Poly(*tert*-butyl methacrylate-*b*-styrene-*b*-4-vinylpyridine) Triblock Copolymers: Synthesis, Interactions, and Self-Assembly

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ABSTRACT: Using atom transfer radical polymerization (ATRP), poly(*tert*-butyl methacrylate-*b*-styrene-*b*-4-vinylpyridine) or P*t*BMA-*b*-PS-*b*-P4VP linear triblock copolymers were synthesized. Different homopolymer and diblock copolymer macroinitiators were used for different block copolymerizations. For a selected triblock copolymer the self-assembly was studied with transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and thermal analysis. Indications were found for a core−shell hexagonal ordering of coaxial cylinders with P4VP cylinders separated from the P*t*BMA matrix phase by a PS shell layer. To further support this, the interaction parameter between styrene and *t*BMA was investigated by a random copolymer blend miscibility study on blends of P(S-*co*-*t*BMA) random copolymers with PS and found to satisfy $0.08 < \chi_{S,tBMA} < 0.10$.

Introduction

Well-defined homogeneously dispersed nanostructures with long-range order have a huge potential in the field of nanotechnology. It is, therefore, no surprise that the number of investigations into the synthesis and morphological behavior of block copolymers continues to be large.[1–9] Such systems in either bulk or solution spontaneously self-assemble into various nano-ordered structures. For diblock copolymers, cylindrical, lamellar, spherical, and bicontinuous gyroid morphologies are the most commonly found microstructures, whereas for triblock copolymers many more structures were discovered.[2,10] A careful balance between the different parameters involved, such as the block sequence, the block volume fractions, the interaction parameters, the chain architecture, and even the casting solvent,[11,12] determines the morphology obtained. Several applications involve the presence of nanoporous structures that can be obtained in various ways from the self-assembled systems. Especially in the area of functional membranes, long-range homogeneous porosity is a requirement.[13,14]

Here we report on the synthesis of a class of ABC triblock copolymers that has the specific property that after self-assembly of ABC triblock-based supramolecules the A and C block may be derivatized to obtain systems containing two different types of charged pores. The copolymer selected is poly(*tert*-butyl methacrylate)-*block*-polystyrene-*block*-poly(4-vinylpyridine) (P*t*BMA-*b*-PS-*b*-P4VP). The possibility to use this kind of triblock copolymers as building blocks for such applications rests on the following observations. First, it is well-known that the addition of low molecular weight amphiphiles, notably pentadecylphenol (PDP), results in a noncovalent side-chain architecture of the P4VP block due to hydrogen bonding between the phenol and pyridine group. The principal advantage in relation to membrane applications is the fact that these amphiphiles can be simply washed away afterward, thus rendering a nanoporous P4VP phase.[15–18] After quarternization at the nitrogen atom of the pyridine moiety, positive charges may be obtained within these domains. Besides these positively charged nanopores, negatively charged ones may be constructed from the *t*BMA phase. As reported,[19–21] the bulky *tert*-butyl ester groups can be easily hydrolyzed into methacrylic acid groups via reaction in the gaseous phase. This results in an additional porous phase, which in turn can be negatively charged by washing with a basic solution, at which point a polymethacrylic base is obtained. Using these relatively mild derivatizing methods, we may thus create so-called charge-mosaic membranes from suitably self-assembled P*t*BMA-*b*-PS-*b*-P4VP(PDP) systems. A number of groups used block copolymers for this purpose in the past, but the procedure of derivatizing the block copolymers usually required rigorous methods such as (γ-ray-assisted) cross-linking and sulfonation.[22,23] The derivatization procedure proposed is illustrated in Scheme 1.

In the present work we focus on two issues. First, we present in some detail the synthesis of P*t*BMA-*b*-PS-*b*-P4VP triblock copolymers via atom transfer radical polymerization (see Scheme 2),[24,25] which is a relatively undemanding technique with respect to purification of the materials used and the polymerization procedure compared to, for example, anionic polymerization.[26,27]

The second issue concerns the self-assembly in these triblock copolymer systems. It has been reported that the interaction between P*t*BMA and PS is only very slightly unfavorable. Using neutron reflectivity data to determine the interfacial width between these homopolymers a value of $\chi_{tBMA,S} \cong 0.025$ was reported.[28] The same value was also found from the solubility parameter approach using estimated values of the solubility parameters.[29] Such a small value would require a relatively large molar mass for the PS and P*t*BMA blocks ($M \gg 20$ kg/mol) to obtain a segregated state. However, it is well-known that different experimental techniques actually address different interaction parameters.[30,31] In the past random copolymer blend miscibility studies have been frequently used to determine interaction parameters,[32,33] and recently it was shown to produce values that agreed quite well with the phase behavior observed in the corresponding diblock copolymers.[34,35] Therefore, P(S-*co*-*t*BMA) random copolymers were synthesized to determine the interaction between these components from a PS/P(S-*co*-*t*BMA) random copolymer blend miscibility study. The results show that the actual unfavorable interaction is considerably larger of the order of $\chi_{tBMA,S} \cong 0.08-0.1$ Hence, block molecular weights of the order of 10 kg/mol should be enough to obtain microphase separation between styrene (St) and *t*-BMA in the case of block copolymers. That this seems indeed to be the case is corroborated by the self-assembly study of one particular P*t*BMA-

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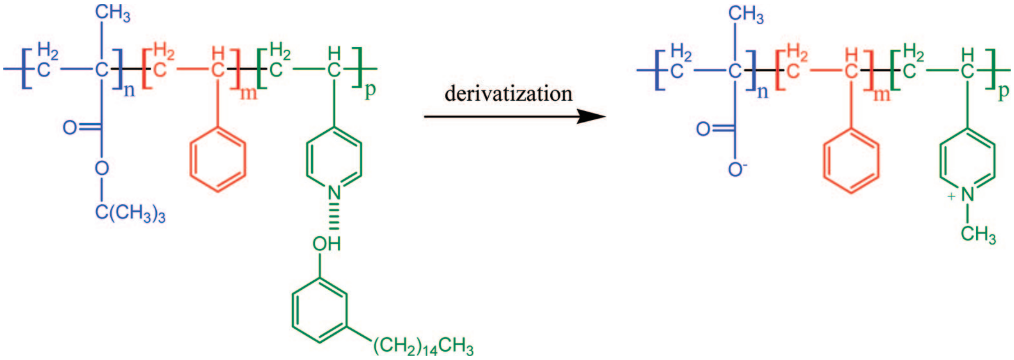
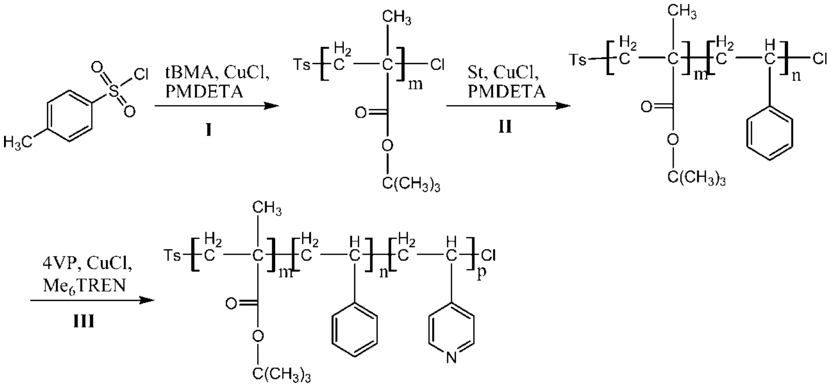
Scheme 1. Two Oppositely Charged Blocks after Derivatization of P*t*BMA-*b*-PS-*b*-P4VP(PDP)



Scheme 2. Synthesis Route of the P*t*BMA-*b*-PS-*b*-P4VP Triblock Copolymer



b-PS-*b*-P4VP triblock copolymer system using TEM, SAXS, and DSC.

Experimental Section

Materials. Styrene (St, ACROS, 99%), 4-vinylpyridine (4VP, Aldrich, 95%), and *tert*-butyl methacrylate (*t*BMA, Aldrich, 98%) were dried over calcium hydride, distilled under reduced pressure, and stored under nitrogen at 6 °C. Toluene (LABORATORY-SCAN, 99.5%), acetone (LABORATORY-SCAN, 99.5%), and dimethylformamide (DMF, Acros, >99%), were distilled and stored under nitrogen at room temperature. Tetrahydrofuran (THF, Acros, 99+%) was used as received.

CuCl (Aldrich, 97%), CuBr (ACROS, 98%), and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were used as received. Tris[(2-dimethylamino)ethyl]amine (Me_6TREN) was synthesized according to literature[36] and purified by multiple short path distillations.

Methyl-2-bromopropionate (MBrP, ACROS, 99%), *p*-toluenesulfonyl chloride (*p*TsCl, Aldrich, 97%), α,α-azobis(isobutyronitrile) (AIBN, Fluka, ≥98%), and hydroquinone (Merck, >99%) were used as received. Aluminum oxide 90 active basic and silica gel (239−400 mesh) were obtained from Merck and used without purification. DOWEX MARATHON MSC (H) ion-exchange resin (Aldrich) was used for copper removal from the triblock copolymers. All polymerizations were performed under an atmosphere of dry nitrogen.

The polystyrene sample used for the copolymer blend miscibility study was obtained from Tosoh Corp. (M_n = 2800 g/mol, PDI = 1.05).

Copolymer blends were made by dissolving both polymers in chloroform in a 1:1 weight ratio and drop-casting the solution directly into a DSC pan (dry sample weight about 10 mg).

Characterization. Gel permeation chromatography (GPC) measurements were performed in DMF with 0.01 M LiBr at 70 °C (1 mL/min) on a Waters 600 Powerline system, equipped with two columns (PL-gel 5 μ, 30 cm mixed-C, Polymer Laboratories) and a Waters 410 differential refractometer. Measurements in THF were performed at 25 °C (1 mL/min) on a Spectra-Physics AS 1000 LC-system applying universal calibration using a Viscotek H-502 viscometer and a Shodex RI-71 refractive index detector and Trisec software (Viscotek). PLGel 5 μ 30 cm mixed-C columns (Polymer Laboratories) were used. The polymer samples were calibrated using narrow disperse polystyrene standards (Polymer Laboratories).

Bright-field transmission electron microscopy (TEM) was performed on a JEOL-1200EX transmission electron microscope operating at an accelerating voltage of 90 kV. Block copolymer films were cast from chloroform. The solvent was slowly evaporated, and the sample was annealed for a day in a saturated chloroform vapor. A piece of film was then embedded in epoxy resin that was cured overnight at 40 °C. The sample was subsequently microtomed to a thickness of about 70 nm using a Leica Ultracut UCT-ultramicrotome and a Diatome diamond knife at room temperature. The microtomed sections were floated on water and subsequently placed on copper grids. To obtain contrast during TEM, the samples were stained with iodine (3 h) or RuO_4 (1 h).

Small-angle X-ray scattering (SAXS) measurements were performed at the Dutch-Belgian Beamline (DUBBLE) at ESRF in Grenoble, France. The sample−detector distance was about 7.3 m, while the X-ray wavelength was 1.24 Å (E = 10 keV). The scattering vector q is defined as $q = (4\pi/\lambda) \sin \theta$, where θ is half of the scattering angle.[37]

^1H NMR spectra in $CDCl_3$ were recorded on a 300 MHz Varian VXR operating at room temperature.

Temperature-modulated differential scanning calorimetry (M-DSC) was performed with a TA Instruments Q1000. A modulated mode with heating/cooling rate of 1 °C/min, an amplitude of 0.5 °C, and a period of 60 s was used.

Random Copolymerization of S and *t*BMA. Random copolymers of styrene and *t*BMA were synthesized by free radical polymerization. A 250 mL three-necked, round-bottom flask was degassed, and via a septum, styrene, *t*BMA, and toluene were added

Table 1. ATRP of *t*BMA with PMDETA as the Ligand and [I]:[CuX]:[L] = 1:1:1

entry	initiator	catalyst	[M]/[I]	solvent (vol %)	T (°C)	time (min)	yield (%)	$\overline{M}_n$ (g/mol)^a	PDI
1	*p*TsCl	CuCl	45	50 (toluene)	90	360	50	12500	1.08
2	MBrP	CuBr and CuBr$_2$^{b}	35	14 (acetone)/43 (toluene)	60	310	72	13600	1.09
3	*p*TsCl	CuCl	30	50 (toluene)	60	960	68	9100	1.04
4	*p*TsCl	CuCl	60	50 (toluene)	90	300	72	8700	1.04
5	*p*TsCl	CuCl	30	50 (toluene)	60	960	62	6400	1.08

^{a} Measured by GPC, calibrated against PS standards. ^{b} [CuBr]:[CuBr$_2$] = 20:1.

using a syringe. The total amount of monomers was about 12 g. The mixture was stirred and subjected to three freeze−thaw cycles, after which it was placed in an oil bath thermostated at 80 °C. In a 50 mL three-necked flask, about 40 mg of AIBN was dissolved in 5 mL of toluene, and the mixture was also subjected to three freeze−thaw cycles. Then the initiator solution was added to the polymerization flask using a syringe. The polymerization was carried out for 2−3 h, making sure that the monomer conversion was never above 10% to avoid composition drift in the resulting copolymer. The polymerization was terminated by adding hydroquinone. Toluene was evaporated, and the polymers were precipitated twice in a 10-fold excess of methanol. All polymers were then dried for a few days at 40 °C in vacuo. The monomer ratios were calculated from the ^{1}H NMR spectra using the aromatic protons of styrene.

Homopolymerization of *t*BMA (I). A typical procedure to prepare a chlorine end-functionalized P*t*BMA is as follows. A dried 100 mL three-necked flask was degassed by evacuating and backfilling with nitrogen three times. To this flask was added 0.455 g (4.60 mmol) of CuCl, and it was evacuated and backfilled another three times. Now 22.5 mL (0.14 mol) of *t*BMA, 20 mL of toluene, and 0.97 mL (4.63 mmol) of PMDETA were added using degassed syringes. The mixture was stirred for at least 20 min to let the complex form, having a cloudy green color. After the complex formation, the flask was put into a thermostated oil bath at 60 °C. In a 50 mL three-necked flask, 0.881 g (4.62 mmol) of *p*TsCl was dissolved in 10 mL of toluene. This initiator solution was added to the 100 mL flask, and the polymerization was carried out for 16 h. Next, the mixture was dissolved in THF and passed through a basic alumina column to remove copper species. The solvents were evaporated, and the polymer was precipitated in a 10-fold excess of cold hexane (−60 to −50 °C). The polymer was isolated by filtration over a pore size 3 glass filter. Finally, the polymer was dried in a vacuum oven overnight. GPC analysis revealed that $\overline{M}_n$ = 6400 g/mol and PDI = $\overline{M}_w/\overline{M}_n$ = 1.08.

Polymerizations were performed at different temperatures, for different periods of time. Also, CuBr and CuBr$_2$ were used, together with MBrP as initiator, to obtain bromine end-functionalized P*t*BMA. With these homopolymers, the use of halogen exchange is possible[38] for the next block copolymerization.

Diblock Copolymerization (II). The P*t*BMA-*b*-PS diblock copolymerizations were performed using the same setup as the homopolymerizations. To give a representative example, the following quantities of substances were taken for a certain diblock copolymerization: 1.26 g ($\overline{M}_n$ = 6400, 1.97 × 10^{-4} mol) of chlorine-terminated P*t*BMA (I), 17.3 mg (1.75 × 10^{-4} mol) of CuCl, 38 μL (1.88 × 10^{-4} mol) of PMDETA, and 2.8 mL (24.4 mmol) of St. The polymerization was carried out for 190 min at 100 °C. Next, the mixture was dissolved in THF and passed through a silica column to remove copper species. The polymer was precipitated in a 10-fold excess of methanol and was isolated by filtration over a pore size 3 glass filter. After drying, GPC analysis revealed that $\overline{M}_n$ = 14 200 g/mol and PDI = 1.20. The polymerizations were performed at different temperatures, for different periods of time, and with or without solvent.

Triblock Copolymerization (III). The P*t*BMA-*b*-PS-*b*-P4VP triblock copolymerizations were performed using the same setup as the homo- and diblock polymerizations. To give a representative example, the following quantities of substances were taken for a certain triblock copolymerization: 0.399 g ($\overline{M}_n$ = 14 200 g/mol, 2.81 × 10^{-5} mol) of chlorine-terminated P*t*BMA-*b*-PS (II), 3.0 mg (3.0 × 10^{-5} mol) of CuCl, 0.5 mL of 4-vinylpyridine (4.68 mmol), 7.0 μL (2.9 × 10^{-5} mol) of Me$_6$TREN[39] in 4 mL of DMF. The polymerization was carried out for 330 min at 80 °C. The mixture was the dissolved in chloroform and passed through a silica column to remove copper species. After precipitation in a 10-fold excess of cold hexane (0 °C), the polymer was isolated and dried. GPC analysis revealed that $\overline{M}_n$ = 19 300 g/mol and PDI = 1.18.

The copper content was reduced by dissolving the polymer in chloroform and stirring overnight with an ion-exchange resin and reprecipitation in cold hexane. After this, the triblock copolymer has a copper content of about 30 ppm as opposed to 330 ppm before purification, as shown by elemental analysis.

Determination of Molecular Weights. The molecular weight data presented are obtained using both GPC and ^{1}H NMR measurements. It is known that molecular weight determinations using GPC are rarely correct for block copolymers. This is of course due to the fact that GPC is based on the difference in elution times versus the hydrodynamic radius of the polymer; it is well-known that block copolymers behave differently in solution than monodisperse linear homopolymers. For the P*t*BMA homopolymers the molecular weights could be determined directly using GPC. Furthermore, the molecular weights of the P*t*BMA-*b*-PS diblock copolymers were estimated using GPC in both THF and DMF, which were in agreement. For block copolymers containing 4-vinylpyridine, however, it was evident that the molecular weights could not be estimated using GPC. For our triblock copolymers, the data obtained from GPC in DMF gave an overestimation of the actual molecular weight values by at least a factor 2. From ^{1}H NMR, the relative fractions of 4VP and St may be easily calculated, using the different aromatic proton signals for 4VP and St.

Results and Discussion

We start with the synthesis of the P*t*BMA-*b*-PS-*b*-P4VP triblock copolymers following the synthesis route presented in Scheme 2.

Homopoly(*tert*-butyl methacrylate) (I). Different P*t*BMA homopolymers were synthesized with molecular weights in the range 4.4−13.6 kg/mol. Table 1 lists a number of representative examples. It is clear that the *p*TsCl/CuCl/PMDETA system results in well-defined polymers with low polydispersities.[40] When applying a MBrP/CuBr/PMDETA system in toluene/acetone with a small amount of Cu[II] to accelerate deactivation, a good control over the polymerization was obtained as well. Using a more polar solvent, in this case adding acetone, has a positive effect on the control of the polymerization, as was already shown by Krishnan et al.[41] The molecular weights obtained are significantly higher than may be expected on the basis of the yield and [M]/[I]. This can be explained by the fact that the initiator efficiency in the case of tosyl chloride and PMDETA is never 100%, as was shown by Gurr.[42]

Diblock Copolymers (II). Using P*t*BMA macroinitiators, diblock copolymers of P*t*BMA-*b*-PS were synthesized. Table 2 shows that these block copolymers are well-defined (PDI ≅ 1.2) and can be synthesized in a range of molecular weights. Several different ratios of [I]:[CuCl]:[PMDETA] were tried, but it could be shown that a ratio of 1:1:1 is the most effective. In all cases, a certain amount of P*t*BMA was not chain extended, while in theory, methacrylates should be able to initiate the polymerization of styrene.[25] This problem in theory may be overcome by using the halogen exchange technique, as the use

Table 2. Diblock Copolymerization of P*t*BMA-*b*-PS Initiated with Different P*t*BMA-Cl Macroinitiators ([I]:[CuCl]:[PMDETA] = 1:1:1)

						weight fractions			
entry	[M]/[I]	solvent (%)	T (°C)	time (min)	yield (%)	P*t*BMA	PS	$\overline{M}_n$ (g/mol)[a]	PDI
1	59	50 (toluene)	80	360	41	0.51	0.49	12 500	1.20
2	138	bulk	100	190	29	0.50	0.50	14 200	1.20
3	90	50 (toluene)	100	270	44	0.49	0.51	17 700	1.22
4	95	50 (toluene)	60	270	20	0.48	0.52	19 100	1.23
5	94	50 (toluene)	60	270	22	0.44	0.56	20 700	1.24
6	86	50 (DMF)	100	290	41	0.39	0.61	22 300	1.25
7	64	50 (toluene)	100	360	55	0.38	0.62	16 900	1.25

[a] Measured by GPC, calibrated against PS standards.

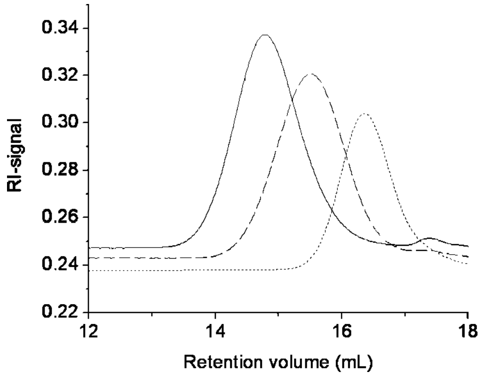


Figure 1. GPC traces of P*t*BMA-*b*-PS-*b*-P4VP (solid line) and its precursors P*t*BMA (dotted line) and P*t*BMA-*b*-PS (dashed line); $\overline{M}_n$ = 18 400, PDI = 1.19.

of a bromine end-capped homopolymer would ensure faster and thus more effective initiation. However, experiments with bromine end-capped P*t*BMA showed no improvement. The percentage of unextended homopolymer after a certain period of time at the same temperature was comparable to the percentage without the use of the halogen exchange technique. This may be explained by slow consumption of the macroinitiator, which was shown before for the polymerization of styrene with a methacrylate macroinitiator.[43] However, any residual homopoly(*t*BMA) was easily washed away by precipitation in methanol, so that there was no problem for the next polymerization step. This can also be seen in Figure 1, which clearly shows that there is no homopolymer left in the diblock copolymer after precipitation.

Triblock Copolymers (III). With the use of the synthesized diblock copolymers as macroinitiators, triblock copolymers of P*t*BMA-*b*-PS-*b*-P4VP were synthesized using a CuCl/Me$_6$TREN catalyst system. Selected results are shown in Table 3. In Figure 1, a representative GPC diagram for successive polymerizations of a triblock copolymer is shown. It is clear that monomodal, narrow distributions are obtained for the three polymerizations and that no precursors are left in the precipitated polymers. For high fractions of 4VP, the polydispersity increases somewhat, probably due to solvability problems such as micellization during polymerization and interactions with the GPC column. This is a known phenomenon for amphiphilic triblock copolymers.[44]

Interactions and Self-Assembly. It is well-known that besides the copolymer composition the relative values of the three different χ parameters involved is an additional important factor for the type of self-assembled structure of triblock copolymers formed.[45–47] The first question to be answered is whether the block molecular weights are large enough to result in phase separation between all three species involved. For the P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer systems under investigation this is particularly relevant given the small value of $\chi_{S,tBMA} \cong 0.025$ reported for the interaction between P*t*BMA and PS based on neutron reflectivity data[28] as well as solubility parameter estimates.[29] If true, this would imply that in the triblock copolymer systems synthesized no phase separation between the styrene and *tert*-butyl methacrylate blocks should be expected since the blocks have molecular weights of the order of 10 000 g/mol. However, it is well-known that different experiments probe different interaction parameters.[30] A striking example is given in ref 31, where the determination of the Flory−Huggins interaction parameter between styrene and 4-vinylpyridine from a variety of observations was discussed, including micelle spacing in microphase-separated PS-*b*-P4VP diblocks, contact angle measurements of droplets of PS on a thin P4VP film, and the PS/P4VP interfacial width. The values obtained were 7.5, 3.5, and 1.4 as well as a lower bound of 1.0. A subsequent random copolymer miscibility study on blends of PS with P(S-*co*-4VP) random copolymers led to $0.30 < \chi_{S,4VP} < 0.35$.[34] This number was confirmed by a small-angle neutron scattering study on PS-*b*-P4VP diblocks,[35] thereby demonstrating that data obtained from random copolymer blend miscibility studies allow a much more reliable prediction of microphase separation in the corresponding block copolymer systems. Therefore, we decided to perform a similar random copolymer miscibility study to determine $\chi_{S,tBMA}$. Table 4 summarizes the properties of the different P(S-*co*-*t*BMA) random copolymers synthesized for this purpose.

We notice that, except for the copolymer with the largest *t*BMA fraction, all copolymers have a glass transition temperature around 100 °C, which is very close to the glass transition temperature of homopolymer polystyrene with a molar mass of 10 000 g/mol or higher. For this reason a PS sample of a molar mass of $\overline{M}_n = 2800$ g/mol, with $T_g \cong 70$ °C, was selected for the PS/P(S-*co*-*t*BMA) copolymer blend miscibility study. Figure 2 shows a series of DSC curves for four different 50/50 wt % PS/P(S-*co*-*t*BMA) blends. It demonstrates that PS is miscible with the copolymer with a weight fraction of 55.5% *t*BMA (one T_g), whereas phase separation occurs in a mixture with the copolymer containing 62.3% tBMA (two T_gs). Given the relatively low molar mass of PS, 50/50 wt % is most likely not the critical blend composition. This is not relevant for the observed immiscibility but could in principle affect the conclusion of miscibility reached for the 55.5 wt % *t*BMA copolymer blend system. Experiments with different blend compositions, however, showed this not to be the case. The effective χ parameter for a P(A)/P(A$_x$-*co*-B$_{1-x}$) random copolymer blend is related to the χ_{AB} by[48]

$$\chi = (1 - x)^2 \chi_{AB} \tag{1}$$

Phase separation occurs for[49]

$$\chi > (1/\sqrt{N_{w,1}} + 1/\sqrt{N_{w,2}})^2/2 \tag{2}$$

where $N_{w,1}$ denotes the weight-average chain length expressed as the number of appropriately selected segments. Using these expressions, it follows from the observed phase separation for the 62.3 wt % *t*BMA copolymer blend system that $\chi_{S,tBMA} > 0.08$. Note that this number is based on taking styrene (St) as the segment and taking equal densities for St and *t*BMA.

Table 3. Triblock Copolymerization of P*t*BMA-*b*-PS-*b*-P4VP in DMF with CuCl/Me$_6$TREN as the Catalyst System

						weight fractions				
entry	[M]/[I]	solvent (%)	T (°C)	time (min)	yield (%)	PtBMA	PS	P4VP	$\overline{M_n}$ (g/mol)[a]	PDI
1	150	89	100	240	24	0.40	0.53	0.07	15 800	1.17
2	170	89	80	330	27	0.40	0.49	0.11	16 000	1.18
3	80	89	100	240	62	0.33	0.54	0.13	19 500	1.23
4	100	93	100	270	29	0.36	0.48	0.16	17 400	1.16
5	400	80	100	280	25	0.27	0.49	0.24	23 000	1.24
6	170	89	80	330	43	0.33	0.41	0.26	19 300	1.18
7	450	89	60	1020	10	0.42	0.30	0.28	27 400	1.20
8	80	91	60	330	51	0.20	0.36	0.44	31 800	1.24

[a] $\overline{M_n}$ of the P4VP block was calculated on the basis of ^{1}H NMR and the value of $\overline{M_n}$ of the diblock precursor.

Table 4. Characteristics of the P(S-*co*-*t*BuMA) Random Copolymers

entry	fraction *t*BMA (wt %)	fraction St (wt %)	T_g (°C)	$\overline{M_n}$ (kg/mol)	PDI
1	10.7	89.3	99	23.9	1.58
2	16.0	84.0	100	28.4	1.57
3	28.2	71.8	98	25.6	1.56
4	38.7	61.3	98	23.7	1.43
5	49.0	51.0	101	27.6	1.36
6	52.6	47.4	100	27.7	1.42
7	55.5	44.5	100	28.1	1.36
8	62.3	37.7	103	32.2	1.35
9	78.7	21.3	107	43.8	1.34

Likewise, the observed miscibility for the 55.5 wt % *t*BMA copolymer provides an upperbound of 0.1. Hence, from the random copolymer blend miscibility study we conclude

$$0.08 < \chi_{S,tBMA} < 0.10 \qquad (3)$$

Since all DSC scans were taken with a scanning rate of 1 °C/min, from room temperature up to 140 °C, and the second scan is used to judge miscibility, the behavior observed is characteristic for the temperature range 100−140 °C. Therefore, inequality (3) is expected to hold for this temperature interval.

On the basis of $0.08 < \chi_{S,tBMA} < 0.10$, we should expect microphase separation between the PS and P*t*BMA blocks, at least for some of the P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer systems synthesized. To verify this, the self-assembly of one particular triblock copolymer system, entry 7 from Table 3, with a total number-averaged molecular weight of 27 400 g/mol and a block molecular weight ratio PS:P*t*BMA:P4VP = 0.42:0.30:0.28, was investigated with SAXS, TEM, and thermal analysis.

Figure 3 presents the SAXS data showing scattering peaks at a ratio of 1:$\sqrt{4}$:$\sqrt{7}$, indicative for a hexagonally ordered cylindrical structure. The absence of the $\sqrt{3}q^*$ scattering peak is presumably due to the form factor scattering. Because the electron density difference between PS and P*t*BMA is very small,[29] SAXS merely reveals the contrast between P4VP and the rest of the system. Hence, we may conclude that P4VP is present in the form of hexagonally ordered cylinders. From the value of the first-order peak $q^* = 0.20$ nm^{-1}, the characteristic (10) distance is calculated to be 31.4 nm.

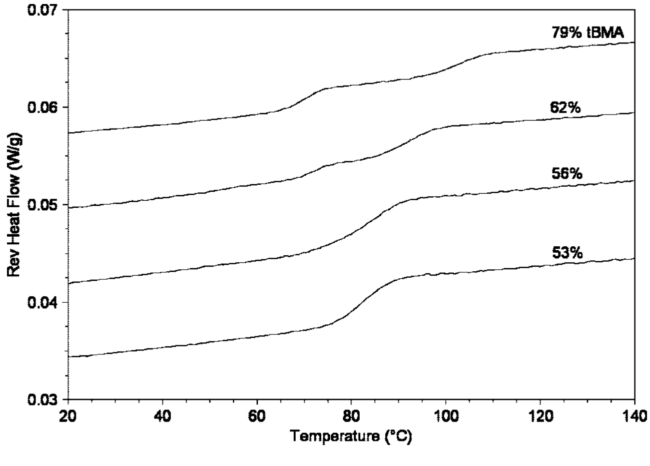


Figure 2. Reversible heat flow curves for blends of PS ($\overline{M_n}$ = 2800 g/mol, PDI = 1.05) with four different P(S-*co*-*t*BMA) random copolymers.

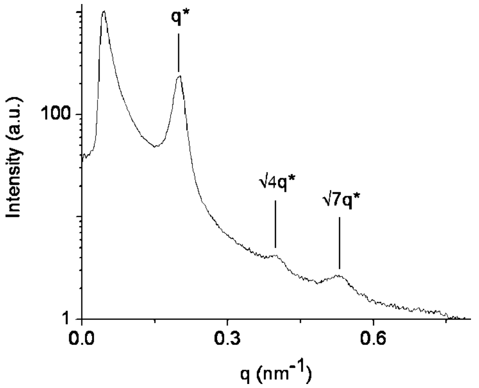


Figure 3. SAXS intensity profile for a P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer ($\overline{M_n}$ = 27 400 g/mol, $f_{tBMA} = 0.42$, $f_{St} = 0.30$, $f_{4VP} = 0.28$).

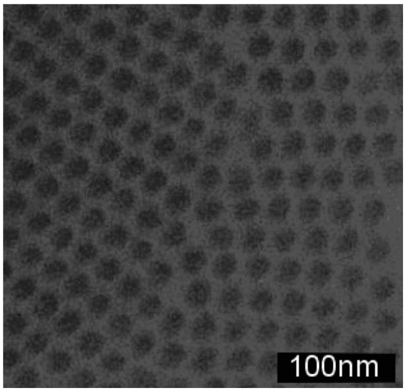


Figure 4. Bright-field TEM image of P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer ($\overline{M_n}$ = 27 400 g/mol, $f_{tBMA} = 0.42$, $f_{St} = 0.30$, $f_{4VP} = 0.28$) stained with I$_2$.

Figures 4 and 5 show the TEM results for this triblock copolymer stained with iodine and RuO$_4$, respectively. After I$_2$ staining the P4VP phase appears dark, and the hexagonally ordered P4VP cylinders can be easily recognized. The distance (10) between the cylinder planes satisfies 23 ± 2 nm, which is considerably smaller than the value found from SAXS. This is most likely due to the fact that the P*t*BMA matrix shrinks very fast under the electron beam in the vacuum of the electron microscope. Figure 5 shows the TEM image for the RuO$_4$-stained system. Because of this staining agent, the PS and P4VP phases are expected to appear dark and gray, respectively. The figure indicates a possible hexagonally ordered P4VP−PS core−shell cylindrical structure within a P*t*BMA matrix, i.e., a

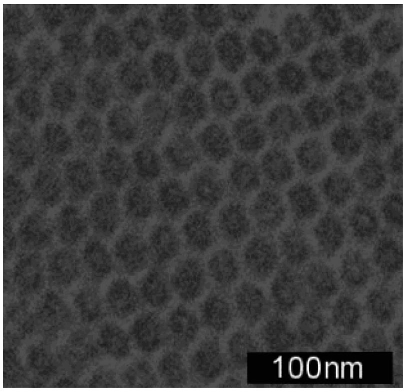


Figure 5. Bright field TEM image of P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer ($\overline{M_n}$ = 27 400, $f_{tBMA} = 0.42$, $f_{St} = 0.30$, $f_{4VP} = 0.28$) stained with RuO_4.

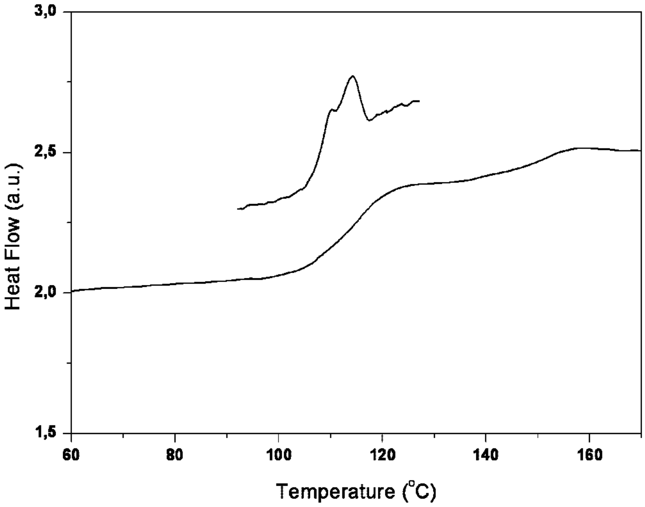


Figure 6. DSC scan of P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer ($\overline{M_n}$ = 27 400 g/mol, $f_{tBMA} = 0.42$, $f_{St} = 0.30$, $f_{4VP} = 0.28$). Inset shows the two enthalpy recovery peaks after annealing for 32 days at 90 °C.

so-called coaxial cylinder phase.[45] In particular, we note that the average cylinder diameter increases from 17 ± 2 nm in the iodine-stained sample to 20 ± 2 nm in the RuO_4-stained sample.

To further support the presence of three microphases, a thermal analysis study of this P*t*BMA-*b*-PS-*b*-P4VP triblock copolymer system was performed. Figure 6 shows a characteristic DSC scan, showing what appears to be two T_g's: one at ca. 110 °C and one at 150 °C. The latter corresponds to the P4VP phase, whereas the former is due to both PS ($T_g \cong 100$ °C) and P*t*BMA ($T_g \cong 120$ °C). To demonstrate that it really corresponds to two nonresolved T_g's rather than to a single mix T_g, we thermally annealed the system at 90 °C for 32 days. The physical aging that has occurred is subsequently recovered during a DSC scan in the form of an enthalpy relaxation peak. As Figure 6 demonstrates, actually two enthalpy recovery peaks are observed, a clear signal for the presence of two phase-separated phases.[34,50,51]

Concluding Remarks

In summary, the synthesis of P*t*BMA-*b*-PS-*b*-P4VP triblock copolymers using ATRP was performed successfully. With a variety of experimental variables the three successive polymerizations were investigated, and for every polymerization, suitable procedures were established. This resulted in a series of low-polydispersity triblock copolymers (PDI ≅ 1.2) with different molecular weights and compositions. From a PS/P(S-*co*-*t*BMA) random copolymer blend miscibility study the interaction parameter between S and *t*BMA was determined to satisfy $0.08 < \chi_{S,tBMA} < 0.10$. This order of magnitude indicates that at least for some of the P*t*BMA-*b*-PS-*b*-P4VP triblock copolymers synthesized we should expect microphase separation between PS and P*t*BMA to occur. Even though the precise value of $\chi_{tBMA,4VP}$ is not known yet, there is no doubt that P4VP will microphase separate from either component. The analysis of a specific triblock copolymer gave strong indications that microphase separation between the three species involved indeed occurred and that a P4VP−PS core−shell cylindrical morphology was formed. The fact that the P*t*BMA and P4VP phases are separated from each other by the PS phase indicates that these polymers might be suitable candidates for the desired charge-mosaic membrane application.

In future work we will study the self-assembly in these triblock copolymer systems in more detail. PDP will have to be added to the system so that nanoporous charge-mosaic membranes may be prepared along the lines discussed in the Introduction. Of course, this requires a further study into the self-assembly of P*t*BMA-*b*-PS-*b*-P4VP(PDP) supramolecules. Since the amount of PDP may be varied and thus not necessarily has to be very large, we feel confident that self-assembled systems may be obtained from the triblock copolymers synthesized with the P4VP(PDP) domains separated from P*t*BMA domains by PS domains. The latter being a first requirement for the charge-mosaic membrane preparation envisioned.

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