

Tailoring of polymer properties in segmented block copolymers

Doris Pospiech*, Liane Häußler, Kathrin Eckstein, Dieter Voigt, Dieter Jehnichen, Antje Gottwald, Wolfram Kollig, Andreas Janke, Karina Grundke, Carsten Werner, Hans R. Kricheldorf[#]

Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

[#] Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

SUMMARY: Linking segments of two different polymers in block copolymers offers the opportunity to combine their macroscopic properties and to design tailor-made materials. This is shown for segmented block copolymers (A-B)_n in which the basic segment is polysulfone. Incorporation of either hydrophilic and or hydrophobic segments results in a dramatic change of surface properties which is also correlated to the bulk structure of the block copolymers.

Introduction

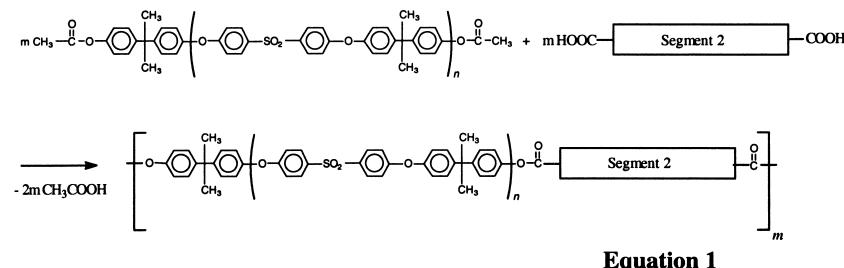
Block copolymers (BCP) have been intensively studied for more than 30 years. The intention was always to combine properties of two or more polymers in a new polymer, resulting in materials with tailor-made property profiles. Thus, a variety of block copolymers with different structure was reported and the phase separation between the block copolymer segments was shown to cause property combinations and synergisms¹⁻³⁾. Properties to be adjusted can be processing behavior (melt and solution viscosity), mechanical and thermal performance and also surface properties (e.g., to achieve biocompatibility)⁴⁾. Tools to design new materials by block copolymer formation are to choose the polymeric segments to be incorporated with respect to their macroscopic properties, i.e., to select which properties should be developed in the new material, and, on the other hand, the knowledge of the phase separation behavior because the properties of block copolymers are mainly controlled by the microphase-separated morphology. The conditions for phase separation are relatively well-known for certain diblock copolymers (e.g., polystyrene-*b*-polyisoprene) expressed in phase diagrams that were obtained both experimentally and by calculations⁵⁻⁷⁾.

We have been investigating segmented block copolymers of the structure $(A-B)_n$ having polysulfone (PSU) blocks as building blocks in order to introduce the advantageous properties of PSU, e.g., excellent mechanical strength, temperature- and oxydation stability and chemical resistance, into block copolymers. It could be shown that incorporation of liquid-crystalline polyester and poly(ester imide) segments actually resulted in a combination of mechanical properties in phase separated samples, whereas non-phase separated BCP developed property synergisms particularly with respect to the glass transition temperature⁸⁻¹⁰⁾. The processability in the melt as well as the thermostability could generally be improved by block copolymer formation in comparison to the homopolymers.

In this work we will discuss the influence of phase separation in segmented block copolymers with surface active segments. Both, hydrophilic poly(tetramethylene oxide) segments and semifluorinated polyester segments having low surface energy were built into the polysulfone chain. The investigations were performed to address the questions whether it is possible to understand the phase separation behavior of these rather complicated structures and, on the other hand, to investigate whether or not the degree of phase separation in the bulk influences the surface properties of the polymers.

Synthesis of the segmented block copolymers

The segmented block copolymers were synthesized by a transesterification polycondensation process in the melt, as it was described for several LC block copolymers in our earlier work⁸⁻¹¹⁾. Thus, acetoxy-terminated PSU oligomers with molecular weights ranging from 1000 to 10000 g/mol were reacted with carboxy-terminated oligomers, as schematically shown in Equation 1.



Relative molecular weights were calculated using PS calibration. The GPC molecular weights obtained for different types of segmented block copolymers are given in Tab. 1.

Table 1. Molecular weights of different types of segmented block copolymers.

Type of segmented block copolymer	M_w (GPC) g/mol	M_w/M_n
Polysulfone-Poly(tetramethylene oxide) 1	18-45,000 ^{a)}	1.8-2.9
Polysulfone-(Semifluorinated polyester) 2	20-40,000 ^{b)}	1.7-2.7
Polysulfone-Poly(ethylene terephthalate-co-oxybenzoate) 3	100,000 ^{c)}	1.7-3.9
Polysulfone-Poly(ethylene terephthalate-co-polyester imide) 4	50,000 ^{c)}	2.1-2.6
Polysulfone-Poly(ester imide) 5	45-70,000 ^{c)}	2.3-5.2

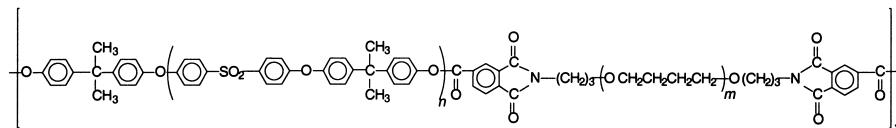
^{a)} GPC: Knauer; eluent: CHCl_3 ; separation column: Merck LiChrogel PS 40; RI detection

^{b)} GPC: Knauer; eluent: pentafluorophenol/ CHCl_3 (1/3 vol/vol); separation column: PSS-SDV linear; RI detection

^{c)} GPC: Knauer; eluent: cresol/ CHCl_3 (1/3 vol/vol); separation column: Waters Styragel HT3/HT6E; RI detection

For the results presented here, two different series of segmented block copolymers **1** and **2** (chemical structure as given in Formulae **1** and **2**) have been investigated. The chemical characterization of the samples is given in Tab. 2.

Polysulfone - Poly(tetramethylene oxide) (PSU-PTMO) block copolymers



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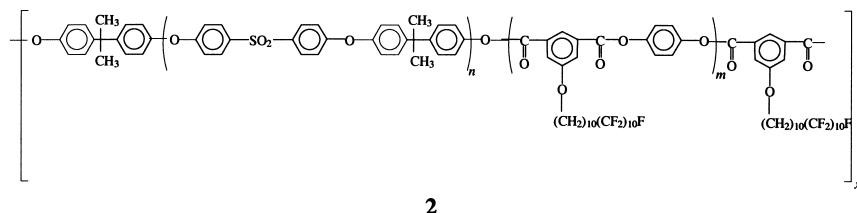
Polysulfone - semifluorinated polyester (PSU-SF-PES) block copolymers**2**

Table 2. Characterization of the segmented block copolymers under discussion.

Block copolymer	PSU segment M _n g/mol	Second segment M _n g/mol	BCP M _w (GPC) g/mol	BCP M _w /M _n
PTMO				
1-1a	1150	283	32,300	3.80
1-1b	1150	1150	17,700	2.83
1-1c	1150	2500	18,400	2.49
1-1d	1150	3600	25,600	3.44
1-1e	1150	5200	45,200	1.75
1-1f	1150	9100	35,800	2.07
1-2a	2500	283	43,500	2.54
1-2b	2500	1150	22,300	2.93
1-2c	2500	2500	23,000	2.38
1-2d	2500	3600	19,300	2.12
1-2e	2500	5200	26,600	1.80
1-2f	2500	9100	43,300	1.82
SF-PES				
2-1a	2300	840	10,600	2.36
2-1b	2300	1750	29,000	1.82
2-1c	2300	3600	20,100	2.63
2-1d	2300	9000	21,000	2.13
2-2a	9000	840	44,000	2.16
2-2b	9000	1750	30,400	2.64
2-2c	9000	9000	27,400	1.68

^{a)} GPC: Knauer; eluent: CHCl₃; separation column: Merck LiChrocel PS 40; RI detection^{b)} GPC: Knauer; eluent: pentafluorophenol/CHCl₃ (1/3 vol/vol); separation column: PSS-SDV linear; RI detection

Incorporation of hydrophilic poly(tetramethylene oxide) segments

The synthesis and characterization of segmented PSU/PTMO block copolymers was reported in detail in a previous paper¹²⁾. The block copolymers of series 1-1 with short PTMO segments (1150 g/mol) have a non-crystalline, homogeneous bulk structure, showing a single T_g according to the miscibility rule. The block copolymers of series 1-2 containing PTMO segments with a molecular weight of 2500 g/mol are separated into two amorphous phases. Samples with low molecular weight polysulfone segments contain additionally crystallized PTMO. However, the amorphous phases, although phase-separated, are significantly mixed resulting in a strong decrease of the T_g of the PSU phase. The phase separation behavior of the PSU/PTMO block copolymers observed experimentally agrees well with phase diagrams obtained by Mean Field calculations for polydisperse segmented block copolymers¹³⁾.

Introduction of hydrophilic PTMO units into the PSU chain actually leads to a significant hydrophilization of polysulfone. The dynamic contact angles (advancing and receding contact angles) measured on thin films prepared by spin coating increase continuously in the first, non-phase separated series (Fig.1).

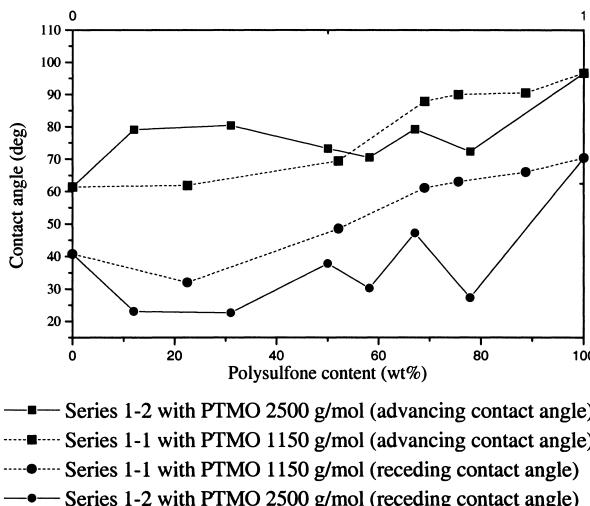


Fig. 1: Contact angles of water on segmented PSU/PTMO block copolymer films

By XPS investigation an enrichment of the surface with PTMO units was observed. The depth profiles show a continuous drop of the S/C ratio with decreasing sampling depth. The phase separated block copolymers (series 1-2) show a discontinuous increase in contact angle with increasing PSU content of the block copolymers. The contact angle hysteresis is much higher than in homogeneous BCP thus indicating that the phase separation in the bulk also produces chemically heterogeneous surfaces having both, hydrophilic as well as hydrophobic parts at the surface. The XPS depth profiles (S/C ratio, indicating the relative concentration of PSU in different sampling depths) depend on the BCP segment molecular weights. The S/C ratio increases, as in series 1-1, in samples with short PSU segments (enrichment with PTMO) whereas samples with long PSU segments show higher relative concentrations of PSU at the surface than in greater depth (enrichment with PSU).

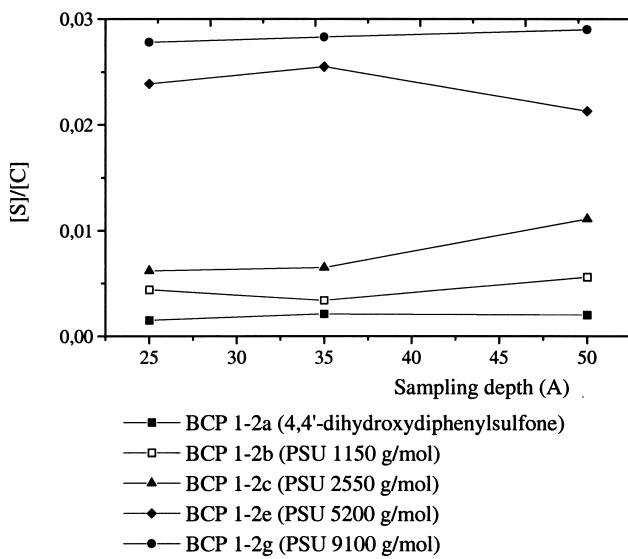


Fig. 2: XPS analysis of the surface composition of block copolymers 1-2 (depth profile).

This is probably caused by the presence of PTMO crystallites near the surface (Fig. 3, left). In contrast, the PSU segments as low energy component are able to segregate to the surface in BCP with long PSU spacers producing a more uniform surface morphology (Fig. 3, right).

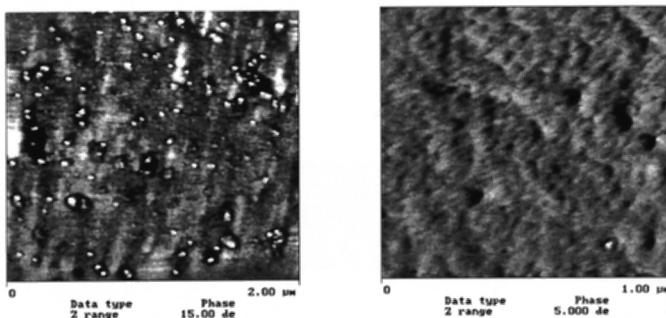


Fig. 3: AFM micrographs of surfaces of BCP 1-2c (left) and BCP 1-2g (right), phase contrast by stiffness; bright: hard.

A next question was whether the hydrophilic properties of PTMO/PSU BCP could be retained in physical mixtures with polysulfone. Thus, 50/50 wt/wt blends of PSU and block copolymers of series 1 were prepared by solution casting. DSC analysis revealed that different states of miscibility (demixed to completely homogeneous) can be achieved by just selecting the appropriate molecular weight of polysulfone segments in the BCP¹⁴. The wetting behavior of thin films on Si wafer was investigated by contact angle measurements (Fig. 4). The contact angles obtained for the blends are significantly lower than that of pure polysulfone, i.e., the hydrophilic properties of the block copolymers determine the surface properties of the blend. The state of miscibility is reflected by the contact angle hysteresis (i.e., the difference between advancing and receding dynamic contact angle). The hysteresis is higher for completely immiscible blends (~ 45 deg for BCP 1-1a), indicating chemically heterogeneous surfaces, whereas on partially miscible and miscible blends the contact angle hysteresis typically obtained is between 25 and 30 deg. This result offers also a tool to create chemically heterogeneous surfaces.

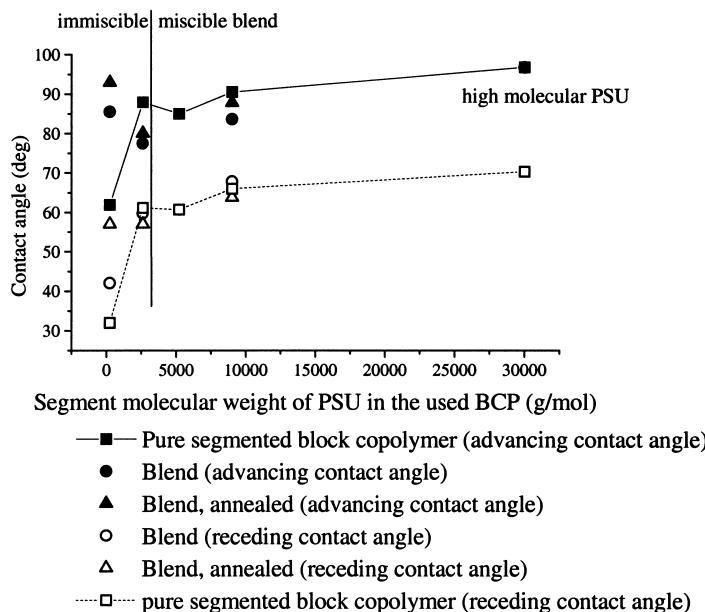


Fig. 4: Advancing and receding contact angles using water as probe obtained on thin films of blends from PSU and PTMO 1150/PSU segmented block copolymers

Incorporation of low surface energy segments (SF-PES)

Poly(p-phenylene-1-oxydecylperfluorodecyl-isophthalate) has been synthesized to introduce semifluorinated side chains to a polyester with fully aromatic backbone¹⁵. Due to microphase separation between the alkyl- and the perfluoroalkyl part of the side chain, the polymer forms a self-organizing, layered solid phase structure and thermotropic liquid-crystalline behavior. The highly ordered bulk structure results also in a highly ordered surface structure having CF₃-groups at the surface which consequently leads to an extremely low surface energy ($\gamma_{sv} = 9.8 \text{ mN/m}$). Linking such segments to polysulfone units in block copolymers should change the surface properties of polysulfone dramatically, though retaining the excellent film-forming properties of PSU. The huge Flory-Huggins interaction parameter calculated for the block copolymer ($\chi = 13.6$) indicates that phase separation in these BCP would occur at very low segment molecular weights. The onset of phase separation was examined by DSC. Fig. 5 displays the DSC curves for PSU-SF-PES BCP of series 2-1.

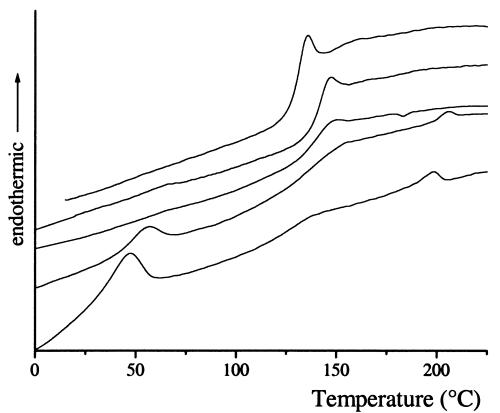


Fig. 5: DSC curves (2nd heating) of PSU-SF-PES block copolymers (series 2-1).

- 1: Polysulfone (2300 g/mol)
- 2: BCP 2-1b: SF 1750/ PSU 2300
- 3: BCP 2-1c: SF 3600/ PSU 2300 BCP 2-1c: SF 3600/ PSU 2300
- 4: BCP 2-1d: SF 9000/ PSU 2300
- 5: Semifluorinated polyester

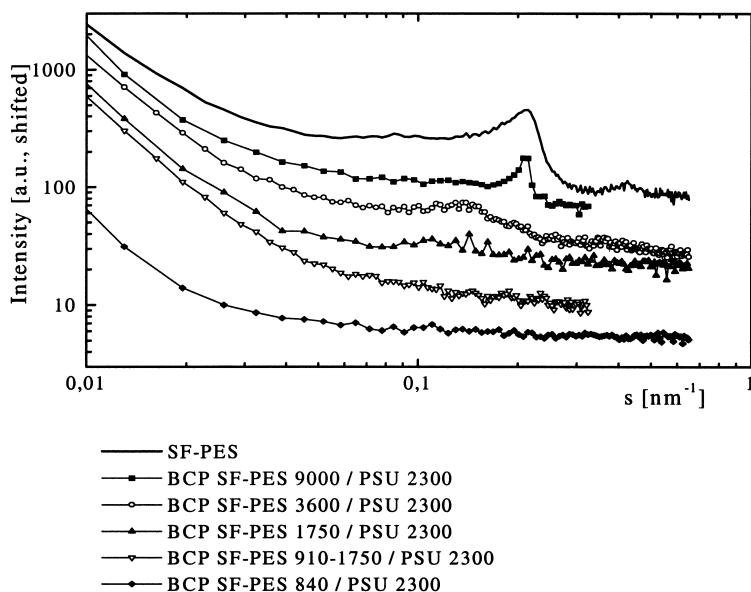


Fig. 6: SAXS curves of polysulfone-semifluorinated polyester block copolymers

After the state of phase separation in the PSU/SF-PES block copolymers was unambiguously ascertained, the surface properties of thin film were characterized by XPS, contact angle measurements and SFM. The XPS depth profiles of films after annealing for 4 h at 200°C, i.e., 20 K above the T_g of the PSU phase, reveal a significant enrichment of the surface with fluorine, as seen by the ratio F/C (Fig. 7).

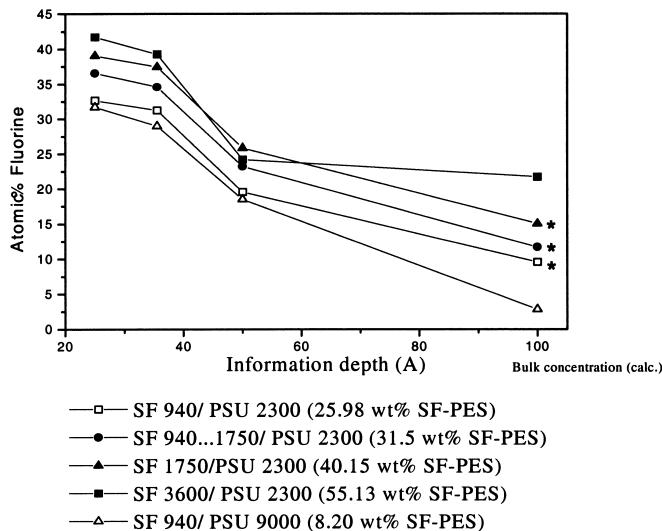


Fig. 7: XPS depth profiles of PS/SF-PES block copolymers
(*: phase separated in the bulk)

Plotting the surface free energies of the block copolymer samples obtained by contact angle measurements (calculation by the Equation-of-State approach¹⁶) versus the actually measured fluorine contents at the surface (Fig. 8) shows that the bulk morphology obviously does not influence the surface energy, i.e., it depends only on the fluorine concentration at the surface which is determined by the strong tendency of the fluorinated segments to segregate to the surface. The fluorinated segments of the block copolymer form disperse domains at the surface as detected by Scanning Force Microscopy. The size of the domains depends on the molecular weight of the semifluorinated polyester segment, i.e., on the block copolymer composition, as

discussed recently¹⁷⁾. The contact angles raise with increasing bulk concentration of fluorinated segments. The surface free energies of block copolymers are in the range of 12 to 16 mN/m which is much less than that of polysulfone. That means, introduction of hydrophobic segments into polysulfone again leads to a significant alteration of surface properties of the block copolymer.

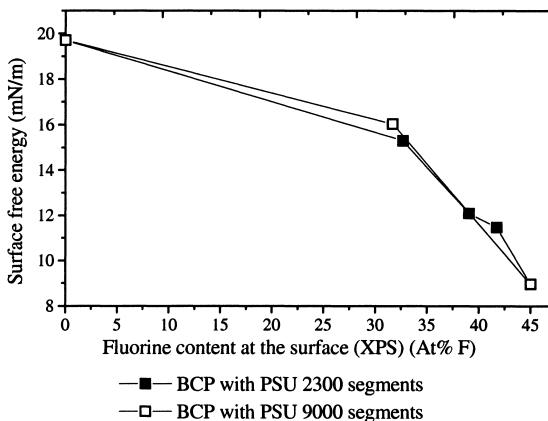


Fig. 8: Surface free energies of PSU/SF-PES block copolymers versus the fluorine content at the surface, obtained by XPS
(0 %F: polysulfone; 45 % F: semifluorinated polyester)

Adsorption of model proteins

Both, hydrophilic as well as strongly hydrophobic materials can prevent the adsorption of proteins which is a significant point to prevent biofouling, e.g. for membranes. Therefore, the interaction of the modified polysulfone surfaces with two model proteins, Human Serum Albumin (HSA, molecular weight: 68,000 g/mol) and Fibrinogen (Fib, molecular weight: 360,000 g/mol), in phosphate buffer solution was examined by variable angle spectroscopic ellipsometry (VASE). VASE allows to determine time-resolved the thickness of the protein layer, shown in Fig. 9 for a polysulfone film. It can be seen that the thickness of the protein film increases continuously reaching a maximum after certain time. The surface concentration of protein on the polymer film at the maximum was then calculated according to de Feijter¹⁸⁾.

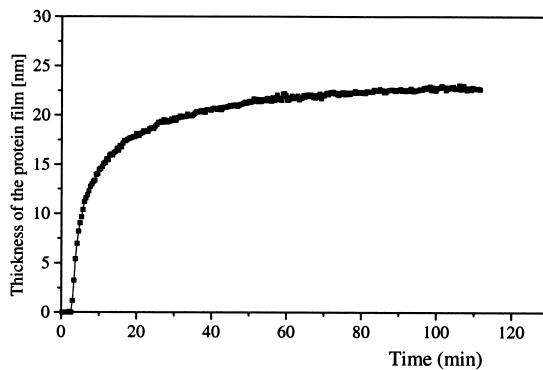


Fig. 9: Time-resolved measurement of the thickness of Fibrinogen adsorption (Fib concentration: 200 ppm in buffer) to a polysulfone film (spincoated, dried in vacuum and annealed for 4 h at 200 °C).

Fig. 10 compares the surface concentration Γ of HSA on different block copolymer films (plotted versus the surface free energy of the BCP).

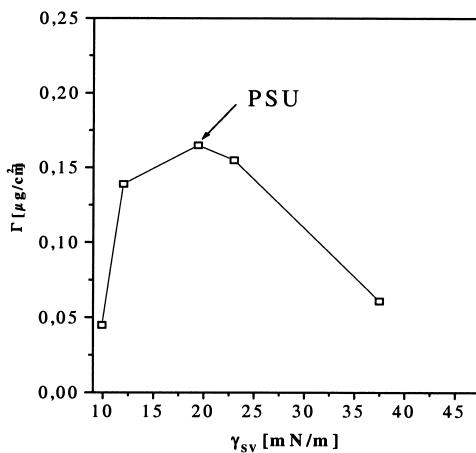


Fig. 10: Surface concentration of Human Serum Albumin (concentration: 100 ppm in buffer) after 150 min measuring time versus the surface free energy of different polysulfone block copolymer films (value at $\gamma_{sv} = 19.5$ mN/m: polysulfone)

The surface concentration of Human Serum Albumin on the block copolymer films is lower than that on the pure polysulfone film. Both, hydrophilic as well as strongly hydrophobic modification results in a decrease of protein adsorption. The same

tendency was found when using the larger Fibrinogen as model protein. Obviously, protein adsorption is significantly prevented by the ultralow surface free energies of the fluorinated samples, whereas on the other hand the low surface tension between the hydrophilic PSU/PTMO block copolymers and the protein in solution has the same effect. Detailed investigation is in progress and the results will be published soon elsewhere.

Conclusion

It was demonstrated that the synthesis of multiblock copolymers of polysulfone containing either hydrophilic PTMO segments or ultrahydrophobic semifluorinated polyester segments leads to a significant modification of surface properties of polysulfone. The state of phase separation of the block copolymers in the bulk can be controlled by the segment molecular weights of the blocks used. In the case of segmented PSU/PTMO block copolymers phase separation in the bulk produces chemically heterogeneous surfaces. In contrast, block copolymers having semifluorinated polyester segments in the chain show surface segregation of the fluorinated segments independently on the state of phase separation resulting in materials with very low surface free energies. Both approaches finally help to reduce the adsorption of model proteins significantly.

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