

SYNTHESIS OF POLY(FLUORINATED STYRENE)-BLOCK-POLY(ETHYLENE OXIDE) AMPHIPHILIC COPOLYMERS VIA ATRP : POTENTIAL APPLICATION AS PAPER COATING MATERIALS

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Abstract

The atom transfer radical polymerization (ATRP) of poly(ethylene oxide)-block-poly(2,3,4,5,6-pentafluorostyrene) (PFS-b-PEO) copolymers (di- and triblock structures) with wide range of poly(ethylene oxide) (PEO) molecular weights of 5000 (5 k), 10,000 (10 k), 35,000 (35 k), and 100,000 (100 k) g/mol was initiated by a poly(ethylene oxide) chloro telechellic macroinitiator. The polymerization, carried out in bulk at 140 °C and catalyzed by copper(I) chloride (CuCl) in the presence of 2,2' -bipyridine (bipy) ligand (CuCl/bipy), led to A–B–A amphiphilic triblock and A-B amphiphilic diblock structures with polyfluorinatedstyrene (PFS) as the A block and poly(ethylene oxide) (PEO) as the B block. With most of the macroinitiators, the living nature of the polymerizations led to block copolymers with narrow molecular weight distribution ($1.09 < M_w/M_n < 1.33$), and well-controlled molecular structures. These block copolymers turned out to be water-soluble through the adjustment of the content of PEO blocks (PEO content >90% by mass). The printability of the treated paper was evaluated with contact angle measurements and felt pen tests. From our study, it is observed that chain length of the hydrophilic block and/or the amount of hydrophobic block play an important role in modification of the paper surface. Among all of block copolymers synthesized, the PFS-b-PEO(10k)-b-PFS containing 10 w-% PFS was found to retarded water absorption considerably.

Introduction

Amphiphilic polymers and block copolymers are typical nonionic polymeric surfactants which have attracted considerable attention because of their outstanding solution properties and a wide range of applications. These materials are very interesting from the point of view of fundamental research, as they exhibit self-assembling properties in the presence of a selective solvent or surface. The increasing interest in hydrophilic-hydrophobic block copolymers is due to the improvement of the synthesis techniques and to their application possibilities as biomaterials, drug carriers, stabilizers in suspensions or emulsions, surface modifying agents, adhesives and coatings, etc.¹

One of the most successful synthetic techniques is atom transfer radical polymerization (ATRP) which was first reported by Matyjaszewski, Sawamoto, and others.²⁻⁶ ATRP has been used to produce polymers with controlled architecture in the synthesis of block copolymers from macroinitiators.⁷⁻⁹ Several research groups have reported ATRP for synthesis of block copolymers using poly(ethylene oxide)^{8,9,10,11} and other hydroxy terminated oligomers¹² as precursors by this technique. Most of the amphiphilic block copolymers of this type have poly(ethylene oxide) (PEO) as hydrophilic blocks, whereas the hydrophobic blocks are poly(methyl methacrylate) (PMMA), polystyrene (PS), and so forth.^{8,9,13,14} PEO, in addition to its adjustable water solubility, has the advantage of being biocompatible.

Earlier we reported the ATRP polymerization of styrene and methylmethacrylate initiated with

poly(ethylene oxide) chloro telechelic macroinitiator and catalyzed by (CuCl/bipy).^{15,16} Our results showed that the block copolymers synthesized proceeded in a controlled manner, leading to A-B-A triblock and A-B diblock copolymers with narrow molecular weight distribution ($1.07 < M_w/M_n < 1.39$) for most of the copolymers synthesized. These water soluble/dispersible polymers showed possible applicability as coating materials on paper surfaces. From our study, it was observed that chain length of the hydrophilic block and/or the amount of hydrophobic block play an important role in modification of the paper surface. Among all of block copolymers synthesized, the PS-*b*-PEO-*b*-PS containing 10 w-% PS was found to retarded water absorption considerably.

Fluoropolymers have attracted significant attention due to their high thermal stability and oil and water repellency. They are extremely hydrophobic materials, exhibiting large contact angle values.¹⁷ An even more hydrophobic surface can be created with fluorinated styrene, than with hydrocarbon styrene.¹⁸ Fluorinated block copolymers with well-defined structures can be generated by ATRP. Hvilsted et al.¹⁹ demonstrated fast controlled polymerization of 2,3,4,5,6- pentafluorostyrene (FS) by this technique. Furthermore, they reported on the preparation of two novel, highly fluorinated styrene monomers and how well-defined homo- as well as block copolymers with styrene and FS can be prepared by ATRP in addition to the preliminary investigations of the surface characteristics of these new polymers.²⁰ In other study, Jankova and Hvilsted²¹ demonstrated a strategy for preparation of BAB triblock copolymers with a poly(ethylene glycol) (PEG) A, middle block flanked by PS end blocks (B) by ATRP. The concept was based on quantitative conversion of the terminal hydroxyl groups in PEG to 2-bromo propionates. The bromine in this environment serves as an effective

initiator for ATRP. The resulting bromine ester terminated PEG then performs as a difunctional microinitiator employed in the preparation of PS-*b*-PEG-*b*-PS copolymers. This strategy was adapted and exploited in utilizing 2-bromoisobutryl bromide for the design of triblock copolymers with PFS blocks replacing the PS blocks. A number of PEGs with molecular weights ranging from 2×10^3 to 10×10^3 g/mole were employed. To the best of our knowledge, we are the first to report the synthesis by ATRP of poly(ethylene oxide)-block-poly(2,3,4,5,6-pentafluorostyrene) (PFS-*b*-PEO) copolymers (di- and triblock structures) with wide range of poly(ethylene oxide) (PEO) molecular weights of 5000 (5 k), 10,000 (10 k), 35,000 (35 k), and 100,000 (100 k) g/mol). Also, to the best of our knowledge, none of the above mentioned articles have studied the possibilities of applying these synthetic block copolymers as coating materials on paper surface or model surfaces. This paper aims at two objectives: first to prepare a well-defined water-soluble/water dispersible amphiphilic di and triblock copolymer (PFS-*b*-PEO-*b*-PFS), and secondly to study the influence of the polymer on the paper surface.

Experimental Section

Materials. Fluorinated Styrene (FS) (Aldrich, 99%) was purified by passing it through a column of activated basic alumina to remove inhibitor. It was then stored under nitrogen at -15 °C. 2,2' -bipyridine (bipy) 99% (Aldrich) and copper(I)chloride (CuCl) 98% (Aldrich) were used without purification. PEO (5000 (5 k), 10,000 (10 k), 35,000 (35 k), 100,000 (100 k) g/mol) (Aldrich) was dried in vacuum for 24 h before use. 4-Dimethyl amino pyridine (DMAP) 99% (Fluka) was recrystallized from toluene. Triethyl amine (TEA) 99% (Acros) was refluxed with p-toluene sulfonyl chloride, distilled and stored over CaH₂. 2-Chloro propionyl chloride

97% (Fluka) was used without further purification. All other reagents were used as received.

Preparation of PEO Macroinitiators. Telechelic PEO macroinitiators were prepared by an esterification reaction between PEO and 2-chloro propionyl chloride as outlined previously in details.¹⁶

Copolymerization of PEO macroinitiator with fluorostyrene. Polymerization of block copolymers was carried out under dry nitrogen in a dried Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the required amount of macroinitiator and catalyst (1 molar equiv. of CuCl and 3 molar equiv. of bipy), sealed with a rubber septum, and then degassed under vacuum to remove oxygen and then purged with dry nitrogen. The precipitated polymer was immersed in cold diethyl ether and then dried in vacuum at room temperature to a stable weight. The separation of the block copolymers from possible homo PFS and PEO macroinitiator was carried out as follows: the crude product was extracted three times with cyclohexane at room temperature for 3 days (one extraction/day) to remove possible present PFS homopolymer or unreacted fluorostyrene. The residue was purified (after drying and weighing) by washing twice with distilled water at room temperature to remove possible unreacted PEO macroinitiator.

Preparation of model surfaces. Silicon wafers were used as model surfaces. The silicon wafers were cleaned by a RCA cleaning sequence. The wafers were immersed into a $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2 ml NH_4OH (25 %):4 ml H_2O_2 (35 %):14 ml H_2O) mixture at $75^\circ - 85^\circ$ for 10 – 20 min, and then rinsed with water. Subsequently, they were immersed into a $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2 ml HCl (37 %):4 ml H_2O_2 (35 %):16 ml H_2O) mixture at $75 - 85^\circ$ for 10 – 20 min, and then rinsed with water. Polymers were applied on silicon wafers by spin coating from 3 w- % aqueous solutions.

Instruments. The dried product was characterized by proton nuclear magnetic resonance ($^1\text{H-NMR}$), and size exclusion chromatography (SEC) techniques and the conversion was determined by gravimetry. Chloroform was used as solvent and eluent. The samples were filtered through a $0.5 \mu\text{m}$ Millex SR filter. Injected volume was $200 \mu\text{l}$ and the flow rate was 1 ml min^{-1} . Nearly monodisperse polystyrene standards in the range $2 \times 10^6 - 150 \text{ g/mol}$ were used for primary calibration.

The $^1\text{H-NMR}$ spectra of the polymer were recorded using a Varian Inc. (Palo Alto, CA) Gemini 2000XL NMR spectrometer operated at 300 MHz. The polymer solution was prepared by dissolving about 50 mg of polymer in 3 ml of deuterated chloroform (CDCl_3) and in deuterium oxide (D_2O) solvents.

Polymers were characterized by optical microscopy and contact angle measurements. The optical images were recorded with a digital camera combined to Leica MZ6 stereomicroscope. The static contact angles of water (distilled and deionized) were measured using a CAM 200 computer-controlled video based instrument (KSV Instruments Ltd, Finland), and was analyzed with software based on Young-Laplace equation.

Results and Discussion

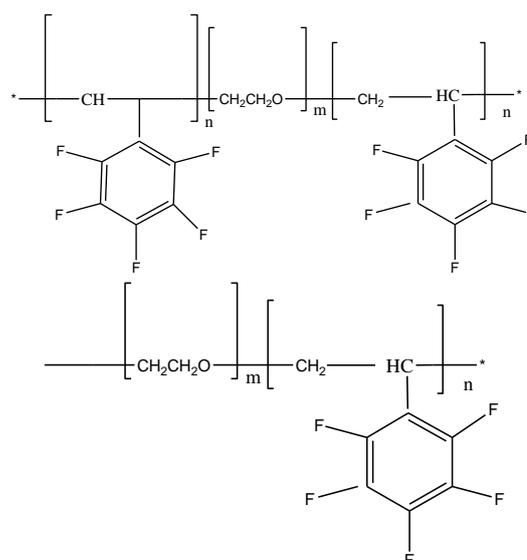


Fig. 1. Synthesis of PFS-b-PEO tri- and diblock copolymers.

Table 1. Results for the synthesis of amphiphilic di and triblock copolymer (PFS-b-PEO-b-PFS).

Entry	%wt FFS	Mn g/mol	Mw/Mn	Solubility in water
1	9	9500	1.19	Soluble
2	10	9600	1.13	Dispersible
3	15	9700	1.12	Dispersible
4	20	10300	1.14	Dispersible
5	30	12000	1.17	Dispersible
6	40	12300	1.14	Dispersible
7	10	21000	1.11	Dispersible
8	15	22000	1.09	Dispersible
9	25	24000	1.16	Dispersible
10	20	43000	1.12	Dispersible
11	20	100500	1.33	Dispersible

Synthesis of PEO-b-PFS di- and triblock copolymers
 The synthesis of PFS-b-PEO-b-PFS triblock or PEO-b-PFS diblock copolymers were carried out from the telechelic PEO macroinitiator as depicted in Fig. 1.

Controllability of Copolymerization. A series of PFS-b-PEO-b-PFS triblock and PEO-b-PFS diblock copolymers with different molecular weights and compositions were synthesized by ATRP technique, as shown in Table 1. Molecular weight of PEO for samples 1 to 6, is 5,000 g/mol (5 k); for samples 7 to 9, is 10,000 g/mol (10 k); for sample 10, is 35,000 g/mol (35 k); and for 11, is 100,000 g/mol (100 k). Table 1 also shows the molecular characteristics data of water-soluble/dispersible di- and triblock copolymers of PEO-b-PFS (when weight percentage of the hydrophobic comonomer becomes higher than 10 w-%, the corresponding copolymer is water-insoluble).¹⁵ The Table reveals that well-controlled copolymers with narrow molecular weight distribution (M_w/M_n as low as 1.09) have been synthesized by means of (CuCl/bipy) catalytic system. According to the results in Table 1 some M_n (SEC) values are higher than theoretical molecular weights (not shown in Table 1). This may be attributed to two reasons: first the high molecular weight macroinitiator produced a low radical concentration in the polymerization system. This low radical concentration slowed the rate of polymerization and decreased the conversion of the fluorostyrene monomer. Other reason is that SEC calibration was carried out with PS standards. Similar results were published by Haddleton et al.²²

Fig. 2 shows the SEC curves of PFS-b-PEO-b-PFS triblock and PEO-b-PFS diblock copolymers, to comprise single and symmetric peaks. A narrowing of molecular weight distribution with conversion, as exhibited in this figure, suggests formation of a controlled polymer structures and, at the end of the reaction, molecular weight distributions are unimodal and narrow ($1.09 < M_w/M_n < 1.33$ see Table 1).

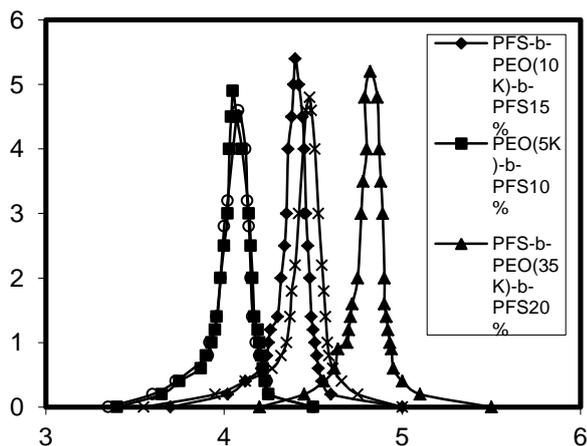


Fig. 2. SEC traces of some PFS-b-PEO tri- and diblock copolymers.

Hydrophilic/Hydrophobic characteristics of spin coated model silicon surfaces by contact angle measurements.

The contact angles of water on different PFS-b-PEO-b-PFS triblock and PEO-b-PFS diblock copolymers are shown in Fig. 3. The polymers were spin coated on hydrophilic silicon strips at the concentration of 3 %. The solutions of PFS triblock copolymers were more turbid in comparison to the solutions of the diblock copolymers indicating a more hydrophobic nature of the triblock copolymers. However, at equilibrium state, at $t = 3$ s, no significant difference can be observed in the contact angles. At time $t = 0$ s, however, it is seen that the triblock copolymers induce more surface than the diblock copolymers (contact angle for PFS-b-PEO(10K)-b-PFS, is about 72° , whereas it is about 55° for PEO(5K)-b-PFS, entries 7 and 2 in Table 1, respectively). PFS-b-

PEO(10K)-b-PFS and PEO(5K)-b-PFS with 10 % PFS in each polymer are chemically the same but one is a triblock copolymer whereas the other one is a diblock structure. The diblock structure allows the formation of more ordered micelle-like particles in comparison to less ordered aggregates that the triblock copolymers form. Thus, the hydrophobic fraction of the diblock copolymers may be more protected by the hydrophilic PEO segments which could induce the slight reduction in the contact angle at $t = 0$ s on the diblock comparison to the triblock structure.

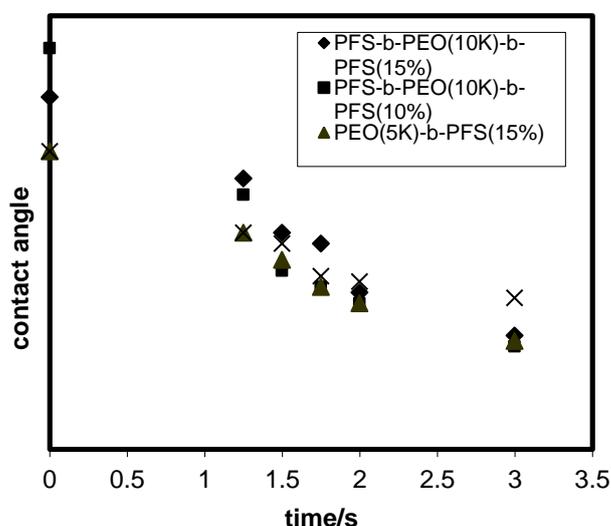


Fig. 3. Contact angle of water on different block copolymers spin-coated at a concentration of 3 w% on hydrophilic silicon strips.

Hydrophilic/Hydrophobic characteristics of spin coated paper surfaces by felt pen test.

Optical microscope images of PEO-coated (up) and PFS-b-PEO(10K)-b-PFS-coated (down) paper samples are shown in Fig. 4. When the paper was treated with PEO homopolymer, the ink penetration was stronger in the PEO-coated zone (Fig. 4 up) than in the polymer-coated zone (Fig. 4 down). The figure shows that the imprint is more even and lighter when the amphiphilic polymers have been used. The amphiphilic nature of the polymer evens out the fluctuation of surface properties of the base paper and the imprint becomes more even. At the same

time, the penetration depth of the color decreases, which can be seen as a lighter imprint. It can clearly be seen that the block copolymer has strongly hydrophobing effect on the paper.

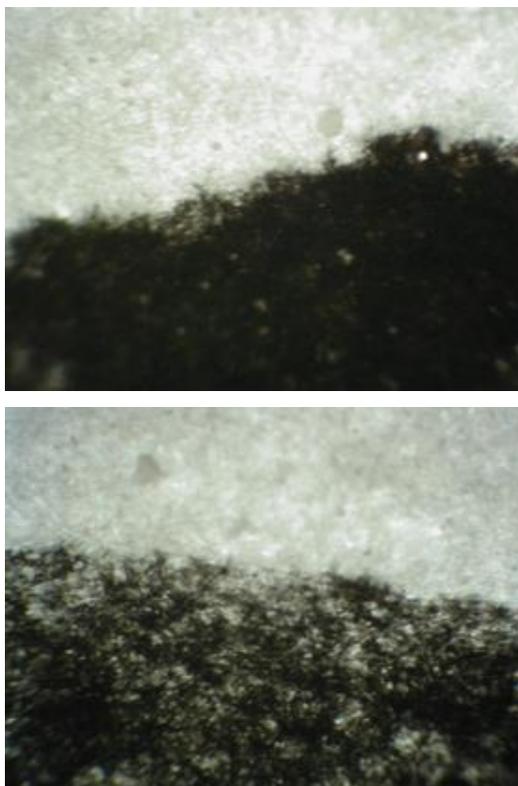


Fig. 4. Water-based felt pen tests of PEO-treated (up) and PFS-b-PEO(10K)-b-PFS-coated (down) paper samples.

In order to study the effect of the molecular weight of the PEO-blocks in the amphiphilic copolymers on the paper surface, the base paper has been coated with two different molecular weight PEO-based triblock copolymers PFS-b-PEO(35K)-b-PFS (entry 10), and PFS-b-PEO(100K)-b-PFS (entry 11) keeping the weight percent of PFS constant at 20 as shown by Fig. 5. Fig. 5 reveals that both polymers has hydrphobized the paper surface (Fig. 5 b, c) in comparison with pure water-coated surface (Fig. 5 a). The microscopy images show that the imprint becomes more even and lighter, and the color does not penetrate as deep to the paper when amphiphilic PFS-b-PEO(35K)-b-PFS polymer is used instead of PFS-b-PEO(100K)-b-PFS. This plausibly can be explained based on the fact that

the solubility of PEO(100k)-based block is less than that of the PEO(35k)-based and to the hydrophilicity nature of PEO.



Fig. 5: Microscopic images from felt-pen tests to polymers with different PEO-based molecular weights.

Ink jet printing. It was of interest to perform an ink-jet printing test on base paper coated with PFS-b-PEO(10K)-b-PFS amphiphilic polymer. Fig. 6 shows that the ink-jet printed text on base paper spray-coated with polymer PFS-b-PEO(10K)-b-PFS is less fuzzy (i.e., sharper edged) than that printed on noncoated base paper or commercial copy paper.

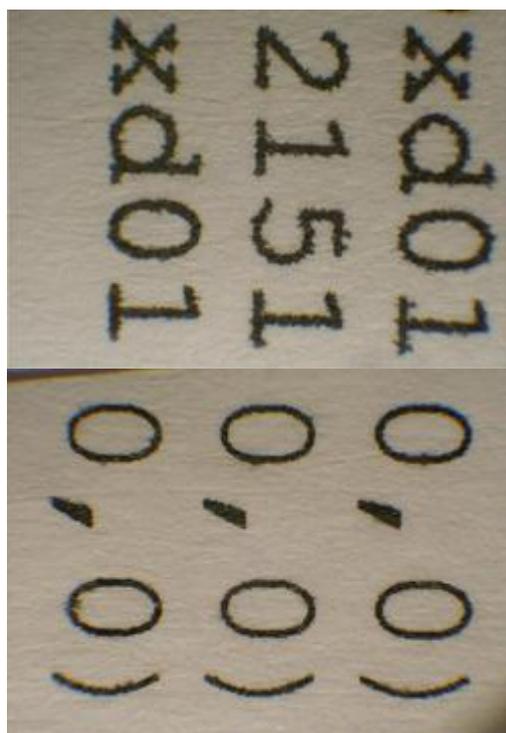


Fig. 6: Ink jet printing test

Conclusions

Water-soluble PFS-b-PEO (di- and triblock structures) block copolymers were prepared through adjustment of the content of PEO blocks (PEO content >90% by mass). Water-soluble PFS-b-PEO-b-PFS and PEO-b-PFS block copolymers showed promise as coating materials in experiments done on silicon model and paper surfaces. On model silicon surface the diblock structure allowed the formation of more ordered micelle-like particles whereas the triblock structure led to less ordered aggregates. On the paper surface, PFS-b-PEO(10k)-b-PFS with 10 w % PFS appeared as the most effective of all synthesized water-soluble block copolymers. The coating hydrophilicity/-phobicity could be modified through change in the PEO/PFS ratio in the block copolymer. Hydrophobicity of the base paper surface was increased when the paper was coated with copolymer when the molecular weight of PEO block was about 10,000 g/mol and the amount of PFS was 10 w %. By coating paper with PEO (35K) the surface becomes more

hydrophobic than coating with PEO (100K) which means that starting with water-soluble block is better as surface modifier.

Finally one could conclude that poly(fluorinated styrene) block copolymers were more hydrophobic and of lower surface energy than with hydrocarbon styrene polymers

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