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Synthesis and Characterization of Semifluorinated Polymers and Block Copolymers

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Summary: The goal of the investigation presented here was to evaluate the influence of semifluorinated side chains on the bulk structure and the surface properties of polysulfones with different chain structure. Thus, segmented block copolymers consisting of polysulfone and semifluorinated aromatic polyester segments as well as polysulfones having semifluorinated side chains randomly distributed over the polymer backbone were synthesized and characterized. Oxydecylperfluorodecyl side chains were used because of their strong tendency for self-organization. The influence of the chain architecture on the self-organization as well as on the surface properties, particularly the wetting behavior, was examined. It could be shown that despite of the higher self-organizing tendency of block copolymers the surface properties of both polymer types are comparable and depend only on the concentration of side chains.

Keywords: polysulfone, self-organization, semifluorinated polymers, ultrahydrophobicity, wetting

Introduction

Structural segments consisting of alkyl and perfluoroalkyl groups covalently linked by a C-C bond, called semifluorinated (SF) compounds, are known for their microphase separation resulting in highly ordered bulk structures.[1] The microphase separation is caused by the thermodynamic immiscibility between alkyl and perfluorinated alkyl segments. Additionally, the strong tendency of the perfluorinated parts in such compounds to surface segregation results in surface structures having $-CF_3$ groups regularly ordered at the surface, yielding in low surface free energy. The same behavior has also been reported for polymers with semifluorinated side chains, for example poly(styrene),[2] poly(methylmethacrylate),[3,4,5] poly(acrylates),[6,7] poly(styrene-*b*-isoprene) diblock copolymers,[8,9] poly(siloxanes),[10] and poly(vinyl ether) analogues.[11] One of the first examples of polycondensation polymers with SF-side chains were semifluorinated aromatic polyesters based on poly(p-phenylene isophthalate).[12] The rigid backbone requires longer ($-O-(CH_2)_{10}-(CF_2)_9-CF_3$, H10F10) semifluorinated side chains with ten C-atoms in the alkyl and ten C-atoms in the

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perfluoroalkyl part to generate a self-ordered structure in the bulk and also at the surface,[13,14] resulting in an extremely low surface free energy of 9 mN/m. The aim of the work presented here was to use the same semifluorinated side chains to modify the surface properties of another polycondensation polymer, polysulfone (PSU). Therefore, two synthetic concepts have been explored, the first being the synthesis of segmented block copolymers (BCP) having the semifluorinated side chains in the polyester segments, connected by PSU segments, and the second way being the synthesis of polysulfones with semifluorinated H10F10 side chains randomly distributed along the PSU backbone. The schematic structures of both types of polymers are given in Figure 1. Thus, the influence of the chain architecture on both, the self-organization in the bulk as well as the surface properties could be explored.

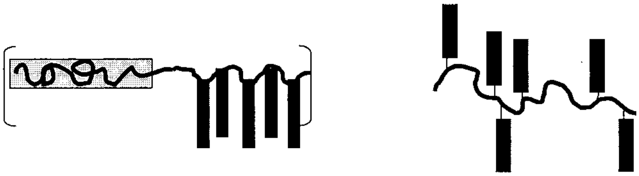

Fig. 1. Schematic representation of the chain architectures of the semifluorinated polymers under investigation (left: segmented block copolymers with PSU and SF-PES segments; right: PSU with randomly distributed SF-side chains).

Experimental

The synthesis of segmented BCP with PSU and SF-PES was performed as described in refs.[16,17] The polysulfones with randomly distributed SF-side chains were prepared by nucleophilic aromatic substitution using bisphenol A, 4,4'-bis(chlorophenyl) sulfone, and 4,4'-bis(hydroxy-phenyl valeric acid), according to Koch et al.[18] The semifluorinated side chains were attached by Mitsunobu conditions[19] using HO-H10F10 (1mol), diethyl azodicarboxylate (1.5 mol/COOH-side group), triphenyl phosphine (1.2 mol/COOH-side group) in dry THF (50°C, 24 hrs).

SEC was carried out using a modular built Knauer SEC with RI detection. Solvents and separation columns as given in Tables 2 and 3. The molecular weights are relative to narrowly distributed polystyrene standards. NMR was performed on a Bruker DRX-500 spectrometer using $CDCl_3$/TFA-d (1:1 v/v) as solvent. The spectra were referenced on the $CHCl_3$ signal ($\delta(^1H) = 7.26$ ppm, $\delta(^{13}C) = 77.0$ ppm). DSC measurements were carried out on a Perkin Elmer DSC 7 (heating and cooling rate: 20 K/min). Temperature-dependent SAXS/WAXS measurements were performed at beamline A2 (DESY Hamburg, HASYLAB), heating and cooling rate 3 K/min. Thin films for surface characterization were prepared by spin coating (Headway Inc., USA, 2000 rpm/60 s) of polymer solutions (c_{pol}: 1 wt%, solvents: pentafluorophenol/ chloroform for BCP and chloroform for random copolymers) on precleaned silicon wafers. The films were dried at 50 °C for 4 h and then annealed at 200 °C in vac. for 4 h. Dynamic contact angles were measured using ADSA-P[15] and water as probe.

Results and Discussion

Synthesis of Segmented Block Copolymers Having PSU and SF-PES Segments

The SF polyester originally reported[12] was synthesized by Higashi polycondensation to prevent the cleavage of the ether linkage to the substituents. The low molecular weights obtained thus suggested the use of melt polycondensation of the semi-fluorinated isophthalic acid and hydroquinone diacetate (HQDA, in excess to compensate sublimation), resulting in higher molecular weights in the range of 50,000 g/mol for M_w.[16] Comparable conditions were applied to the synthesis of the segmented BCP copolymers with PSU and SF-PES blocks, recently reported by us in ref.[17] Two ways were explored: the synthesis of BCP with preformed oligomers (acetoxy group-terminated PSU and COOH-group-terminated SF-PES), and *in situ* preparation of the semifluorinated blocks during block copolymer synthesis with acetoxy-terminated PSU, as outlined in Figure 2. Different molecular weights of starting PSU and SF-PES blocks were used.

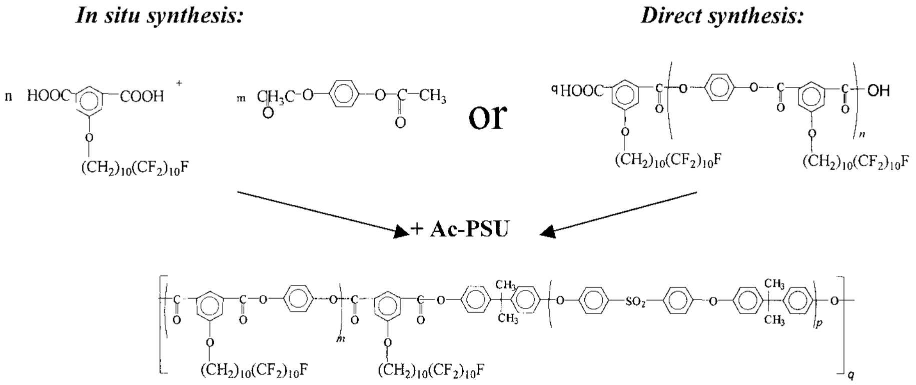

Fig. 2. Synthesis scheme of segmented block copolymers having polysulfone and semifluorinated polyester blocks.

The linking groups can be detected by their carbonyl signals at 166.9 – 167.6 ppm in the ^{13}C NMR spectrum. The ^1H NMR spectra gave additional information about the linkage between SF-PES and PSU. The signal of the 2-proton in the SF-IPA-ring at about 8.7 ppm, as shown in Figure 3, is split into three signals, where the first one at 8.71 ppm is caused by the triad HQ-SF-IPA-HQ, the second one at 8.68 ppm is caused by the triad PSU-SF-IPA-HQ and the third one at 8.67 ppm by the triad PSU-IPA-PSU. A comparable splitting is observed for the 2/6-protons (Figure 3).

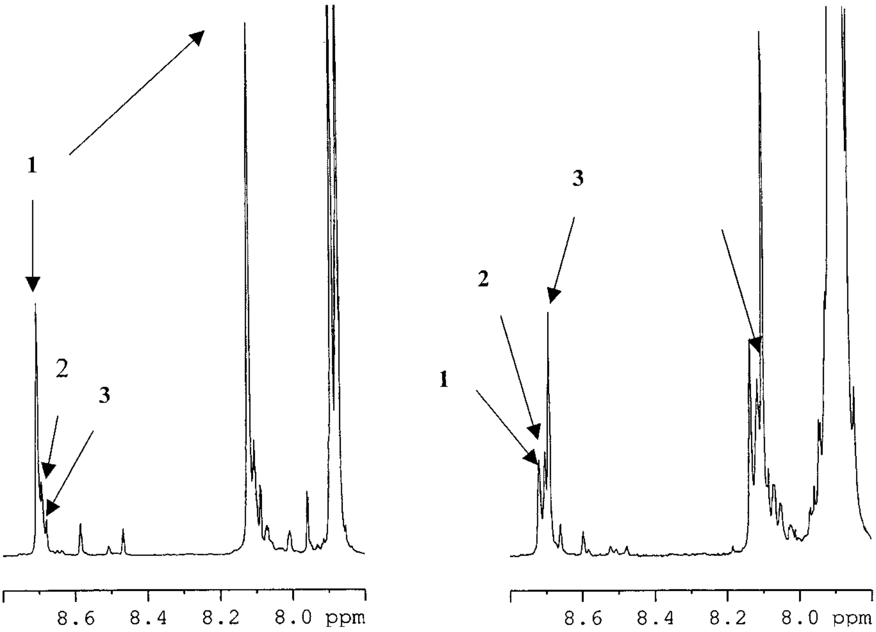

Fig. 3. ^1H NMR spectra of segmented block copolymers consisting of polysulfone and semifluorinated polyester segments (triads: 1-HQ-IPF-HQ; 2-PSU-IPA-HQ; 3-PSU-IPA-PSU).

Table 1 contains the concentration of triads obtained from the intensities of these protons in selected samples. The triad HQ-IPA-HQ can only occur within the semifluorinated polyester block. Triad PSU-IPA-HQ is the linkage desired for block copolymer formation and the triad PSU-IPA-PSU refers to the direct coupling of two PSU segments by a single semifluorinated IPA unit which can be generated by transesterification reactions. The content of PSU-IPA-PSU triads shows that transesterification within the SF-PES blocks occurs at times during direct synthesis. The direct coupling of SF-IPA to PSU is preferred during *in situ* synthesis of the SF-PES blocks, indicating that the reactivity of acetoxy-PSU to SF-IPA is obviously higher than the reactivity of HQDA. The concentration of this triad shows that the molecular weights of SF-blocks formed during *in situ* synthesis are lower than calculated from the initial ratio of IPA/HQDA (Table 2).

Table 1. Intensities of triads detected in ^{1}H NMR spectra of segmented PSU-SF-PES BCP, synthesized by the *in situ* method and by direct polycondensation.

PSU a) (g/mol)	COOH-SF b) (g/mol)	Ratio HQDA/SF-PES	HQ-IPA-HQ/ (%)	PSU-IPA-HQ/ (%)	PSU-IPA-PSU (%)
2,300	5,400	-	84	12	4
2,300	2,500	-	56	22	22
4,900	2,300	-	82	7	11
9,000	8,330	-	90	10	0
2,300	-	5/4	26	21	53
4,900	-	5/4	3	25	72

a) Molecular weight M_n of the acetoxy-terminated PSU, obtained by titration of OH-groups.
b) Molecular weight of COOH-terminated SF-PES blocks, obtained by ^{1}H NMR.

Table 2. Characterization of PSU-SF-PES block copolymers.

Ac-PSU	**SF-Oligomer**		**Block copolymer**		**Phase**
M_n a) (g/mol)	M_n (g/mol)	ratio SF/HQDA c)	M_w e) (g/mol)	M_w/M_n e)	**separation?**
2,400	2,500 b)	-	19,300	3.33	yes
2,400	-	4/3	20,000	2.63	yes
2,400	5,400 b)	-	33,200	2.89	yes
2,400	1,850 d)	5/4	32,200	2.84	yes
2,400	-	10/9	21,000	2.13	yes
4,900	1,800 d)	5/4	42,100	2.63	yes
4,900	2,300 b)	-	13,000	2.71	yes
9,000	840	-	44,000	2.16	no
9,000	-	2/1	30,400	2.64	no
9,000	8,330 b)	-	18,800	3.36	yes

a) Determined by titration of OH-groups of the OH-terminated PSU and from ^{1}H NMR spectra.
b) Determined by ^{1}H NMR of COOH-terminated SF-oligomers.
c) Ratio of the monomers used in the *in situ* synthesis of SF-PES blocks during block copolymer formation.
d) Molecular weight of SF-blocks calculated from ^{1}H NMR spectra.
e) SEC in pentafluorphenol/chloroform mixture, PL Mini MIX P separation columns.

Synthesis of PSU with Randomly Distributed Semifluorinated Side Chains

A two-step synthesis to obtain these polymers have been exploited. In the first step, copolymers of bisphenol A based polysulfone with 4,4'-bis(hydroxyphenyl) valeric acid with different concentration of valeric units have been synthesized by nucleophilic aromatic substitution using K_2CO_3 in NMP/toluene as solvent, according to Koch et al.[18] In the second step, the COOH groups were esterified by perfluorodecyldecanol according to Mitsunobu et al.[19] as shown in Figure 4.

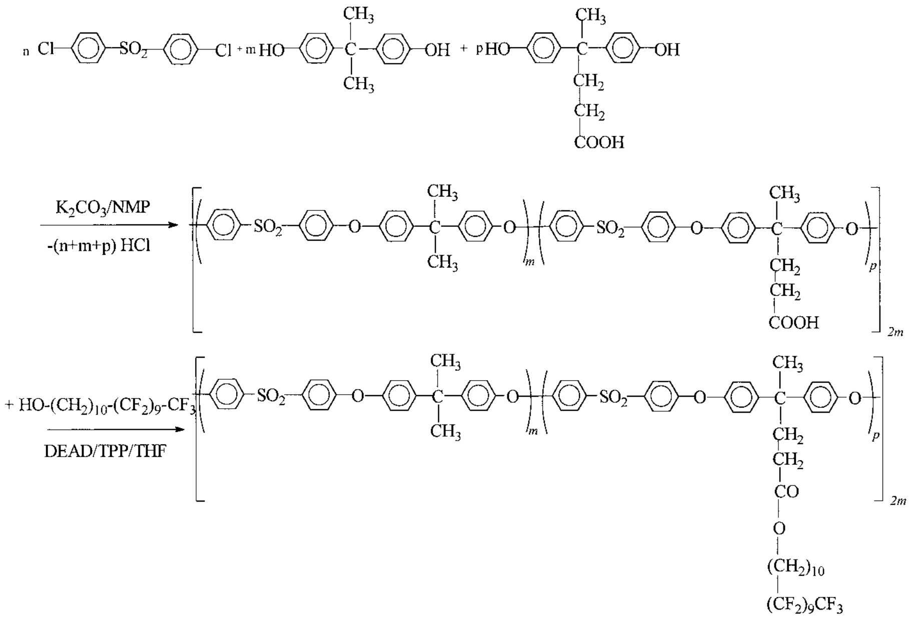

Fig. 4. Synthesis scheme of semifluorinated polysulfones with random chain structure.

The PSU's with COOH-side groups are very polar and only soluble in solvents as THF and DMSO. Esterification with the semifluorinated alcohol OH-H10F10 gives unpolar polymers, soluble in chloroform which could be characterized by SEC (Table 3).

The valeric acid comonomer is incorporated almost according to the stoichiometry used. At low side chain concentration, the polymer analogous reaction proceeds completely. High concentration of COOH-side chains obviously shields the reactive centers due to the polyelectrolyte character of the copolymer[20] and results, thus, in incomplete conversions of the esterification. The molecular weights of the copolymers are high, with broad molecular weight distributions that can be assumed from the synthesis method. The ^1H NMR spectra of a COOH-containing PSU and a H10F10-containing PSU are illustrated in Figure 5. The protons of CH_2-groups on the valeric acid (1 and 2) are slightly shifted after esterification with OH-H10F10 (1' and 2' in Figure 5b) in addition to the protons of the CH_2-groups of the SF side chain next to the ester bond (4).

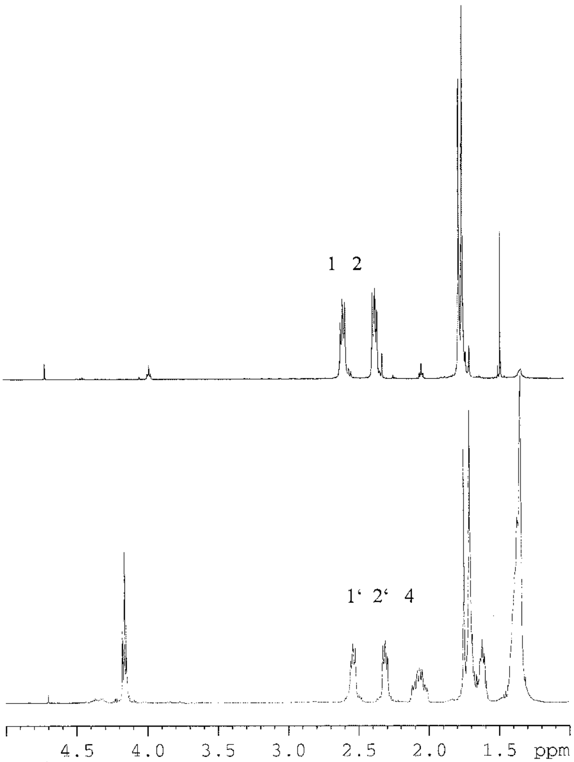

Fig. 5. ^{1}H NMR spectra of random a semifluorinated polysulfone (above: COOH-side chains, below: semifluorinated side chains).

Table 3. Characterization of polysulfone copolymers with randomly distributed COOH- and H10F10 side chains.

Concentration of COOH comonomer during polycondensation (mol%)	Concentration of COOH comonomer in the product [a] (mol%)	Concentration of H10F10 side chains [b] (mol%)	M_w [c] (g/mol)	M_w/M_n [c]
0	0	0	62,300	5.93
10	13		13,300	5.58
25	24	24	46,000	4.13
50	54	33	36,200	3.48
75	67	42	40,800	4.27
100	100	85	41,900	3.31

a) Calculated from 1H NMR spectra from the intensity ratio of aromatic protons (6.5-8.0 ppm) to CH_2 protons (2.06 ppm).

b) Calculated from 1H NMR spectra from the intensity ratio of CH_2 protons of valeric acid (2.06 ppm, 2H) to CH_2 protons of semifluorinated side chain (4.02 ppm, 2H).

Bulk Structure of Block and Random Copolymers

The structure of PSU-SF-PES block copolymers is determined by microphase separation. As indicated in Table 2, phase separation between the amorphous PSU phase and semifluorinated polyester domains occurs at very low molecular weights of SF segments having only a few monomeric units. The reasons therefore are the high interaction parameter between SF-PES and PSU (13.6)[16] as well as the high tendency for self-organization of the semifluorinated polyester itself, driving to a highly ordered bulk structure. The structure of the SF poly(p-phenylene isophthalate) was reported earlier.[21] By a combination of methods, the structural changes upon heating and cooling could be understood.[14,22] Phase separated block copolymers of PSU and the SF-PES should have both, the glass transition of polysulfone as indication of an amorphous matrix, as well as the thermal transitions of the SF-PES.[22] Based on the results obtained by DSC, SAXS, and TEM, a structural model was proposed recently[16,17] showing a random distribution of well-ordered SF domains within an amorphous matrix (Figure 6).

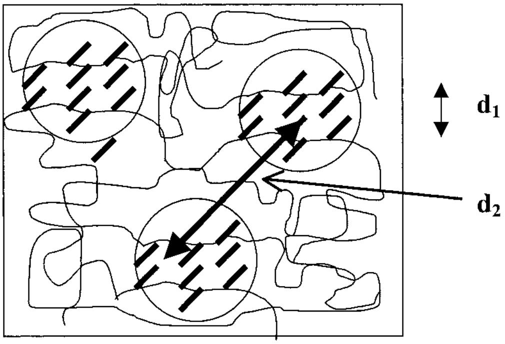

Fig. 6. Structural model of segmented PSU-SF-PES block copolymers, as published in ref.[16] indicating the periodic distances obtained in the SAXS measurements.

The SAXS curves show two scattering maxima at d_1 being exactly the layer distance obtained in the pure SF-PES. The larger scattering maximum d_2 (Figure 6 and 7) refers to the periodic distance between the SF-PES domains in the PSU matrix. A correlation between this distance and the domain size was postulated recently.[17] The random semifluorinated polysulfones show a somewhat different structure compared to the BCP. In DSC investigations, only a glass transition can be found, without indications of side chains melting and isotropization.

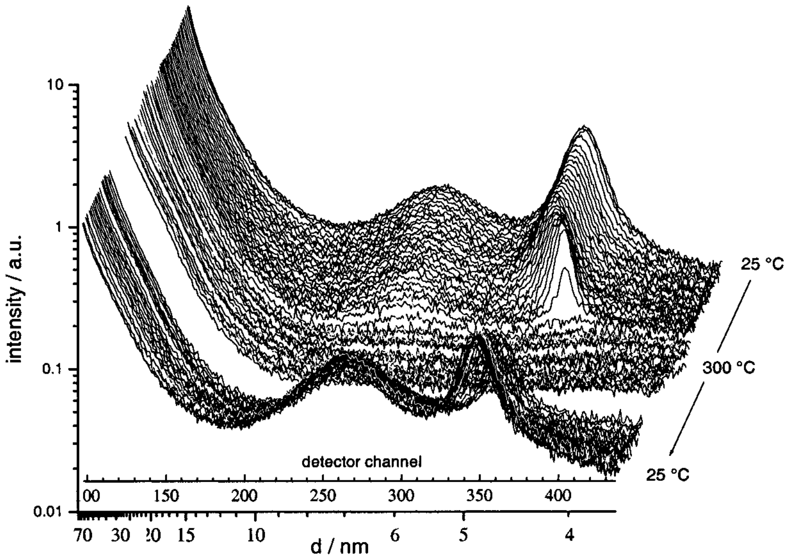

Fig. 7. Temperature-dependent SAXS curves of a BCP with PSU 2300 g/mol and SF-PES 2300 g/mol segments.

The T_g's strongly depend on the structure of the side chains (Figure 8). The T_g of PSU with COOH-side chains increases slightly with the side chain concentration referring to higher intermolecular interactions. In contrast, the T_g's of PSU with SF-side chains drop down significantly with increasing side chain concentration, showing that the SF-side chains alter the amorphous rigid structure of unmodified PSU.

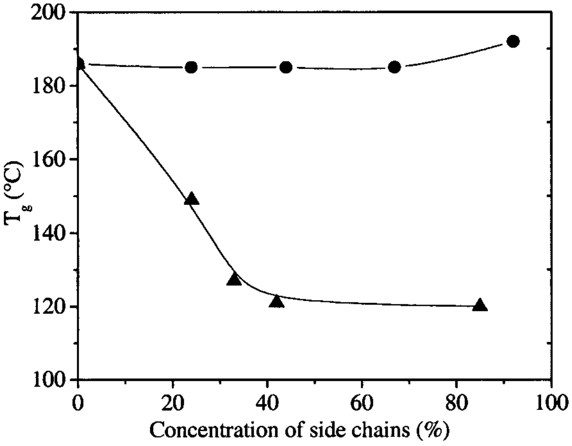

Fig. 8. Glass transitions temperatures of COOH-terminated polysulfones (circles) in comparison to polysulfones with semifluorinated side chains (triangles).

In contrast to the DSC results, temperature-dependent SAXS measurements clearly indicate the existence of an ordered phase having semifluorinated layers (Figure 9). At high side chain concentrations, this phase is already detected in the as-synthesized samples and at lower side chain concentrations, the phase develops upon heating. Even in the polymer with only 25 % SF-side chain, this phase can be detected, as illustrated in Figure 9.

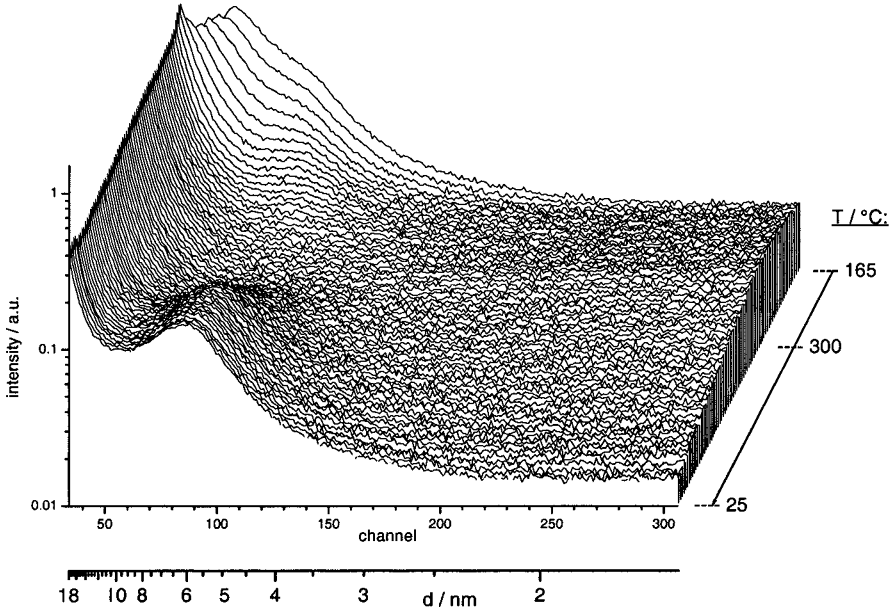

Fig. 9. Temperature-dependent SAXS curves of a random semifluorinated polysulfone (concentration of side chains: 25 mol%, 1st heating to 300 °C with 3 K/min).

The influence of side chain concentration is particularly reflected by the slight shifts in layer distance (Table 4). Higher concentration of semifluorinated side chains forces the side chains to arrange stronger into the smectic layers, thus giving lower layer distances. The copolymer with the highest concentration of SF side chains (85 mol%) shows about the same layer distance than the semifluorinated polyester synthesized by melt polycondensation.[22]

Table 4. Layer distances in the semifluorinated domains obtained for random semifluorinated polysulfones with different molar concentration of SF-side chains (after the first heating to 300 °C and cooling to 25 °C).

Molar concentration of SF-side chain (mol%)	Structure at room temperature?	Layer distance d after cooling (nm)
85	yes	5.2
42	yes	5.3
33	no	5.5
25	no	6.6
0	no	-

Surface Properties of the Block and Random Copolymers

Thin films were prepared by spin coating to investigate the wetting behavior of the polymers. Using similar concentrations of the polymers for spin coating should confirm comparable thickness of the produced copolymer films. The wetting behavior was examined by contact angle measurements using water as probe.

Figure 10 shows the results obtained for PSU-SF-PES BCP and Figure 11 the contact angles for PSU's with randomly distributed COOH- and SF-side chains with different concentration. Regarding the difference in the wetting behavior of both polymer types, it has to be stated that the segmented BCP's show a stronger dependence on the polymer composition than the random copolymers with SF-side chains. Whereas the BCP's show a clear increase of water advancing contact angle with the molecular weight of the SF-PES block (but without dependence on the molecular weight of PSU blocks), a clear dependence on the concentration of SF-side chains in the random copolymers cannot be found. All polymers with SF-side chains have high contact angles between 115 and 120°, that means, a clearly more hydrophobic behavior than the unmodified PSU, but a dependence on SF-side chain concentration does not appear. In contrast, PSU's with COOH-side chains show a more hydrophilic behavior as compared to PSU, as it was expected, but again without dependence on side chain concentration. The reason therefore might be discussed in terms of the much lower bulk order of the PSU copolymers.

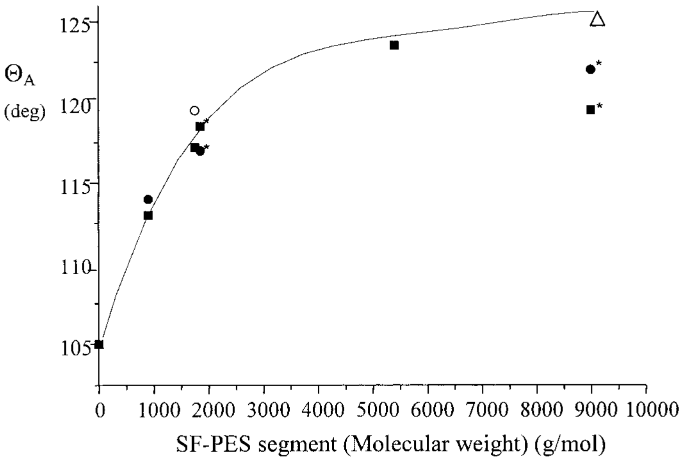

Fig. 10. Advancing contact angles of water on thin films of PSU-SF-PES block copolymers (*: molecular weights calculated by ^{1}H NMR, see Table 2; △: SF-PES; ■: PSU block molecular weight – 2,300 g/mol; ○: PSU block molecular weight – 4,900 g/mol; ●: PSU block molecular weight – 9,000 g/mol) plotted versus the molecular weight of the semifluorinated polyester blocks.

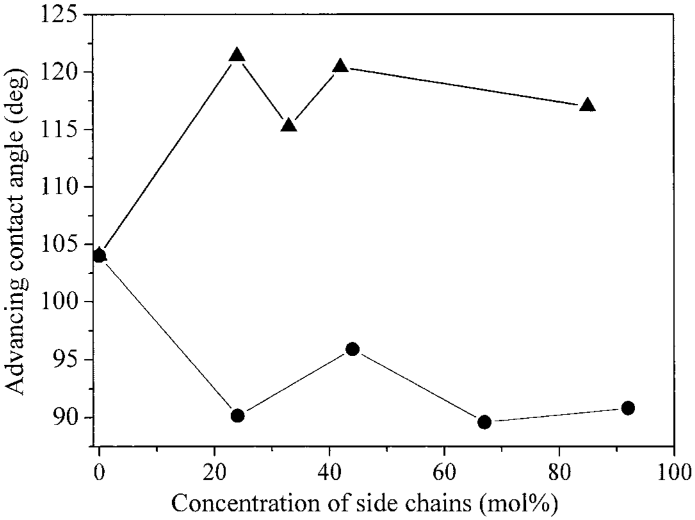

Fig. 11. Advancing contact angles of water on thin films of polysulfones with COOH- and SF-side chains (●: COOH-side chains; ▲: SF-side chains) plotted versus the molar concentration of semifluorinated side chains.

Conclusions

BCP with PSU and SF-PES segments show a stronger tendency of self-organization of semifluorinated side chains than PSU's with randomly distributed SF-side chains, which can be understood in terms of a lower distance and therefore higher interaction of the fluorinated parts in the BCP, leading to a higher ordered structure in the bulk. The surface properties of both polymer types are almost comparable, showing extremely high water contact angles, i.e., low surface free energies, at high concentration of SF-side chains. In both cases, the contact angle can be controlled by the chemical composition (i.e., the concentration of semifluorinated side chains) of the polymer. Both types can be used in blends, as reported recently.[23]

Acknowledgements

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