution Dielectric Alpha-analyzer (Novocontrol),  $10^{-1} - 10^7$  Hz, 120 – 500 K, isothermal measurements in steps of 2 K ( $\pm 0.02$  K).

## Results and discussion

In order to verify the influence of the flexibility of the backbone on the structure, the diol chain length was altered from two CH<sub>2</sub> groups (ethyl) to ten (decyl). The thermal structure behaviour shows similarities to aromatic SF-PES [1], because both possess a layered structure (1D) at temperature below and above the side chain melting [2-3]. Small angle X-ray scattering was performed temperature-dependent (Figure 1b: SAXS, represented as a topographic contour-plot of the scattered intensity *I* vs. *T* and *t* as well as vs. *s* and *d*).

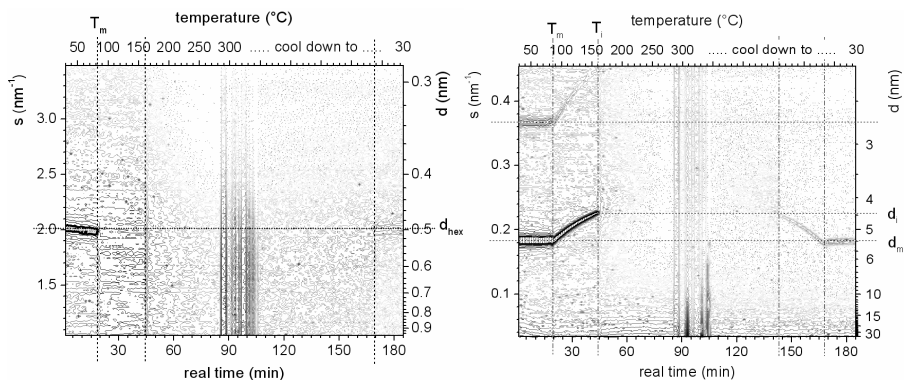


Figure 1. IPA-H10F10-H5 as an example for the typical scattering behaviour of the polyesters under investigation; a) T-WAXS pattern (left), b) T-SAXS pattern (right); min. max. intensity .

SAXS indicates a layered structure (reflections of 1<sup>st</sup> and 2<sup>nd</sup> order at  $d = 5.50$  nm and  $d = 2.75$  nm, respectively, with mirror-like thermal behaviour for all polyesters. Typically, the disappearance of the WAXS reflection at  $\sim 0.5$  nm (which is similar to the (100) reflection of PTFE with  $d_{\text{hex}} = 0.491$  nm) in Figure 1a can be correlated with the side chain melting ( $T_m$ ) and a transition to a smectic structure. The assignment of the thermal transitions (melting -  $T_m$ ; isotropisation -  $T_i$ ) are in good agreement with DSC investigations (Figure 2a). The transition temperatures are significantly dependent on the spacer length ( $x$  in Formula 1) and decrease with increasing flexibility of the backbone (Figure 2b). However, some geometrical parameters (e.g., layer distances  $d$ ) show a more complicated behaviour versus spacer length:  $d_i$  ( $d$  at  $T_i - \Delta T$ ) increases, however  $d_m$  ( $d$  at  $T_m - \Delta T$ ) is more likely to show a weak odd-even behaviour (Figure 2b). Additionally, up to  $T_m$  the layers expand only marginally, then jump to a slightly larger  $d$  and finally pass into a range with negative thermal expansion coefficient up to the vanishing of the layers at  $T_i$ .

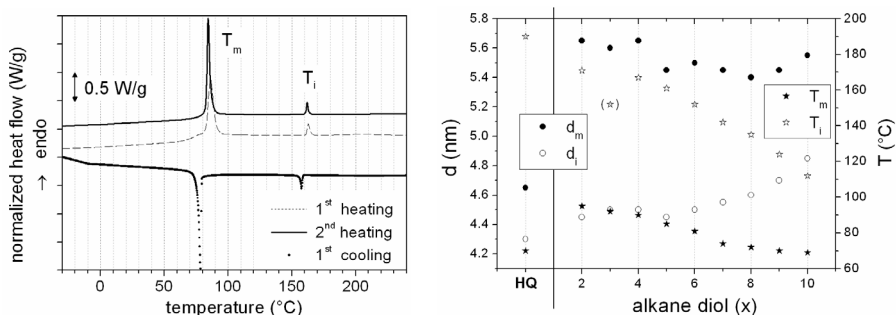


Figure 2. a) DSC curves of the polyester IPA-H10F10-H5 (left); b) Dependency of structural parameters (SAXS: layer distances, transition temperatures) on the diol length (right). HQ – hydroquinone, given for comparison, is taken from [4].

From DSC, two main endothermic peaks can be found, which can be assigned to melting/crystallization ( $T_m$ ) of the semifluorinated side chains and the isotropisation temperature ( $T_i$ ), where the ordered layered structure disappears. The glass transition temperature ( $T_g$ ) of the polymer backbone is decreasing with the diol spacer length  $x$  and is often below the lower measuring limit or overlapped with the side chain melting (and thus not clearly visible) [5]. The corresponding polymers cited in [5], i.e., identical main chain and no side chains, are amorphous as only  $T_g$  occurs in the DSC curves at  $\sim 5 \dots 15$  °C. Furthermore, dielectric relaxations were measured to get more information about the mobility of groups or segments in the polymer structure, also their thermal dependence. In this dynamic context, four relaxation regions are detectable (Figure 3) [6]: the  $\alpha$  being assigned to the dynamic glass transition process (backbone motions), the  $\beta$  - a local process originating from the main chain (i.e., fluctuations of dielectrically active carbonyl groups together with the phenyl ring, “intra-IPA”), the  $\gamma_{\text{SF}}$  is a local process assigned to librational fluctuations of the  $-\text{CF}_3$  group at the terminal position of the side chain, and the  $\delta$  - process being a “glass transition”-like cooperative motion of the SF microphase. The  $\alpha$ -process becomes faster with increasing length of diols due to an internal plasticization effect. Increasing the main chain flexibility slows down

the  $\beta$ -relaxation and subsequently manifests itself as an  $\alpha$ -process. The  $\gamma_{SF}$ -process is influenced by the backbone flexibility, too. The dynamic glass transition temperature – conventionally defined as temperature at which the relaxation time is 100 s (extrapolation in the activation plot, compare Figure 3) – of the SF domains,  $T_g^{SF}$  is estimated to be 40 °C (as expected for all polymers) using the Vogel-Fulcher-Tammann equation (compare also Figure 3, right column).

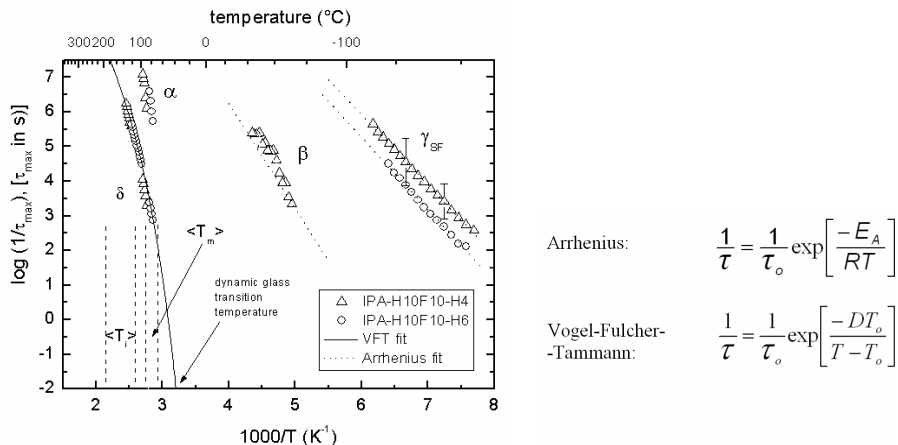


Figure 3. Representative examples of activation plots and their fits; right: common fit equations after Arrhenius and Vogel-Fulcher-Tammann, resp.).  $\alpha$ ,  $\beta$ ,  $\gamma_{SF}$  and  $\delta$  are explained in the text.

The investigations of the morphology or solid state structures were expanded to samples having more or less short main chains (low molecular weight types) to prove the influence of different (strong) interactions originating from both the main and side chains on the ordering. For this purpose, also the dicarboxylic acid IPA-H10F10 as one component of the synthesis was measured by means of scattering methods, due to the expectation that the decyl-perfluorodecyl side chains play an important role. In comparison to the real polymer samples, scattering patterns were found that were very similar to those of rather oligomeric types, but having additional reflections in the SAXS region, which can be interpreted as higher symmetry morphologies: hexagonal (2D) and cubic (3D): cylinders and spheres, resp.. Mostly, these structures coexist (up to  $T_i$  of the real polymer) with the layered structure (smectic, 1D) as the morphology of the high molecular weight polymers in a temperature range from about 115 to 157 °C. The SAXS pattern as a function of temperature for the oligomeric IPA-H10F10-H5 is shown in Figure 4. In the WAXS region there are no significant changes with respect to the real polymer. Figure 4 includes also the assignment of these structures to known symmetries of classic cubic and hexagonal crystals. Applying the d-ratios of the first strong reflections (see the left-hand side of Figure 4) a classification as hexagonal close-packed cylinders (hcp) as well as face-centred cubic packed spheres (fcc) could be done. The lattice parameters are  $a_{hcp,1} \sim 4.52 \dots 4.48$  nm and  $a_{fcc} \sim 4.52 \dots 4.48$  nm, respectively, for the phases with a negative coefficient of linear expansion up to  $\sim 260$  °C,

and  $a_{\text{hcp},2} \sim 4.23$  nm being about constant in the temperature region around 300 °C. That implies, no real isotropic melt of the oligomeric types was found up to  $\sim 300$  °C. Higher temperatures are not applicable because of the beginning of the thermal decomposition.

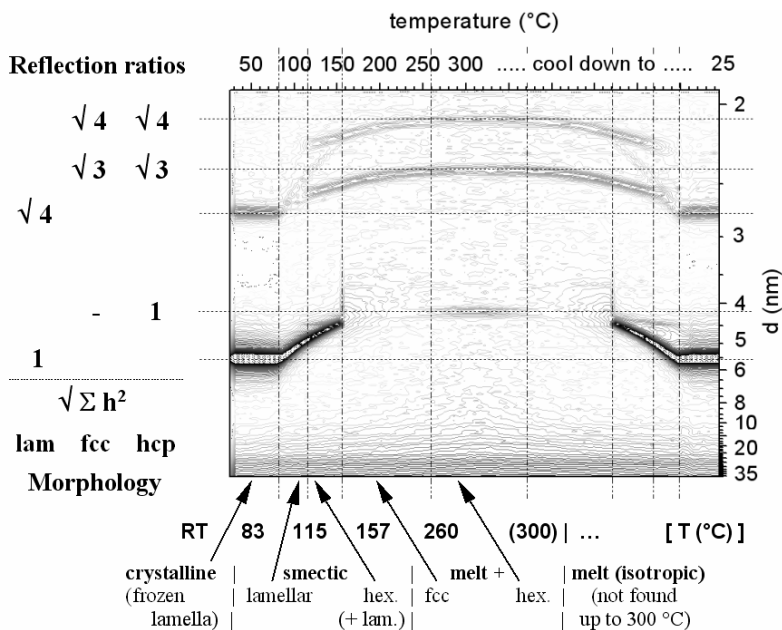


Figure 4. T-SAXS pattern (topography) of low molecular IPA-H10F10-H5 (even as an example too) showing additionally several high-temperature modifications and their classification (left and below).

The structures at higher temperatures (i.e., hcp and fcc) are originated by the side chain possessing dicarboxylic acid IPA-H10F10 (compare Formula 1) in the polymers with shorter main chains, as known from similar scattering pattern of the pure monomer IPA-H10F10. Even though the transition temperatures, as well as the number and the kind of these morphologies, of both monomer and low molecular weight polymer are different. Considering these findings, it can be concluded that the side chain has a pre-eminent influence. Just as the layered structures at lower temperatures found in both the oligomeric and real polymer types, also these structures show mirror-like patterns during scattering experiments with symmetric heating-cooling cycles, what may be a good hint to the high speed and the thermodynamic stability of the phase transitions investigated here.

## Concluding remarks

The solid state structure of all polyesters under investigation is dominated by the tendency of self-organization of the semifluorinated side chains forcing the perfluoroalkyl parts to aggregate closely in a layered structure which is caused by the strong interaction between the perfluoroalkyl parts. Thus, the general behaviour of the polymers is almost independent on the

chemical structure of the polymeric backbone. It could be observed that the number of structural changes (i.e., transitions between kinds of structures) taking place upon heating increases with increasing flexibility of the backbone. It seems to be that at least at higher temperatures even with increasing flexibility of the main chain the intensive interacting polymer segments feel freer to take a structure, which is more and more similar to that of the dicarboxylic acid attached with a semifluorinated side chain (i.e., IPA-H10F10). This result is in agreement with the findings of polymers with fully aromatic backbone (e.g., with the diol HQ [4]), where more or less the rigid main chains foremost control the structure. The same sub-layers generated by intra- and intermolecular phase separation will represent the solid as well as smectic state. First of all, the incompatibility (immiscibility) of the polymer segments can be considered as the main driving force. Noteworthy, the reproducibility of the scattering pattern for several repeating heating-cooling cycles (thermal reversibility) is remarkable, even for polymer types with both the high and low molecular weights. The negative expansion coefficient of the layer distance above  $T_m$  is not understood in detail. First model calculations as well as logic considerations favour two reasons: interdigitation of the side chains (also their changes with temperature) and their “line of sight” in relation to the sub-layer of main chains. It is very probable that a more and more flat tilt of the side chains is the main reason, whereas a stronger interdigitation seems to play an underpart (since investigations on non-fluorinated side chain polymers show the same behaviour). Further work is in progress directed to solve this problem with new models and investigations applying other analytical methods (e.g., NMR, IR spectroscopy).

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