

Triblock copolyampholytes from 5-(N,N-dimethylamino)isoprene, styrene, and methacrylic acid: Synthesis and solution properties^{*}

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Abstract. ABC triblock copolymers of the type poly[5-(N,N-dimethylamino)isoprene]-*block*-polystyrene-*block*-poly(*tert*-butyl methacrylate) (AiST) were synthesized and hydrolyzed to yield poly[5-(N,N-dimethylamino)isoprene]-*block*-polystyrene-*block*-poly(methacrylic acid) (AiSA) triblock copolyampholytes. Due to a complex solubility behavior the solution properties of these materials had to be investigated in THF/water solvent mixtures. Potentiometric titrations of AiSA triblock copolyampholytes showed two inflection points with the A block being deprotonated prior to the Ai hydrochloride block thus forming a polyzwitterion at the isoelectric point (iep). The aggregation behavior was studied by dynamic light scattering (DLS) and freeze-fracture/transmission electron microscopy (TEM). Large vesicular structures with almost pH-independent radii were observed.

PACS. 61.16.Bg Transmission, reflection and scanning electron microscopy (including EBIC) – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 81.05.Lg Polymers and plastics; rubber; synthetic and natural fibers; organometallic and organic materials

1 Introduction

Amphiphilic block copolymers [1] are an interesting class of material and find applications as stabilizers, emulsifiers, dispersants, foamers, thickeners, compatibilizers, membranes [2], in microencapsulation [3] as well as in oil recovery applications and nanomaterial hybrids [4,5]. Moreover, they are of theoretical relevance for studying principles of macromolecular self-assembly [6–16]. Several studies on the solution behavior of amphiphilic ABC triblock copolymers have been reported. Patrickios *et al.* investigated the solution properties of a system composed of an insoluble, a partial soluble, and a soluble block in water, namely poly(vinyl ethylether), poly(vinyl methylether) and poly(triethylene glycol) [17]. The influence of the block sequence was investigated and it was found that the position of the water soluble block governs the micellization behavior. Kriz *et al.* [18] found core-shell structures for poly(2-ethylhexyl acrylate)-*block*-poly(methyl methacrylate)-*block*-poly(acrylic acid) in mixed solvents of THF and water. While in that system the water-soluble endblock poly(acrylic acid) was the major component, Yu *et al.* [19] studied polystyrene-*block*-poly(methyl methacrylate)-*block*-poly(acrylic acid) with the water insoluble endblock polystyrene being the major component. They used different solvents (dioxane,

THF, or DMF) which were continuously diluted by addition of water and found micelles of different shapes as a function of the water content. Ishizone *et al.* [20] synthesized ABC triblock copolymers containing perfluorinated alkyl methacrylates, *tert*-butyl methacrylate and 2-(trimethylsilyloxy)ethyl methacrylate with various block sequences. The block copolymers then were converted into amphiphilic systems by removing the trimethylsilyl protecting group to give a poly(2-hydroxyethyl methacrylate) block.

Crosslinking of micelles formed by ABC triblock copolymers in solution can lead to nanospheres, which can be further modified to hollow nanospheres in a selective degradation step, as was shown by Liu's group [21]. Also crosslinked micelles with two different faces, so-called Janus Micelles have been reported recently [22]. In this case the spherical polybutadiene (B) domains located at a lamellar interface between polystyrene (S) and poly(methyl methacrylate) (M) of an SBM triblock copolymer were crosslinked in the bulk state. Amphiphilic block copolyampholytes in which two of the blocks possess opposite charges besides a third, hydrophobic block constitute a small and scarcely investigated but highly interesting class within the amphiphilic block copolymer family. Patrickios *et al.* [23–25] studied ABC triblock copolyampholytes consisting of 2-(dimethylamino)ethyl methacrylate, methyl methacrylate/2-phenylethyl methacrylate, respectively, and methacrylic acid. Giebler *et al.* [26] investigated the polyelectrolyte complex formation of triblock copolyampholytes from styrene, vinylpyridine and methacrylic

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acid. As part of our work on block polyampholytes we synthesized poly[5-(*N,N*-dimethylamino)isoprene]-*block*-polystyrene-*block*-poly(methacrylic acid) (AiSA) triblock copolyampholytes to gain a deeper insight into the pH-dependent properties of such materials in solution.

2 Experimental

2.1 Materials

5-(*N,N*-dimethylamino)isoprene (DMAi) was prepared and purified as reported before [27]. Styrene (technical grade; BASF AG) was degassed twice and condensed onto dibutylmagnesium (1 M solution in heptane, p.a., Aldrich) followed by stirring for several hours. The yellow color resulting from slow oligomerization indicates sufficient dryness. *Tert*-butyl methacrylate (tBMA) (technical grade; BASF AG) was degassed three times and condensed onto triethylaluminium (1 M solution in heptane, p.a., Aldrich) where it was stirred until a slight yellowish-green color remained. Toluene (p.a., Merck) was purified by degassing and condensing onto dibutylmagnesium followed by stirring for several hours. THF (p.a., Merck) was degassed twice, then *sec*-butyllithium (1.3 M solution in cyclohexane/hexane, Acros) was added leading to an instantaneous yellow coloring of the solution. THF was regarded as pure as soon as this color had completely disappeared after stirring for several hours. Monomers and solvents were then condensed into glass ampoules for transfer into the reaction vessel. All purification procedures were carried out under N₂ inert atmosphere. *Sec*-butyllithium (1.3 M solution in cyclohexane/hexane, Acros) was used as initiator without further purification.

2.2 Polymerization procedure

Triblock copolymers were synthesized in amounts of 20–30 g. Anionic polymerizations were carried out in a 1000 ml stirred glass reactor (Büchi) with a thermostated cooling jacket under N₂ inert gas atmosphere. The desired amount of DMAi and about 300 ml toluene were added *via* glass ampoule and cooled to –40 °C. The required amount of *sec*-butyllithium was charged *via* syringe through a rubber septum. After 40–50 minutes the polymerization solution was cooled down to –65 °C, about 100 ml of THF were added and after renewed cooling the desired amount of styrene was transferred into the reaction vessel. After 5 to 6 hours the styrene polymerization was found to be complete and the desired amount of tBMA was added. The polymerizations were terminated by addition of 1 ml of degassed methanol after 15–20 minutes. 2,6-Di-*tert*-butyl-*para*-cresol was added as radical stabilizer, then solvent was carefully removed from the polymer solutions until they reached about 1/3 of their original volume. This solution was precipitated in a 10-fold excess of methanol/water yielding colorless powdery polymer in all cases. 2–3 precipitation cycles were carried out in methanol/water after dissolution of the polymer in THF.

2.3 Hydrolysis

AiSA triblock copolyampholytes were obtained by hydrolysis of the poly(*tert*-butyl methacrylate) block of AiST triblock copolymers with hydrochloric acid. To this end, 3 g AiST triblock copolymer were dissolved in 100 ml 1,4-dioxane (p.a., Merck) and heated to 80 °C. Then 5 ml of a 10% aqueous hydrochloric acid (p.a., Merck) were added turning the solution turbid instantaneously. After a reaction time of 6–8 hours the solution was cooled down, the polymer was precipitated in cold *n*-hexane, washed several times and dried under vacuum. AiSA triblock copolyampholytes obtained this way proved to be highly hygroscopic.

2.4 Characterization of AiST triblock copolymers

¹H- and ¹³C-NMR spectra were obtained using a Bruker AC 250 spectrometer (250 MHz for ¹H-nuclei, 62.9 MHz for ¹³C-nuclei). The CDCl₃ solutions had concentrations between 25–70 mg/ml for ¹H- and 120–250 mg/ml for ¹³C-spectra. All NMR measurements were carried out at 298 K using tetramethylsilane as internal standard.

Size exclusion chromatography (SEC) was performed on a WATERS system with refractive index and UV (254 nm) detection. Since poly[5-(*N,N*-dimethylamino)isoprene] adsorbs to regular polystyrene gel column materials we used columns filled with polyester gel (GR-AM columns from Polymer Standards Service, PSS) with pore sizes of 100, 3 × 10³ and 10⁴ Å and a particle size of 10 μm. As elution solvent THF was used, the flow rate being 1 ml/min in all cases. The setup was calibrated with polystyrene standards.

Membrane osmometry was carried out on an Osmomat 090 from Gonotec at 35 °C in toluene using a membrane of regenerated cellulose with a cut off molecular weight of 20 kg/mol.

2.5 Characterization of AiSA triblock copolymers

IR spectra were recorded on a Bruker Equinox 55/S FTIR spectrometer. Spectra of unhydrolyzed samples were obtained by solvent evaporation of 1% chloroform solutions on NaCl or KCl windows. Water-soluble samples were obtained from 1% THF/water solution on CaF₂ windows. Completely insoluble samples were ground and spectra were recorded after preparation of KBr pellets.

Potentiometric titrations were carried out with a digital titration apparatus DIGI 610 from WTW. All titrations were performed in THF/water (2/5 weight/weight) at 25 °C using polymer solutions with a concentration of 0.015 weight-% and titrating with aqueous 0.01N sodium hydroxide.

Dynamic light scattering was performed using a Spectra-Physics Stabilite TM 2060 IIs Kr laser (647.1 nm), ALV goniometer Sp-86 and an ALV 3000 digital correlator at room temperature. All investigated solutions were

Table 1. Molecular characteristics of the AiSA triblock copolyampholytes.

block copolymer ^(a)	x_{Ai} ^(b)	x_{S} ^(b)	x_{A} ^(b)	w_{Ai} ^(c)	w_{S} ^(c)	w_{A} ^(c)	$M_{\text{n}}/\text{kg mol}^{-1}$ ^(d)
Ai ₁₄ S ₆₃ A ₂₃	0.14	0.59	0.27	0.16	0.65	0.19	52
Ai ₃₁ S ₂₃ A ₄₆	0.30	0.26	0.44	0.35	0.25	0.40	69
Ai ₄₂ S ₂₃ A ₃₅	0.37	0.26	0.37	0.46	0.24	0.30	39
Ai ₅₆ S ₂₃ A ₂₁	0.53	0.21	0.26	0.60	0.22	0.18	51
Ai ₅₇ S ₁₁ A ₃₂	0.51	0.21	0.28	0.61	0.12	0.27	37

^(a) Molar composition from ¹H-NMR spectra of the AiST precursor block copolymers. ^(b) Molar fractions of the hydrolyzed block copolymers calculated from elemental analysis. ^(c) Weight fractions of the hydrolyzed block copolymers calculated from elemental analysis. ^(d) Molecular weight calculated from membrane osmometry and ¹H-NMR of the AiST precursor block copolymers.

filtered three times using 0.2 μm filters (Millipore); the concentration was 0.1 g/l in all cases.

Freeze-fracture investigations were carried out by shock-freezing a drop of the solution in liquid propane at 90 K between two copper supports. The fracture of the sample was accomplished using a Balzers BAF 400 Freeze Etching System (sandwich technique) at 90 K under vacuum. Onto the fracture area a 2 nm layer of platinum was vapor-deposited at an angle of 45° for electron contrast and a 20 nm layer of carbon was vapor-deposited at an angle of 90° for support. The so prepared replicas were washed from the copper support with water and transferred onto a copper grid for TEM investigation. Transmission electron microscopy (TEM) was performed with a Zeiss CEM 902 transmission electron microscope with an accelerating voltage of 80 kV. The micrographs were taken in the bright field modus. The nomenclature used for the triblock copolyampholytes is as follows: Ai_{*x*}S_{*y*}A_{*z*}^{*n*}, where *x*, *y*, *z* describe the molar fractions of the blocks in the triblock copolyampholyte and *n* corresponds to the total molecular weight in kg/mol taken at the isoelectric point.

3 Hydrolysis of AiST triblock copolymers to AiSA triblock copolyampholytes

The hydrolysis of the poly(*tert*-butyl methacrylate) block of AiST triblock copolymers easily yields the corresponding AiSA triblock copolymers with a poly(methacrylic acid) polyelectrolyte block. From the several methods of hydrolysis of poly(*tert*-butyl methacrylate) found in the literature, only the hydrolysis in dioxane with hydrochloric acid led to high conversions [26,28]. Synthetic routes working in organic solvents like methylene chloride [29] or toluene [28,30,31] suffer from premature precipitation of the polymer due to the poor solubility of the hydrophilic poly(methacrylic acid) in these solvents.

The reaction of AiST triblock copolymers with 10% HCl in dioxane yields the hydrochloride of the amine functionality of the Ai block besides hydrolyzing the T block. The degree of conversion can easily be determined by FTIR spectroscopy as shown in Figure 1.

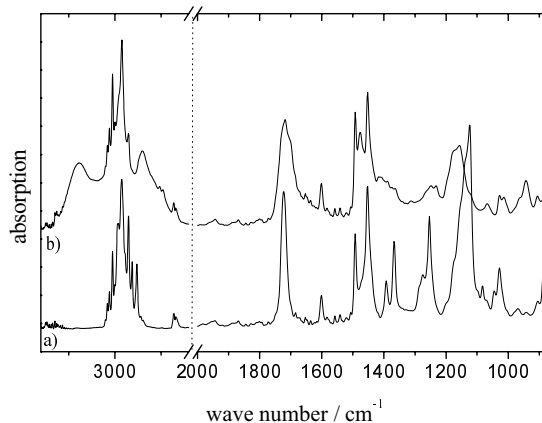


Fig. 1. Hydrolysis of Ai₁₄S₆₃T₂₃⁵²: FTIR spectra before (a) and after (b) hydrolysis.

The C=O absorption band at 1724 cm^{-1} is broadened and shifted to 1718 cm^{-1} and the carbonyl absorption band of the dimeric acid is observed at 1700 cm^{-1} . Between 3500 cm^{-1} and 2400 cm^{-1} the typical broad bands of the O–H valence vibration are obtained. Hydrolysis also leads to a shift of C–O valence vibrations from 1254 cm^{-1} and 1138 cm^{-1} to 1248 cm^{-1} and 1162 cm^{-1} , respectively. The disappearance of the *tert*-butyl double absorption band at 1394 cm^{-1} and 1368 cm^{-1} is by far most characteristic and can be taken for quantitative analysis. Hydrolysis under these conditions was found to be complete after 6–8 hours.

Because they possess a basic (Ai) as well as an acidic (A) end block the functional groups of which are protonated or deprotonated dependent on the pH of the solution AiSA triblock copolymers can be classified as triblock copolyampholytes.

Table 1 lists the investigated AiSA triblock copolyampholytes. Elemental analyses confirm degrees of hydrolysis greater than 91% in all cases. Molecular weights refer to the chemical structure at the isoelectric point without taking into account the counterions.

A determination of the degree of hydrolysis *via* ¹H-NMR spectroscopy turned out to be impossible. As these polyampholytes aggregate in solution the integration of ¹H-NMR signals did not yield the true compositions.

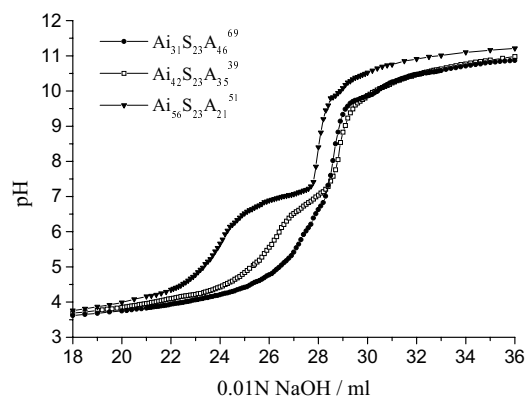


Fig. 2. Potentiometric titrations of three different triblock copolyampholytes.

4 Solution properties of AiSA triblock copolyampholytes

Investigations of the pH-dependent solution properties of the AiSA triblock copolyampholytes in solution had to be performed in solvent mixtures due to a complex solubility behavior of these materials. The hydrochloride of poly[5-(N,N-dimethylamino)isoprene] and the sodium salt of poly(methacrylic acid) are only soluble in water; poly(methacrylic acid) is best soluble in lower alcohols whereas poly[5-(N,N-dimethylamino)isoprene] as well as polystyrene dissolve in organic solvents like THF, toluene, chloroform, or cyclohexane. For the investigation of the AiSA solution behavior THF/water mixtures proved most valuable. In all cases viscous solutions were obtained, the strongly differing solubilities of the three components thereby leading to aggregate formation. Often only highly dilute solutions could be prepared (≤ 0.1 wt.-%); solutions under neutral and basic conditions were generally more difficult to realize than under acidic conditions. Dialysis of THF/water solutions to get pure aqueous solutions proved impossible as the AiSA triblock copolyampholytes precipitated from the dialyzed solutions after several days.

Potentiometric titration curves of AiSA triblock copolyampholytes in THF/water (2/5 weight/weight) are shown in Figure 2 for three copolymers possessing identical mole fractions of hydrophobic polystyrene but different amounts of acidic and basic end blocks.

For all investigated AiSA triblock copolyampholytes two inflection points at $\text{pH} \approx 5.5$ and 9 were detected corresponding to the deprotonation of carbon acid and amine hydrochloride functionalities, respectively. The relative breadths of the buffer plateaus allow an unequivocal assignment of the deprotonation order. $\text{Ai}_{56}\text{S}_{23}\text{A}_{21}^{51}$ with a molar ratio of amine/acid of 56/21 shows the narrower plateau at $3 < \text{pH} < 4$ and the broader one at $\text{pH} = 7$ whereas $\text{Ai}_{31}\text{S}_{23}\text{A}_{46}^{69}$ with a ratio of amine/acid of 31/46 shows inverse plateau widths. From this it follows that during titration with sodium hydroxide poly(methacrylic acid) is deprotonated prior to poly[5-(N,N-dimethylamino)isoprene hydrochloride].

Figure 3 shows the pH-dependent structures of AiSA triblock copolyampholytes.

The same order of deprotonation was observed in copolymers of poly(methacrylic acid) and poly[2-(diethylamino)ethyl methacrylate] [32–35]. In copolymers of poly[(meth)acrylic acid] and poly(2/4-vinylpyridine), on the other hand, deprotonation of the pyridine hydrochloride takes place prior to deprotonation of the carboxyl functionalities [28,36–39] because in comparison to carboxylic functionalities amine hydrochlorides are the weaker acids and vinylpyridinium hydrochlorides the stronger ones. At the isoelectric point (iep) in the first case polyelectrolytes are obtained which possess the highest amount of charges at that pH resulting in a polyelectrolyte complex (PEC) formed mainly by strong electrostatic interactions. In the second case polymers with a minimal net charge built the PEC which is stabilized by hydrophobic interactions often accompanied by hydrogen bonding [28,40–44].

As both poly(methacrylic acid) and poly[5-(N,N-dimethylamino)isoprene hydrochloride] are weak acids their buffer zones are comparatively broad (3.5–4.2 and 6.5–7.3). In contrast to low molecular weight electrolytes the corresponding pK_a values cannot be calculated from these values in a straightforward manner because for polyelectrolytes they are found to depend on the degree of dissociation. As the charge density on the polymer backbone increases during the titration of poly(methacrylic acid) with sodium hydroxide, deprotonation gets more difficult in the course of the titration and the pK_a value increases [45,46].

FTIR spectroscopy investigations (films cast from solution on CaF_2 windows or bulk samples as KBr pellets) confirm the formation of polyelectrolytes at the iep. Figure 4 shows FTIR spectra of $\text{Ai}_{42}\text{S}_{23}\text{A}_{35}^{39}$ obtained at various pH. The acidic sample was taken as it was obtained from hydrolysis after reprecipitation and severe drying. The samples at the iep and at basic conditions were obtained by redissolving the acidic sample and titrating with sodium hydroxide to the desired pH. Especially the basic sample was washed thoroughly to remove all residual sodium chloride.

Under acidic conditions characteristic absorptions of poly(methacrylic acid) are observed, in particular the broad O–H valence band at 3400 cm^{-1} , the C=O valence band of the dimeric acid at 1700 cm^{-1} and of the free acid at 1718 cm^{-1} as well as the C–O valence bands at 1248 and 1162 cm^{-1} [47–50]. The amine functionalities are protonated as can be seen from the N–H absorption band at about 2700 cm^{-1} . The N–H deformation band can be expected around 1717 cm^{-1} but is superimposed by the strong carbonyl band.

At the iep the antisymmetric OC–O valence band caused by the sodium salt of poly(methacrylic acid) is seen at 1575 cm^{-1} and the symmetric OC–O valence band at 1336 cm^{-1} . The deformation band of the ammonium salt is slightly shifted and now appears at 1713 cm^{-1} .

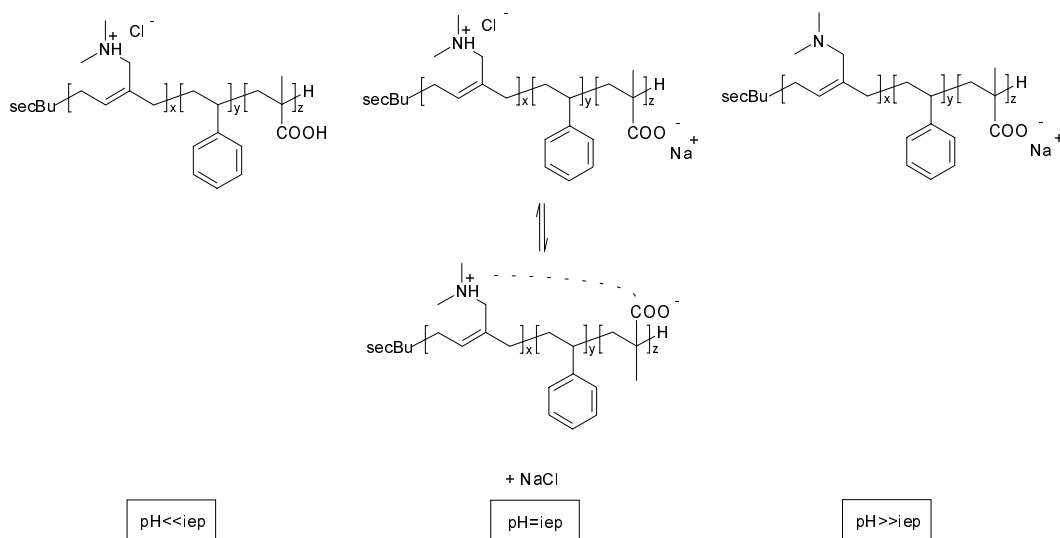


Fig. 3. pH dependence of the functional groups of the triblock copolyampholytes.

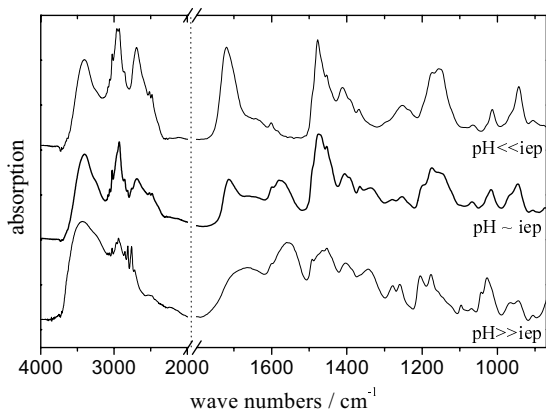


Fig. 4. FTIR spectra of $Ai_{42}S_{23}A_{35}^{39}$ at three different pH.

Under basic conditions the NCH_3 and NCH_2 valence bands of the deprotonated amine appear at 2760 and 2811 cm^{-1} , respectively.

The aggregation behavior of $Ai_{57}S_{11}A_{32}^{37}$ triblock copolyampholyte in THF/water (2/5 weight/weight) solution was investigated by performing pH-dependent dynamic light scattering (DLS) and freeze-fracture/TEM. This system was chosen because it showed the best solubility in a water-rich solvent due to the short polystyrene block. Figure 5 shows the autocorrelation functions of 0.1 wt.-% solutions at different pH. The obtained diffusion coefficients D were converted into the corresponding sphere-equivalent hydrodynamic radii, R_h , via the Stokes-Einstein law, $R_h = kT/(6\pi\eta D)$, where η is the solvent viscosity [51].

The logarithmic plots of the autocorrelation functions are almost linear at all examined pH values so that essentially one defined particle type with low polydispersity can be assumed.

The hydrodynamic radius of these species is found to vary with pH and ranges from 260 to 120 nm showing that highly aggregated structures were obtained. Figure 6

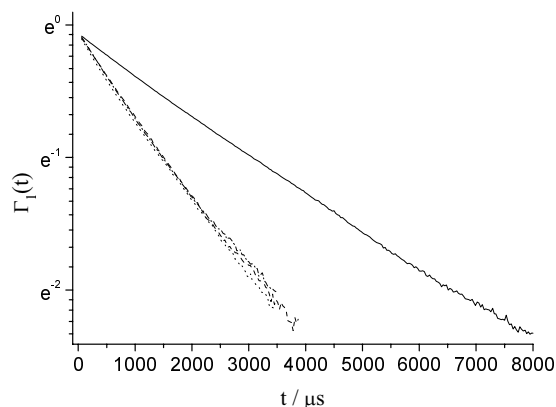


Fig. 5. Autocorrelation functions of $Ai_{57}S_{11}A_{32}^{37}$ at different pH values: (—) pH = 4: $D = 9.5 \times 10^{-9}\text{ cm}^2/\text{s}$; $R_h = 260\text{ nm}$; (---) pH = 7: $D = 1.8 \times 10^{-8}\text{ cm}^2/\text{s}$; $R_h = 136\text{ nm}$; (····) pH = 9: $D = 2.1 \times 10^{-8}\text{ cm}^2/\text{s}$; $R_h = 120\text{ nm}$; (-·-·-) pH = 10.5: $D = 2.0 \times 10^{-8}\text{ cm}^2/\text{s}$; $R_h = 124\text{ nm}$.

shows the titration curve of $Ai_{57}S_{11}A_{32}^{37}$ together with the hydrodynamic radii at different pH values as determined by DLS.

The decrease in the hydrodynamic radius coincides with the first inflection point of the potentiometric titration; a further significantly smaller decrease might be assumed at the second inflection point. In order to ensure the stability of these aggregates in solution, DLS control measurements were performed during the following days; all results were found to be reproducible.

In order to visualize the true shape of these aggregates freeze fracture TEM was carried out. Figure 7 shows bright-field TEM micrographs of freeze fractures of the triblock copolyampholyte $Ai_{57}S_{11}A_{32}^{37}$ in 0.1 wt.-% THF/water (2/5 weight/weight) solution at pH = 4 and 10. At pH = 4 spherical structures with a maximal radius of approximately 120 nm are observed. As the contour length of the polymer chain is only 140 nm (all-trans

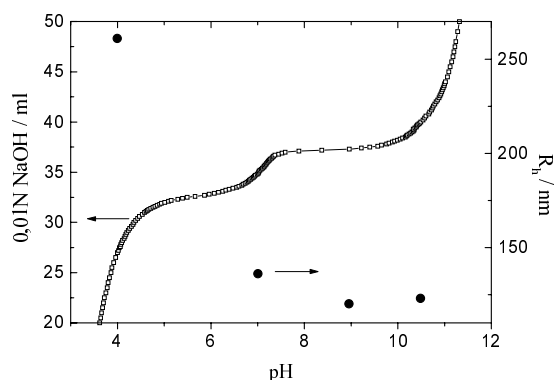
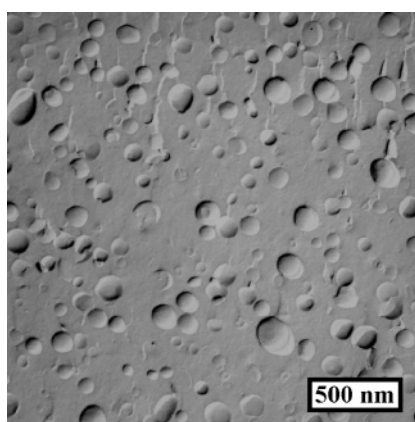
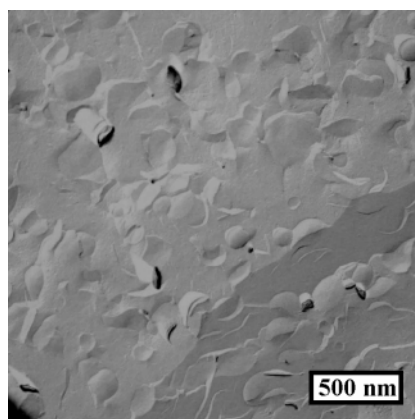


Fig. 6. Titration curve of $\text{Ai}_{57}\text{S}_{11}\text{A}_{32}^{37}$ and dependence of the hydrodynamic radii on pH.



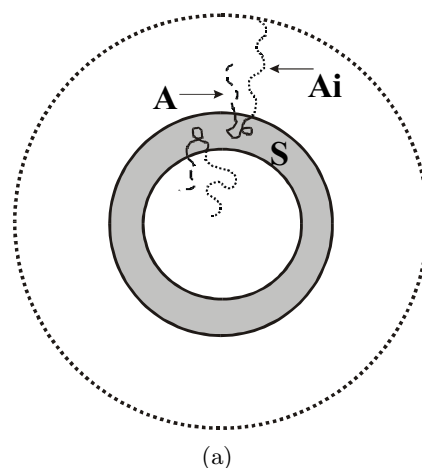
(a)



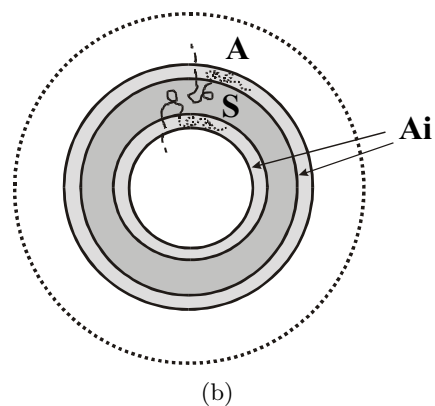
(b)

Fig. 7. Bright-field TEM micrographs of freeze-fractures of $\text{Ai}_{57}\text{S}_{11}\text{A}_{32}^{37}$ at (a) pH = 4, (b) pH = 10.

conformation assumed) these spherical aggregates most probably do not represent simple spherical micelles. More likely vesicles are formed. At pH = 10 also spherical aggregates are found which appear to be less uniform than the ones formed under acidic conditions. Some tendency towards a lamellar superstructure seems possible from the micrograph in Figure 7b although a poorer quality of the



(a)



(b)

Fig. 8. Possible vesicular structures at pH = 4 (a) and 10 (b).

freeze-fracture might also account for that impression. The maximal radius was determined to be about 100 nm under basic conditions.

Suggestions of possible vesicular structures under the two pH conditions are shown in Figure 8. Under acidic conditions both end blocks are soluble and the insoluble shell is formed by the polystyrene block. On the contrary, at basic conditions both polystyrene and PAi are insoluble and only the deprotonated PA-block keeps the vesicular structure in solution.

As the solutions at pH other than 4 were prepared from the corresponding acidic solutions by adding sodium hydroxide solution until the desired pH was reached it is not surprising that the vesicle dimensions are not found to depend on the pH of the solution to a great extent. The glassy polystyrene center-block defines the pH-independent diameter of the inner vesicle shell. At higher pH values the PAi precipitates on the PS shell (Fig. 8b). The only way the diameter of the vesicle can vary with pH is by a change in the conformation of the soluble end block(s) due to changing of the charge density.

Although the determination of the maximal vesicle radius from the freeze-fracture micrographs is bound to contain a certain error, the discrepancy between DLS and freeze-fracture/TEM results at pH = 4 (260 nm and

120 nm, respectively) surely is too large to be explicable by a measuring error. The results at pH = 10 (DLS: 120 nm, freeze-fracture: 100 nm) on the contrary can be taken as identical within a certain error in both methods.

An explanation for the strongly differing results obtained by DLS and freeze-fracture/TEM at pH = 4 could be the weaker ionic strength of the solution in this case as compared to the solutions with larger pH. The lower ionic strength leads to a stronger stretching of the charged A₁ block at pH = 4, because the positive charges along the chain are less shielded due to a larger distance to the chlorine anions in the corona of the vesicle. The latter may diffuse further away because of osmotic pressure. The optical density (or refractive index) in this corona differs from the rest of the solution and thus it is the contrast of this larger structure which is detected by light scattering. In comparison, the freeze-fracture border lines follow most likely along the S shell, which does not change its size with pH.

5 Conclusions

ABC triblock copolyampholytes (poly[5-(N,N-dimethylamino)isoprene]-*block*-polystyrene-*block*-poly(methacrylic acid)) with a basic and an acidic end block separated by a neutral midblock have been synthesized. The titration experiments show different buffer zones the breadths of which depend on the relative amounts of the basic and acidic end blocks. Due to the very different solubility properties of the blocks aggregates form in solution, *i.e.* microphase separation occurs already in solution. In one example the aggregates formed under acidic and basic conditions were characterized by DLS and freeze-fracture/TEM and strong indications for the formation of rather narrow disperse vesicular structures were found. The size of the insoluble polystyrene shell seems to be stable with respect to pH changes, while the conformation of the corona chains (poly[5-(N,N-dimethylamino)isoprene] and poly(methacrylic acid)) are strongly dependent on the pH value, as indicated by DLS.

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