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Amphiphilic Block Copolymer of Styrene and Ionic Acetylene

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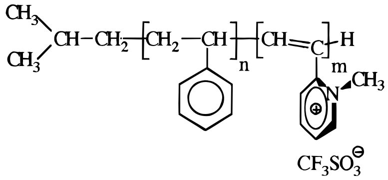
ABSTRACT: A novel amphiphilic block copolymer of an ionic acetylene and styrene was prepared. Initiation of the *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate (2EPyMeTf) by living anionic polystyryl$^-$−Li$^+$ resulted in polystyrene$_{12}$-*block*-poly(2EPyMeTf)$_4$. This amphiphilic block copolymer (PS-PA) contains a conjugated and strongly hydrophilic polyacetylene chain attached to a more flexible hydrophobic polystyrene chain. The structure of PS-PA was confirmed by FT-IR, UV−visible, and ^{1}H, ^{13}C, ^{14}N, and ^{19}F NMR spectroscopy. Gel permeation chromatography (GPC), vapor pressure osmometry (VPO), and viscometry were used to obtain information on the molecular mass and molecular mass distribution. Thermal properties were investigated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). PS-PA was shown to form a stable monolayer at the air−water interface. The positively charged rigid polyacetylene segments are believed to be at the water surface and only partially submerge, while the more flexible hydrophobic polystyrene chains are forced out of the water. Doping with iodine was found to cause a contraction of the monolayer. Uniform and stable multilayers were deposited using both Langmuir−Blodgett and self-assembly deposition techniques without the need for a polyanion. Conductivity measurements of the multilayer assemblies suggested an alternating insulator−semiconductor layer structure of the deposited films.

Introduction

We have recently reported on the synthesis and properties of a new class of mono- and disubstituted ionic polyacetylenes with extensively conjugated backbones.[1−7] The structural features of these polymers are unique with respect to their ionic nature, high degree of substitution, and extensive backbone conjugation. Investigation of the polymerization mechanism of the nucleophile initiated polymerization of the *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate (2EPyMeTf) in polar protic[8] and aprotic media[9] indicated that initiation is the rate determining step. A complex zwitterionic/anionic mechanism and a general reaction scheme were proposed. This rather unusual polymerization mechanism (in which a pyridinium cation containing monomer polymerizes by an anionic route) should lead to an easy preparation of block copolymers by initiating the anionic polymerization of 2EPyMeTf with a “living” polystyryl$^-$ Li$^+$ initiator. Such polymerization should give a polystyrene-*block*-poly(2EPyMeTf), an amphiphilic di-sequential block copolymer containing a strongly conjugated and hydrophilic ionic polyacetylene and a flexible hydrophobic polystyrene (Chart 1). The morphology of films containing such copolymers is interesting because of easy orientation at interfaces of such amphiphilic copolymers. Deposition of monolayers on different substrates could result in an alternate conductive−nonconductive molecular multilayer structure of which the conjugated double bonds of the polyacetylene sequence would form an integral part of one type of layers. The other type would contain strictly nonconductive polystyrene chains. To our knowledge, such block copolymers have not been previously synthesized. We have recently described the preliminary work of synthesis and properties of this copolymer.[10,11] In the above paper this work is discussed in more detail.

Chart 1. General Structure of the Polystyrene-*block*-Poly(*N*-methyl-2-ethynylpyridinium triflates)



Such amphiphilic copolymers are of potential interest in the areas of electronic and electrooptical applications. They can also lead to interesting materials in the fields of surface modification and permeation membranes.

Experimental Section

Materials. 2-Ethynylpyridine, obtained from Lancaster Synth. Inc., was distilled under vacuum in nitrogen atmosphere before use. Pyridine, styrene, benzene (anhydrous), methyl trifluoromethanesulfonate, *sec*-butyllithium solution, KI, and iodine (99.9%) were purchased from the Aldrich Chemical Co. and were used as received. Spectroscopic grade methylene chloride and acetonitrile were freshly distilled from P_2O_5 twice, just before the experiment. Styrene monomer was washed by 10% NaOH solution, and then water, and dried over $MgSO_4$. Final purification was done by vacuum distillation from CaH_2 just before the experiment. Spectroscopic grade methanol was purified by distillation from Mg turnings in the presence of I_2 traces. Deuterated solvents were used as received. Other common solvents were distilled before use.

Methods and Analytical Instruments. Polymerization was carried out in a MBraun 150M stainless steel glovebox (Innovative Technology Inc.) under dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm) at room temperature. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer between CaF_2 plates or as films cast on CaF_2 plates. UV−visible spectra were obtained on a GBC 916 spectrophotometer at room temperature between 200 and 1000 nm. ^{1}H, ^{13}C, and ^{14}N NMR measurements were carried out using a Bruker 270 SY multinuclear spectrometer equipped with a temperature controller. Nitromethane in deuterioacetone solution was used as external reference in the ^{14}N NMR measurements. Dilute

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solution viscosity measurements were made in 1.0 M NaCl solution at 25 °C using a Cannon-Ubbelohde viscometer. Inherent viscosity (η_{inh}) was determined at a concentration of 0.1 g/dL. Thermal analysis was carried out using a Perkin Elmer DSC 7 series instrument. A Du Pont TGA 910 thermogravimetric analyzer was used for the determination of thermal stability. Gel permeation chromatography (GPC) was used for the polystyrene molecular weight measurements (with a polystyrene calibration curve) and for the characterization of copolymers. This GPC consisted of a Waters 510 HPLC pump, a Model U6K universal liquid chromatograph injector equipped with a 20 μL loop, a series of three Ultrastyragel columns (500, 10^3, 10^4 Å) in a Waters TCM temperature controller, and a Hitachi 655A variable wavelength UV monitor. Consecutive runs were recorded on a Kipp and Zonen BD41 dual chart recorder. Vapor pressure osmometry (VPO) was also used for molecular mass measurements (UIC 070 instrument).

PS-PA in undoped, partially doped, and fully doped forms were spread from a chloroform solution (1.9−2.2 mg/mL) onto an aqueous subphase in a commercial Langmuir−Blodgett trough (Lauda FW2) at 20.0 °C.

Doping by iodine was achieved either before spreading (method D-1), during spreading (method D-2), or after spreading (method D-3). In D-1, partial iodine doping was carried out by mixing a known amount of chloroform solution of the copolymer with a calculated amount of I_2 solution in $CHCl_3$. With method D-2, complete doping was accomplished by using 0.1−0.001 M solution of iodine in equimolar aqueous KI ($K[I]_3$ complex) as a subphase. Method D-3 involved exposing transferred polymer films to iodine vapor in vacuo for several days and resulted in full doping.

Film transfer was carried out by vertical dipping at 2 mm/min while holding a constant film pressure of 30 mN/m. Alternating self-assembly layer-by-layer deposition was carried out using a modified technique described in the literature.[12] The polycations were adsorbed for 30 min onto glass and quartz slides from a dilute (10 mg/100 mL) solution in water, with and without using poly(styrenesulfonate) (PSS, M_n = 4 000 000−6 000 000 g/mol) as an alternating polyanion. No inorganic salt was added to avoid the misinterpretation of the conductivity results.

IR measurements of transferred multilayers were carried out using a Perkin-Elmer 1760 X FT-IR, and polarized visible spectra were measured using a Perkin-Elmer Lambda 9 spectrophotometer. An AutoEl^{R}-III (Rudolph Research) ellipsometer was used for thickness measurements. In-plane conductivity was measured with a Keithley 614 electrometer, using interdigitated microsensor electrodes[13] type ABTECH IME 1550-CD-Au-P.

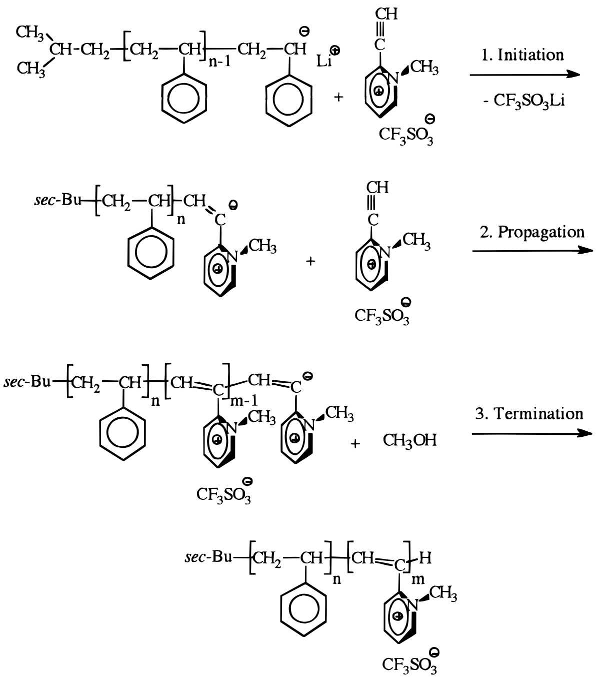
Monomer Synthesis. Synthesis of 2EPyMeTf has already been described by us[7,8] elsewhere.

Copolymerization Method. PS-PA copolymer has been prepared by sequential monomer addition. First, living polystyrene$^-$−Li$^+$ was synthesized in benzene (as indicated below), and this solution was used to initiate the polymerization of 2EPyMeTf previously dissolved in acetonitrile.

Selection of Macroinitiator. 2-Ethynylpyridinium methyl triflate (2EPyMeTf) was shown to polymerize in the presence of weak nucleophiles. Block copolymerization of 2EPyMeTf by the monomer addition method requires a nucleophilic macroinitiator. A suitable system is the well-known living anionic polymer of styrene (PSty$^-$−Li$^+$), where the efficiency of the *sec*-BuLi initiator is close to 100%. Synthesis of nearly monodisperse living polystyrene generally involves the addition of Li salts to narrow even further the molecular weight distribution (MWD ~1.01−1.05) by the common-ion effect (see, e.g., ref 14). In our case, the PSty$^-$−Li$^+$ macroinitiator solution has been prepared without the addition of lithium salts to avoid a possible interference of the inorganic salt during the copolymerization and purification processes.

Synthesis of Living Polystyrene. Typically, 0.6 mL (7.8×10^{-4} mol) of *sec*-butyllithium (1.3 M *sec*-BuLi in cyclohexane) was added to a solution of 0.85 mL (7.42×10^{-3} mol) of styrene in 6.3 mL abs. benzene at room temperature (theoretical M_n ~1000). The solution immediately developed a characteristic deep bright orange color. This solution was then aged for 2 h at room temperature, and aliquots were used to initiate the anionic polymerization of the acetylenic monomer (as described further below).

Scheme 1. Mechanism of Copolymer Formation



Unused portions of living polystyrene were quenched by 1 mL of absolute methanol, and the solvent was evaporated. The resulting white residue was dissolved in CH_2Cl_2 and filtered by means of a glass syringe, first on paper and then on a 0.5 μm pore-size Teflon filter. Solvent evaporation and vacuum drying gave 0.58 g of homopolystyrene as a white powder ($M_{n,\mathrm{GPC}}$ = 960, M_w/M_n = 1.16; $M_{n,\mathrm{VPO}}$ = 1200; $M_{n,\mathrm{NMR}}$ = 1200; η_{inh} = 0.44 g/dL in acetone).

Copolymerization. We have selected as solvent for the copolymerization a mixture of benzene and acetonitrile. This is because 2EPyMeTf is insoluble in apolar solvents. The procedure is as follows:

Two milliliters of initiator solution in benzene (initiator content: 2.0×10^{-4} mol of living polystyrene$^-$−Li$^+$) was added by means of a pipet into a solution of 0.2160 g (9.95×10^{-4} mol) of 2EPyMeTf in 5 mL of acetonitrile at room temperature. The solution immediately turned to reddish-brown, and a precipitate was observed. After 12 h the reaction was quenched by 1 mL of methanol. Addition of 25 mL of diethyl-ether precipitated 0.07 g of homopolyacetylene as a brittle black fine solid. Evaporation of the solvent from the red solution gave 0.46 g of block copolymer as a red solid which was soluble in methanol and dichloromethane without residue. No formation of a homopolystyrene from the anionic polystyrene initiator was observed. The same polymerization procedure involving only *sec*-butyllithium and the acetylenic monomer gave 23% homopolyacetylene as a black solid.

Results and Discussion

Reaction Mechanism. We propose the following reaction scheme (Scheme 1):

In the first step, fast recombination between the Li$^+$ cations and the triflate anions occurs, leading to an adduct formation between macroanions and monomer cations. Since the recombination between the Li cation and triflate anion is fast, the initiation efficiency is practically 100%. In the next step, an internal nucleophilic attack takes place on the substituted triple bond of the monomer, and a carbanion forms. The propagation proceeds via zwitterionic mechanism,[9] in which the 2EPyMe$^+$ monomer cations feed the developing chain.

This propagation can be terminated by MeOH, that transforms the still unreacted acetylenic monomer into dimers.[8]

In addition to the copolymer, formation of various amounts of homopolyacetylene was also observed. Homopolymer formation in an anionic block copolymerization by sequential monomer addition usually indicates protic contaminations or chain transfer. In our case, chain transfer to monomer is not possible during polymerization of the acetylenic bond because proton abstraction from undissociated 2EPyMeTf monomer gives an acetylyde anion that is not able to polymerize.[9] The formation of homopolyacetylene may also be caused by traces of adventitious protic contaminations of the slightly hygroscopic 2EPyMeTf, but in this scenario water would terminate the living polystyrene chain in the initiator and would result in homopolystyrene which was not observed.

The most probable reason of the undesired homopolymerization is a partial hydrolysis of the *sec*-butyllithium before synthesis (note: the relative amount of the homopolymer was different in separate experiments). Presence of LiOH in the reagent suspension essentially does not alter the styrene polymerization, but has a serious effect on the copolymerization as traces of LiOH may generate a competitive homopolymerization of 2EPyMeTf which can partially consume this monomer. This conclusion was confirmed by the following experiment. Copolymerization was initiated by the way described, but the stirring was turned off after 30 min, and the homopolyacetylene was allowed to precipitate and separate. After a 12 h reaction time, an aliquot sample of the clear red solution was added into the solution of 0.267 g (0.001 mol) of 2EPyMeTf in acetonitrile. In 24 h, the absorption of the UV−visible peak moved from 370 to 493 nm without formation of any black precipitate (homopolyacetylene), indicating that the copolymer has increased the length of its polyacetylene sequence, but no formation of the insoluble polyacetylene occurred. Homopolyacetylene formation took place only when the $PSty^{-}-Li^{+}$ macroinitiator solution (contaminated possibly with some LiOH) was mixed with the 2EPyMeTf solution.

The block formation efficiency appears to be 100%, and the homopolyacetylene is originated from hydrolytic impurities in the *sec*-BuLi.

Copolymer Properties and Characterization. PS-PA block copolymer was soluble in solvents of high and medium polarity, such as benzene, $CHCl_3$, methylene chloride, THF, acetone, methanol, DMSO, and DMF. It was not soluble in water upon direct contact; however, when an acetone or methanol solution of the PS-PA copolymer was added into water and the organic solvent was subsequently evaporated, the copolymer displayed water solubility. Film of the copolymer obtained by evaporation of water from such water solutions was again insoluble in water, suggesting that polystyrene forms the external layer of the amphiphilic film while the ionic polyacetylene layer adheres firmly to the surface of the negatively charged substrate. The color of the film cast from solvent on a Si wafer is reddish-brown, in similarity to the bulk material. It is possible that the structures for the bulk and the solvent-cast PS-PA films are similar. Langmuir−Blodgett films of PS-PA deposited on a silicon wafer displayed a uniform color. The color (yellow to blue) depends on the angle of incidence of light and the number of layers. In contrast, the solvent-cast film was brown throughout and did not display iridescence. This could possibly indicate differences in morphology between the two films.

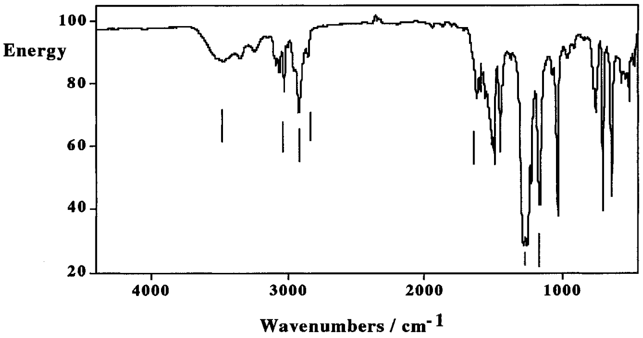


Figure 1. Infrared spectra of the block copolymer (film cast on CaF_2 plate). IR (cm^{-1}): 3466 (polyacetylene backbone =CH), 3082, 3060, 3025 (aromatic ν_{C-H} in PA and PS), 2924, 2850 (aliphatic ν_{CH2} and ν_{CH} in polystyrene), 1625 (polyacetylene backbone -C=C-), 1601, 1585, 1493, 1451 (aromatic skeletal vibrations of PA and PS), 1279, 1258 (S=O unsymmetric stretching in $CF_3SO_3^-$), 1168 (S=O symmetric stretching in $CF_3SO_3^-$).

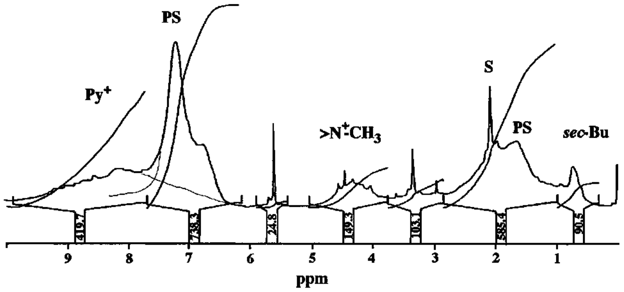


Figure 2. ^1H NMR spectrum of the copolymer in deuteroacetone. *sec*-Bu: CH_3 in the headgroup, A: $-CH_2CH$ units, S: solvent, $(>N^+)-CH_3$: methyl group on the nitrogen, PS: polystyrene, Py^+: pyridinium groups.

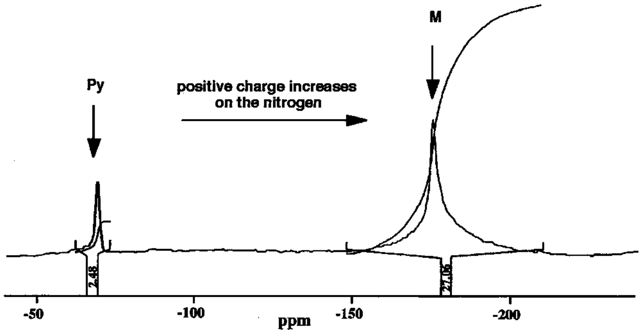


Figure 3. ^{14}N NMR spectrum of the copolymer. Py: ^{14}N resonance of pyridine (−69 ppm); M: ^{14}N resonance of the monomer 2EPyMeTf (−175 ppm).

Spectroscopy. FT-IR spectrum of the product (Figure 1) displayed characteristic absorption bands of polystyrene, of polyacetylene, and of the triflate ions.

Signals of $CH(CH_3)_2$, $>N^+CH_3$, and $-CH_2CH-$ groups were measured by ^1H NMR (Figure 2). The average degree of polymerization was calculated from the ratios of the integrated signals of these groups, which represent the *sec*-butyl headgroup from the initiator, the methyl groups of the polyacetylene sequence, and the polystyrene chain, respectively. The DP of the polystyrene block was found equal to twelve, and the average length of the ionic polyacetylene block was found equal to four ($M_{n,PS} = 1200$ and $M_{n,PA} = 1040$). The ^{13}C NMR spectrum in deuterioacetone corroborated the presence of $-CF_3$ groups (quadruplet centered around 125 ppm).

^{14}N NMR spectrum of the product (Figure 3) confirmed the presence of charged nitrogen atoms with a

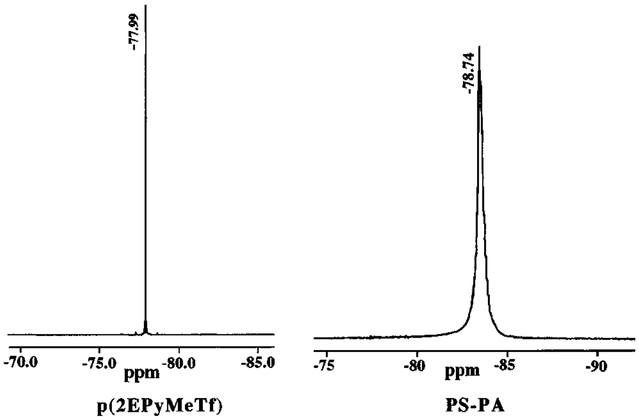


Figure 4. Comparison of ^{19}F NMR spectra of the homopolyacetylene and of the styrene copolymer.

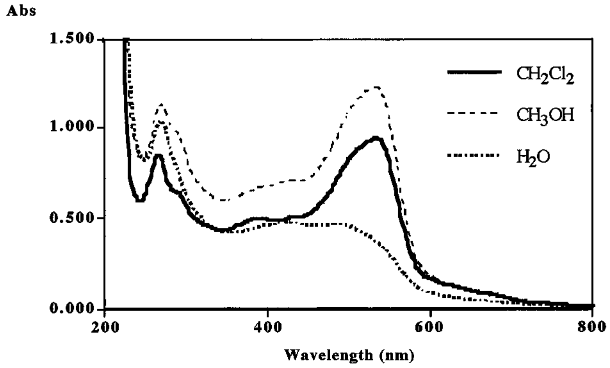


Figure 5. UV−visible spectra of the block copolymer in methanol (continuous line), in methylene chloride (dashed line) and in water (dotted line). $c = 3 \times 10^{-5}$ M.

narrow charge distribution similar to that of the monomer itself. This spectrum also indicated the presence of uncharged nitrogens, amounting approximately to 10% of the total pyridinium rings. Presence of nitrogens virtually without charge in the 2EPyMeTf homopolymers could be related to the formation of stable free radicals on the poly(2EPyMeTf) chain, and their origin will be discussed elsewhere.[15]

^{19}F NMR spectra of the homopolyacetylene and of PS-PA copolymer were also compared (Figure 4). Chemical shifts of the fluorine atoms were practically identical in the homopolymer and in the copolymer, but in the case of the block copolymer the fluorine signal suffers a severe line-broadening due most likely to the more heterogeneous chemical environment of the triflate counterions.

UV−visible spectra of the previously reported homopoly(2EPyMeTf) derivatives synthesized by initiation with nucleophiles[1−9] displayed a broad peak in the visible range, suggesting broad distribution of conjugated sequences. In contrast, PS-PA displays a strong absorption maximum at 532 nm in its UV−visible spectrum (Figure 5). The existence of a distinct major peak in the visible spectrum indicates a narrower distribution of conjugated sequences than in the homopolymer. The position of this peak at 532 nm is not sensitive to the two solvents used such as CH_2Cl_2 (good solvent for polystyrene but a nonsolvent for ionic polyacetylene) and CH_3OH (good solvent for ionic polyacetylene but a nonsolvent for polystyrene). This indicates that in both solvents the PS-PA copolymer is not strongly associated at these low concentrations (3×10^{-5} M). In contrast, the decrease of this peak using water as solvent suggests considerable association of the copolymer in water at the same concentration.

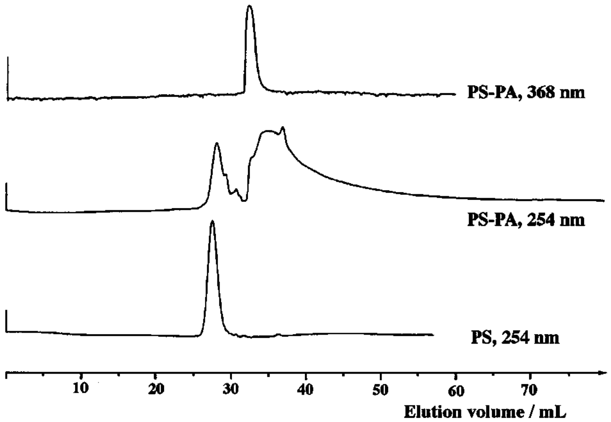


Figure 6. Comparison of GPC (THF, 1.0 mL/min, 500, 10^2, 10^3, 10^4 Å Waters Ultrastyragel columns, ambient temperature) of the styrene block (A) and of the copolymer (A+B) at different detector wavelengths.

Several authors used the Lewis−Calvin equation[16,17] ($\lambda^2{}_{max} = kn$, where n is the conjugation number for low molecular mass polyenes) to estimate the length of the conjugated segment in a polymer,[4,6,7,18] assuming that it is identical with the DP for polyacetylenes. The Lewis−Calvin equation in the case of PS-PA would indicate a DP of ~15 instead of the measured average of 4. It appears therefore that the Lewis−Calvin equation used with some success for conjugated polyenes cannot be applied for this type of strongly amphiphilic block copolymer.

GPC and VPO. As expected, a relatively narrow Gaussian MWD was found for the polystyrene block ($M_w/M_n = 1.16$). However, calculated molecular weight data ($M_n = 720$) disagreed with the ^1H NMR and VPO measurements. (A possible reason is the uncertainty of GPC calibration at these low molecular weights.)

MWD distribution curves were observed at two wavelengths (Figure 6), at 254 nm (where both PS and PA absorb), and at 368 nm. Only the polyacetylene chain absorbs at 368 nm; therefore, this chromatogram proves that the ionic polyacetylene is incorporated into the resulting polymer. (Also, the homopolymer of 2EPyMeTf is insoluble in THF.) Comparison of GPC traces indicated a relatively narrow molecular mass distribution of the ionic blocks in the amphiphilic copolymer, although direct MW determination was impossible because of a very strong adsorption of the ionic segments on the Ultrastyragel packing. This adsorption effect appears to be responsible for the strong tailing of the chromatograms at 254 nm.

Viscosity Measurements. Polystyrene obtained from quenching of the living polystyrene$^-$−Li$^+$ and representing the A-block was characterized by an inherent viscosity at concentration of 1 g/L in acetone of 0.44 dL/g. The PS-PA block copolymer displayed at the same concentration in acetone a lower inherent viscosity of 0.21 dL/g. This value suggests the existence of aggregation of the block copolymer in acetone solution at this concentration.

Thermal Methods. Thermogravimetric data show that there is no weight loss up to 350 °C (total weight loss <1.5%) for PS-PA. However, DSC trace displayed a very broad exotherm starting at 60 °C during the first heating. The intensity of the PS-PA absorption at 532 nm was found to decrease significantly after the DSC run (Figure 7). Both the homopolymer of 2EPyMeTf and the polystyrene A-block are thermally stable up to 300 °C. Since the DSC sample remained soluble, no

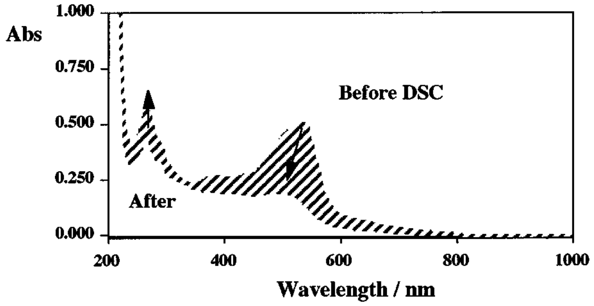


Figure 7. UV−visible spectra of PS-PA before and after DSC run. Shaded area demonstrates intensity changes.

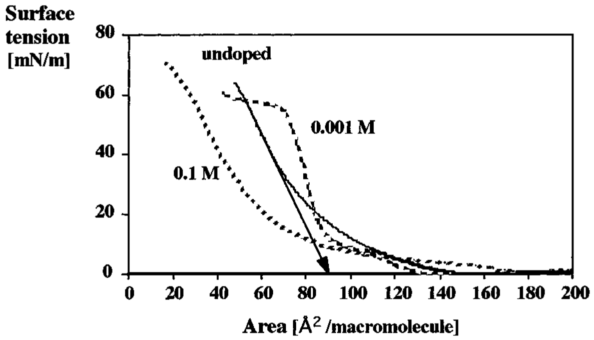


Figure 8. Effect of doping on the occupied area in PS-PA monolayers (using method D-2). Subphases: water and $K[I]_3$ solutions.

cross-linking occurred. The mechanism of this degradation process is not known at present.

Monolayers. The undoped copolymer gave a stable monolayer at the air−water interface with a relatively steep slope (well-defined solid phase) and a high collapse pressure (63 mN/m) as shown by the pressure−area isotherm in Figure 8.

The molecular area calculated from extrapolation of the ascending linear portion of the isotherm to zero pressure gives an unusually high value of 93 Å^2/macromolecule. This suggests that the polyacetylene segments are on the water surface. Modeling by means of molecular (Fischer) models leads to a value of approximately 100 Å^2/macromolecule for the PA sequence.

Dynamic compression−recompression measurements were carried out to determine the mechanical integrity of the monolayers at the air−water interface. A monophasic isotherm was observed in the hysteresis of the monolayer for 6 cycles at a compression rate of 1000 cm^2/30 min. Molecular areas decreased slightly with each cycle indicating a tighter packing of the polymer chains. This hysteresis effect became less with each repeated cycle, indicating the chains are gradually reaching their maximum packing density. This is to be expected for a bulky, rigid polymer system. It is interesting to note that, if the compression rate is slowed to 1000 cm^2/60 min, a biphasic character can be observed in the compression cycle, as given in Figure 9. This may be attributed to allowing sufficient time for the hydrophobic chains in the polymer system to reorient into a more condensed phase.

Isobars of PS-PA at 30 mN/m showed that the monolayer stabilized after 6 h at a final molecular area of 60 Å^2/macromolecule from 93 Å^2/macromolecule. Since the cross-sectional area of a polystyrene chain estimated from models is approximately 64 Å^2, this suggests that at low surface pressures the ionic rigid sequence of the copolymer chain remains primarily on the water surface, but as a result of constant pressure applied over a certain period of time, the PA segments are forced to submerge.

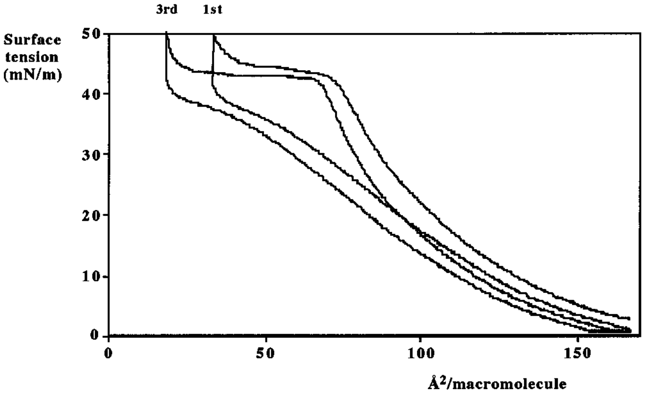


Figure 9. First and third hysteresis of the compression isotherm of PS-PA monolayer. Compression rate: 1000 cm^2/60 min.

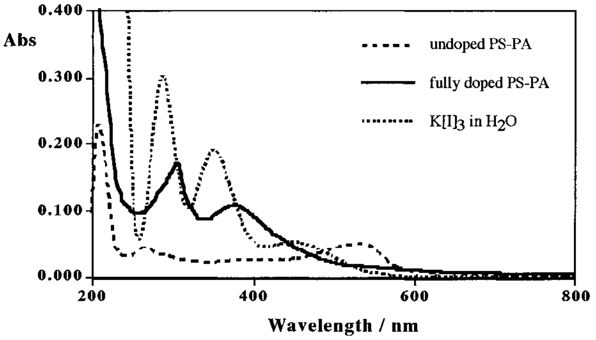


Figure 10. Comparison of UV−visible spectra of the undoped and fully doped PS-PA with the $K[I_3]$ spectrum in MeOH solution.

The effect of iodine doping on PS-PA monolayers was also investigated. In general, increase of the extent of iodine doping resulted in a decrease of the molecular area of the polymer. Using solution doping before spreading (method D-1), contraction of the monolayer was observed when each repeating ionic unit of PS-PA block copolymer was doped by more than 5 equiv of iodine in $CHCl_3$. Using method D-2 (doping during spreading), monolayers prepared over 0.001 M $K[I]_3$ showed little or no decrease in the molecular area while monolayers spread over higher concentrations of $K[I]_3$ subphases exhibited a significant contraction of the monolayer (Figure 8). Comparison of UV−vis spectra of the undoped and doped PS-PA multilayers (Figure 10) showed that the maximum in the visible range had shifted upon doping toward lower wavelengths, and the intensity of the absorption spectra considerably increased. However, ^1H NMR and FT-IR spectra of bulk PS-PA before and after doping were essentially identical. This last observation indicates that only physical interactions take place between the molecules of the dopant and the block copolymer. In the case of a chemical reaction, one would expect both the chemical shifts and the vibrational spectra to change.

Langmuir−Blodgett Multilayers. Undoped and doped L-B multilayers of PS-PA were deposited on various substrates such as glass, silanized glass, quartz, Si(111), and CaF_2 for subsequent characterization. Undoped and doped monolayers of the copolymer were transferred onto the substrates in a Y-type fashion with a deposition ratio of 0.8 during the downward movement (hydrophobic transfer) and of 1.0 during the upward movement (hydrophilic transfer) of the substrate, regardless of the type of substrate.

The number of uniformly transferable layers decreased in the following order: Al > Si > CaF_2 > quartz ~ glass>silanized glass. Multifilm deposition of PS-PA on hydrophilic glass, as observed from the UV−visible spectra, was uniform and reproducible up to 30−40 bilayers for both the undoped and the doped multilayers with similar transfer ratios. Using ellipsometry, a thickness of 65 Å with a refractive index of 1.59 was found for a bilayer of undoped PS-PA. (Predicted length of the fully extended polymer sequences are PA_4 = 11 Å and PS_{12} = 34 Å. Comparison of the experimental and theoretical values indicates either interdigitation of styrene chains or a tilt by 45°.**)** This thickness was found to increase slightly upon doping by method D-1 (doping before spreading) or D-3 (doping after deposition) to 70 Å while the refractive index of the film increased to 1.62.

FT-IR spectrum of the L-B multilayers on CaF_2 showed the presence of trifluoromethanesulfonate counterions, but with a decreased intensity compared to the bulk spectrum of the PS-PA block copolymer. The change of the intensity ratios between the peaks of the aromatic skeletal vibration and the S=O symmetric and unsymmetric stretching indicated a partial exchange of the triflate anions probably with the hydroxide anions of the subphase in the deposited copolymer. Similar exchange of the triflate anions with OH ions can also be observed if we compare the region of S=O vibrations in the FT-IR grazing angle spectrum (GR-FTIR, Figure 11B) to the FT-IR spectrum (Figure 1). These observations confirm the dissociation of the ionic sequence in the monolayer of the copolymer at the air−water interface.

Orientation in the Deposited L-B Multilayers. Deposition of PS-PA copolymer on a silicon wafer gave a transparent film. The color of the L-B multilayers deposited on Si(111) was uniform and changing with the layer thickness and with the angle of light incidence (dark blue to yellow) indicating uniformity of layer thickness.

Absorption spectra of polarized light for PS-PA L-B multilayers indicated only a slight dichroism, i.e., a weak orientation of chromophores within the layers of the undoped copolymer. No orientation of chromophores was found within the iodine doped (method: D-1) multilayers. This suggests that no strong orientation of the ionic polyacetylene sequences does occur within the multilayers.

In contrast, GR-FTIR spectra showed a marked dichroism. With the polarizer perpendicular to the surface of the film, a simple aliphatic resonance can only be seen at 2927 and 2877 cm^{-1} (Figure 11A). We have attributed these absorption peaks to the asymmetric and symmetric methyl valence resonance stretching of the *sec*-butyl end groups of the polystyrene chain. No other possible explanation was found because it is impossible to see the symmetric and asymmetric CH_2 stretching vibrations without observing the aliphatic and aromatic CH valence stretching vibrations. These aromatic and aliphatic vibrations do appear when the polarizer is parallel to the surface of the film and the whole spectrum is then observed (Figure 11B). Consequently, some degree of molecular orientation of the polystyrene sequences in the deposited multilayer does exist while the ionic polyacetylene chains are essentially random.

Polyacetylene sequences in the deposited L-B multilayers of PS-PA become more expanded upon doping and assume a random orientation as evidenced by expanded compression isotherms and absence of dichroism of the UV−visible absorption spectra. The microphase separated and oriented polystyrene chains within the L-B multilayers disorient upon doping; however, their isobutyl end groups still populate the hydrophobic strata of the layers and the external surface of the film itself.

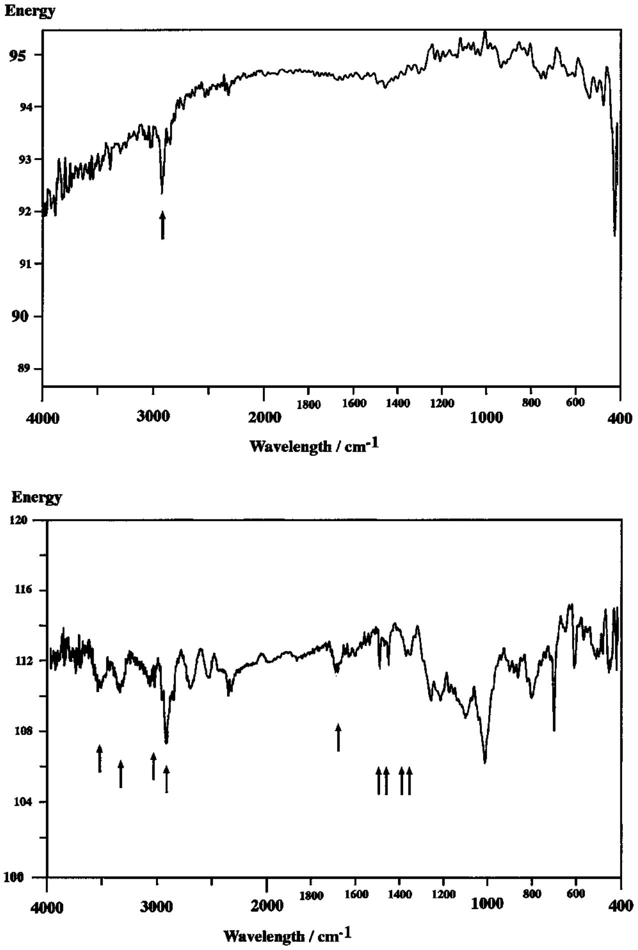


Figure 11. (A) Undoped PS-PA on Al coated glass. 31 bilayers, FT-IR grazing angle measurement with polarizer perpendicular to the plane of the film. IR (cm^{-1}): 2927, 2877. (B) Undoped PS-PA on Al coated glass. 31 bilayers, FT-IR grazing angle measurement with polarizer parallel to the plane of the film. IR (cm^{-1}_: 3555 (polyacetylene backbone =CH-), 3355 (ν_{OH}), 3050 (aromatic ν_{C-H} in PA and PS), 2937, 2877 (aliphatic ν_{CH2} and ν_{CH} in polystyrene), 1506, 1471, 1391 (aromatic skeletal vibrations of PA and PS), 1280, 1260, 1168 (S=O unsymmetric and symmetric stretching in $CF_3SO_3^-$).

Self-Assembly (S-A) Multilayers. UV−visible absorption of alternating S-A multilayers of the undoped block copolymer (on glass, quartz, or CaF_2 substrates) increased with the number of successive immersions. However, when poly(styrenesulfonate) (PSS) was used as the polyanion, the amount of the deposited copolymer decreased progressively to zero after approximately 25 layers. Interestingly, the PS-PA copolymer could be deposited in successive layers without the PSS alternation, i.e., without using a polyanion substrate. This "self-alternation" of PS-PA block copolymer can be easily explained by the strongly amphiphilic and noncompatible nature of the charged PA and the nonpolar PS blocks.

We think that the positively charged PA segments adsorb on the surface of the polar, negatively charged glass when the slide is immersed into the polymer solution first. The surface will be covered then by polystyrene chains. Because of incompatibility of PA and PS, only polystyrene chains can adsorb during the next immersion, leaving polar PA on the surface, which

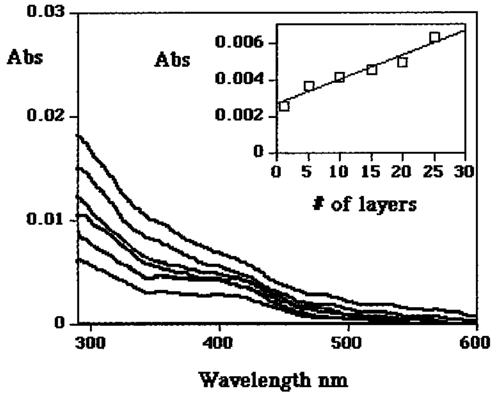


Figure 12. Increase of UV–visible absorbance of deposited self-assembly multilayers of PS-PA on glass substrate without poly(styrenesulfonate) anion. The lines represent subsequent absorbance spectra taken after repeating the deposition procedure 1, 5, 10, 15, 20, and 25 times. Inset: Change of absorbance with the number of of deposited layers at 410 nm.

in turn will adsorb preferentially the PA block, leaving the surface covered with PS, and so on. This leads to an alternation of PS-PA layers. The necessary cohesion between layers is supplied for the polystyrene layers by dispersion forces and for the PA layers by coulombic forces, too. Spectroscopic data in Figure 12 are in direct support of such a multilayer buildup.

In the case of an amphiphilic block copolymer the hydrophilic/hydrophobic character will depend not only on the type of the ionic group, but also on the length of the ionic chain. The ability of PS-PA copolymer to form on different substrates stable monolayers and well-defined multilayers is the consequence of the narrow MWD of both blocks and of a balanced composition of the ionic and hydrophobic segments ($M_{\mathrm{w,PA}} = 1040$, $M_{\mathrm{w,PS}} = 1200$).

Conductivity. In-plane conductivity measurements[13] were carried out on undoped and doped dry PS-PA L-B films. Langmuir–Blodgett films, consisting of three bilayers and fifty bilayers, were deposited on interdigitated electrodes under controlled conditions. The undoped films were found to act as insulators ($k < 10^{-9}$ S/cm). A conductivity of 3×10^{-6}–6×10^{-6} S/cm was found in iodine-doped films prepared by method D-1. Using method D-3, a further increase in conductivity to 2×10^{-4}–6×10^{-4} S/cm was observed. The magnitude of the measured conductivity was of the same order for both the three bilayer and the fifty bilayer films, indicating an insulator–semiconductor "sandwich" structure in these multilayers.

Summary

Living polystyryl anion initiates the polymerization of *N*-methyl-2-ethynylpyridinium triflate and leads to the formation of a novel amphiphilic polystyrene-*block*-poly(*N*-methyl-2-ethynylpyridinium triflate). The molar masses of the individual blocks of the product determined by ^{1}H NMR were typically 1200 and 1040, respectively ($\mathrm{DP_{PSty}} = 12$ and $\mathrm{DP_{PAc}} = 4$). The product was characterized by FT-IR, UV–visible spectroscopy, and ^{13}C and ^{14}N NMR. The formation of blocks confirms the anionic nature of the nucleophile initiated polymerization of *N*-methyl-2-ethynylpyridinium triflate. The resulting amphiphilic block copolymer has an intensive deep red color, and it is soluble in both nonpolar and polar organic solvents. PS-PA can be solubilized in water, and evaporation of water provides a hydrophobic film.

A stable monolayer of PS-PA was formed from chloroform solution at the air–water interface. It was characterized by a compression isotherm with a relatively steep slope and a high collapse pressure. Films of the undoped and iodine-doped copolymer were produced as monolayers, as L-B multilayers, and also by a layer-by-layer self-assembly technique. Doping with iodine induced contraction of the monolayer. Monolayers of PS-PA transferred as Y-type double layers. Good quality L-B films were obtained on hydrophilic glass, quartz, mica, Si(111), Al, and CaF$_2$ substrates. Doping of the deposited multilayers with iodine increased the layer thickness by 10%. Layer-by-layer self-assembly of multilayers of *sec*-butyl-(styrene)$_{12}$-*block*-(2EPyMeTf)$_4$ was achieved on glass using poly(styrenesulfonate) as polyanion in consecutive dippings. More uniform self-assembly was observed without the polyanion.

This work underlines the high propensity of ionic polyacetylenes to form molecular films with possible potential applications in the fields of optoelectronics, polymeric microcapacitors, conductive coatings, and dyes.

The described copolymerization method appears to be a general and easy way to synthesize amphiphilic block copolymers simply by initiating the polymerization of a pyridinium–acetylene salt by an appropriate living anionic system.

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