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ORIGINAL PAPER

Polystyrene-based self-aggregating polymers based on UPy units

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Abstract The synthesis and characterization of a series of polystyrene (PS)-based copolymers, bearing 2-ureido-4[*1H*]-pyrimidinone (UPy) units pendant from the polymer backbone, is reported. The PS-based copolymers are efficiently synthesized by RAFT-mediated free radical polymerization performed on styrene and protected 4-vinylbenzylamine, and post-modification with suitable UPy-derived isocyanates to give the target polymers. Analysis of the samples in solution reveals that the polymer chains aggregate to give organic nanoparticles of discrete and uniform dimensions, whose direct visualization when deposited on surfaces can be achieved using AFM.

Keywords Nanoparticles · Supramolecular structures · Polystyrene
Reversible addition fragmentation chain transfer (RAFT) ·
Atomic force microscopy (AFM)

Introduction

The use of hydrogen bonding interactions for the self-assembly of dynamic materials, showing controlled response to external stimuli, is of great current interest [1, 2]. Several examples of supramolecular polymers obtained through

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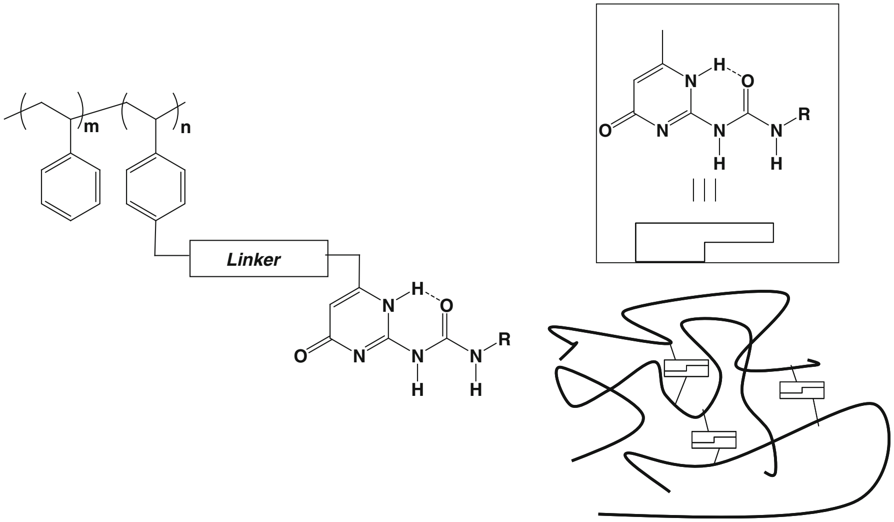

Fig. 1 Schematic representation of self-aggregating UPy PS-based polymers used in this study

hydrogen bonding have been recently reported, using a variety of complementary or self-complementary hydrogen bonding units [3–6]. One of the peculiar features of these dynamic systems is that the aggregation/disaggregation behaviour is mediated by *concentration or dilution of polymer samples*; furthermore, the viscosity and the degree of polymerization increase with concentration. The unit 2-ureido-4[*1H*]-pyrimidinone (UPy) strongly self-associates in solution by means of cleverly designed quadruple hydrogen bonding interactions ($K_a > 10^8$ in toluene at 25 °C) [7, 8]. These units have been successfully placed at the end of oligomeric and polymeric backbones, to form telechelic supramolecular polymers [9, 10]. More recently, UPy self-associating units were introduced as pendant arms onto linear covalent macromolecular backbones. Both polymethacrylates and polyborbornenes have been developed as backbones, and it has been demonstrated that the aggregation of UPy units affords well-defined single chain nanoparticles [11–14].

Solution phase polymeric supports or tags are frequently used in organic synthesis; they are homogeneous in the reaction mixture, overcoming the limitations of solid phase supports, and can be removed and recycled by precipitation/extraction upon the use of an external input.[1,2] Being active in the area of polystyrene (PS)-based supports [17–21], we reasoned that linear PS-based macromolecules functionalized with pendant UPy units could undergo, upon careful structural optimization, [22–24] a change in their aggregation (and possibly solubility and then precipitation) induced

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[1] Most commonly this input is the use of a non-solvent, inducing precipitation and recovery of the support (for example, diethyl ether for PEG-based linear supports, or alcohols for PS-based ones) [15].

[2] Innovative concepts have been proposed in this area, involving the use of an external input for inducing precipitation; for example, photoswitchable organic molecules ("precipitons"), in which the light-induced E/Z isomerization occurring in suitably designed functionalities activates the precipitation phenomena, have been reported [16].

by concentrating a solution of such supports (Fig. 1). In other words, simple solvent removal by evaporation could initiate precipitation of the support, without the need of the addition of the non-solvent.

In this article, we report on the synthesis and characterization of self-aggregating PS platforms containing UPy units, obtained through post-modification from well-defined, narrowly dispersed, linear PS-based macromolecules.

Experimental part

General methods

All commercially available compounds were used as received. THF (CaH_2) and CH_2Cl_2 (CaH_2) were dried and distilled before use. Compounds 4-vinylbenzylamine [25],[3]] 4-[(tert-butoxycarbonyl)amino]methyl]styrene **1** [27], cumyl dithiobenzoate **3** [28], benzyl dithiobenzoate **4** [29] and isocyanate **6** [11] were prepared according to literature procedures. Flash chromatography was carried out using silica gel (0.040–0.063 µm). Infrared spectra were recorded on a FT-IR spectrophotometer using potassium bromide with a diffuse reflectance accessory. ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on 200 or 300 MHz instruments with the solvent residual proton signal or tetramethylsilane (TMS) as a standard.

SEC measurements for copolymers **2** and **5**

Samples obtained after the purification procedures, diluted with stabilized THF, were pre-filtered using 0.45 µm polytetrafluoroethylene (PTFE) filters and then injected. Size-exclusion chromatography (SEC) was carried out on a Waters system equipped with a DRI detector. Low polydispersity polystyrene standards (Fluka) were used for the calibration curve and the mobile phase was tetrahydrofuran (1 mL/min, 40 °C) stabilized with 5 % 2,6-di-*t*-butyl-4-methylphenol (BHT). A bank of two universal columns (Styragel 4E and 5E) in series was used.

SEC-MALS measurements for self-aggregating systems **7** and **8**

Sample solutions in pure $CHCl_3$ or $CHCl_3 + 0.3$ % CH_3COOH solvents were filtered using 0.20 µm PTFE filters prior to injection. The molecular weight distribution (MWD) was characterized by a SEC system equipped with two online detectors: (1) multi-angle laser light scattering (MALS), (2) differential refractometer (DRI) used as concentration detector. The SEC system consisted of: Alliance 2695 separation module from Waters (Milford, MA, USA), columns oven, MALS and a Waters 2414 DRI. The running SEC conditions were the following: two PLgel Mixed C columns, chloroform as mobile phase, 0.6 mL/min of flow rate and 35 °C. The MALS photometer uses a vertically polarized He–Ne laser ($\lambda = 632.8$ nm) and

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[3] An alternative procedure based on nucleophilic substitution (NH_3 in MeOH) on 4-vinylbenzyl chloride as the substrate was much poorer in terms of yields [26].

simultaneously measures the intensity of the scattered light at 16 angles ranging in chloroform from 19.2° to 138.3°. The calibration constant was calculated using toluene as standard assuming a Rayleigh factor of $1.406 \cdot 10^{-5}$ cm^{-1}. The angular normalization was performed by measuring the scattering intensity of a narrow PS standards ($M_p = 10.3$ kg/mol, $M_w/M_n = 1.03$, $R_g = 2.6$ nm) in the mobile phase, assumed to act as an isotropic scatterer. It is well known that the online MALS detector measures, for each polymeric fraction eluted from the columns, the molecular weight and, when the angular dependence of the scattered light is experimentally measurable, also the molecular size, generally known as radius of gyration (R_g). The SEC-MALS system was described in detail elsewhere [30, 31]. The refractive index increment of samples with respect to the solvent (dn/dc) at 25 °C was assumed identical to PS in $CHCl_3$ pure solvent: $dn/dc = 0.161$ mL/g.

Polymer synthesis. General procedure for the free radical polymerization of monomer **1** and styrene

The monomers and the initiator (AIBN, 2 mol% vs. total monomer) were dissolved in toluene (at a total monomer concentration of 0.5 M). The solutions were deoxygenated by bubbling N_2 for 30 min, and then heated under magnetic stirring in a temperature-controlled oil bath at 70 °C for 48 h. The solvent was then removed in vacuo, the remaining solid was dissolved in the minimum amount of CH_2Cl_2, filtered if necessary using 0.45 µm PTFE filters, and the solution was added dropwise to the non-solvent (20 vol). The purified, precipitated polymer sample was filtered and dried.

*Polymer **2a***

From **1** (0.5 g, 2.14 mmol) and styrene (4.27 g, 40.7 mmol). Precipitated from EtOH (3.55 g, 74 %). ^{1}H-NMR (200 MHz, $CDCl_3$) $\delta = 7.4$–6.2 (broad; aryl), 2.1–1.0 (broad; –CH– and $-CH_2-$ polymer chain, $-C(CH_3)_3$). IR (cm^{-1}) = 3412, 2921, 1943, 1874, 1808, 1755, 1686, 1594, 1485, 1446, 757, 696.

*Polymer **2b***

From **1** (0.34 g, 1.41 mmol) and styrene (1.34 g, 12.7 mmol). Precipitated from EtOH (1.03 g, 62 %). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.2$ (bm, aromatic), 128.8–127.3 (bm, aromatic), 126.2–125.4 (bm, aromatic), 85.1 (s, $-\underline{C}(CH_3)_3$), 46.2–40.6 (bm, CH and CH_2 polymer chain), 40.3 (bs, CH and CH_2 polymer chain), 28.4–26.4 (bm, $-C(\underline{C}H_3)_3$).

General procedure for the RAFT-controlled polymerization of monomers **1** and styrene (polymers **5**)

The monomers (0.5 M total concentration in toluene), the initiator (AIBN, mol% vs. monomer as indicated in Table 1) and the RAFT agent (mol% vs. monomer as

Table 1 Effect of polymerization conditions and choice of RAFT reagent in the copolymerization of monomer **1** with styrene

Entry	Time (h)[a]	RAFT (rel. amounts)[b]	PDI	M_n[c]	Th. M_n[d]	Polymer
1	24	(100:0:2)	1.75	4,730	–	**2a**
2	60	C (100:1:0.5)	1.22	3,520	6,450	**5a**
3	60	C (100:2:1)	1.26	2,570	4,160	**5b**
4	60	B (100:1:0.5)	1.27	6,100	9,360	**5c**
5	60	B (100:2:1)	1.17	3,680	4,160	**5d**

PDI polydispersity index

[a] All polymerizations run in toluene at 70 °C with a 95:5 feed ratio of styrene:monomer **1**; the total monomer concentration was 0.5 M

[b] C indicates cumyl dithiobenzoate **4** and B indicates benzyl dithiobenzoate **3**; (100:*x*:*y*) stands for relative molar quantities of monomer, RAFT agent (*x*) and AIBN (*y*)

[c] As determined by SEC relative to PS standards

[d] Theoretical M_n: see "Experimental part" section

indicated in Table 1) were added by using calculated amounts of stock solutions in toluene. The solutions were deoxygenated by bubbling N_2 for 30 min, and then heated with magnetic stirring in a temperature-controlled oil bath. The solvent was then removed in vacuo, the remaining solid was dissolved in the minimum amount of CH_2Cl_2, and the solution was added dropwise to non-solvent (20 vol). Conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixtures, and were in the range 60–85 %. The purified, precipitated polymer samples (reddish powder) were filtered and dried and analyzed by SEC-MALS. Calculated M_n were determined using the monomer average molecular weight (weighted according to composition, 110) by the following equation:

$$\text{Calcd}\, M_n = 110/(\text{RAFT}(\%)) \times (\text{conversion}(\%))$$

Thus, without taking into account the molecular weight of the RAFT agent was added to the polymer.

General procedure for the deprotection reaction

The polymers were dissolved in a 9/1 solution of CH_2Cl_2/CF_3COOH (9/1, ca. 20 mL) and stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was partitioned between CH_2Cl_2 and a saturated Na_2CO_3 solution. The organic layer was dried, the solvent was removed in vacuo and the resulting polymers, obtained in quantitative yield, was analyzed by ^{1}H NMR spectroscopy and used without further purification. For deprotected polymer **2b**: ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.4$–6.2 (broad; aryl), 2.1–1.0 (broad; –CH– and –CH_2– polymer chain). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.2$ (bm, aromatic), 129.0–127.4 (bm, aromatic), 126.6–125.4 (bm, aromatic), 46.2–41.6 (bm, CH and CH_2 polymer chain), 40.3 (bs, CH and CH_2 polymer chain).

General procedure for the post-modification with Upy units (polymers **7** and **8**). Polymer **8c**

Isocyanate **6** (61 mg, 0.21 mmol) was dissolved in DMF (30 mL) and added to deprotected polymer **5c** (0.22 g, 2.1 mmol of polymer, 0.105 mmol of free amine); the clear solution was heated at 50 °C for 72 h. Butylamine (16 mg, 0.22 mmol) was then added to quench residual isocyanate, and heating and stirring was continued for a further 2 h. DMF was removed in vacuo and the residue sonicated for 1 h in EtOH (100 mL), and then decanted for 12 h. The suspension was then filtered and the precipitate dried. ^{1}H NMR (300 MHz, CD_3SOCD_3) $\delta = 7.1$–6.1 (broad; aryl), 5.8 (bs, H of ring UPy), 4.2 (bs, $ArCH_2$), 3.3–3.1 (bs, CH_2 chain UPy), 2.2 (bs, CH_3 of UPy), 2.1–1.0 (broad; –CH– and –CH_2– polymer chain). ^{13}C NMR (75 MHz, CD_3SOCD_3) $\delta = 158.1$, 154.8, 145.0 (bm, PS), 127.9 (bs, PS), 127.2 (bs, PS), 125.6 (bs, PS), 104.5, 45.4, 43.8, 30.0, 29.1, 26.0, 23.2.

AFM measurements

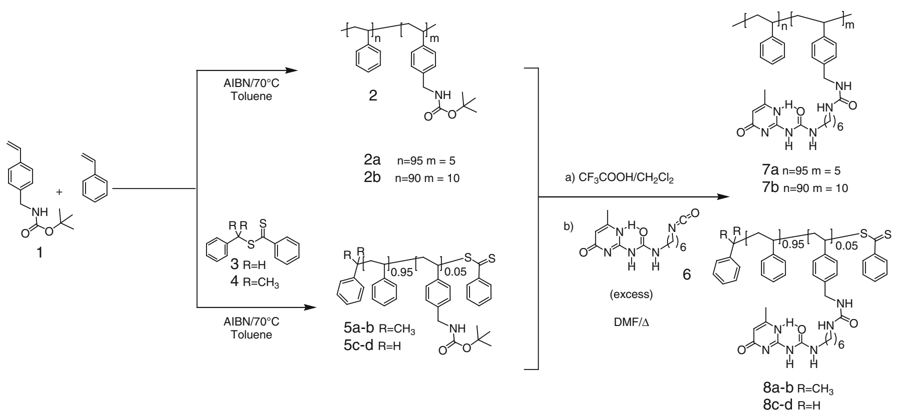
The AFM images were collected with an Autoprobe CP Research microscope (Thermomicroscope-VEECO), operating in non-contact mode, by means of conical silicon tip (curvature radius, 10 nm) onto high-resolution rectangular cantilevers (resonant frequency, 150 kHz; force constant, 5.5 N/m) (NT-MDT). For the analysis, the samples were prepared by spin-casting 3 μL of extremely diluted polymer solutions/dispersions in CH_2Cl_2 (10^{-8}–10^{-9} mg/mL) onto a mica sheet (V-1 grade, SPI Supplies). For each analyzed sample, scans of different areas were carried out with a scan rate of 0.7 Hz. The nanoparticles dimensions were calculated through the analysis of at least 30 line profiles.

Results and discussion

Synthesis

In designing novel PS-based platforms to be post-modified with UPy units, we focused on: (a) the introduction of a chemical functionality on the preformed polymer to which the UPy units could be readily appended with high efficiency and with high reaction fidelity; the availability of isocyanate-derived UPy synthons [11] prompted us to consider amines, which had to be preferred to primary alcohols, for which the use of catalysts is required as they are less reactive with isocyanates; (b) the use of controlled free radical polymerization techniques, which could give low polydispersity samples, to be then subjected to post-functionalization.

Benzylic vinyl substrates with electron withdrawing substituents are known to be not very stable in free radical polymerizations and to cause crosslinking during the polymerization process [32]. Examples of direct polymerizations of vinyl benzyl amine with styrene are rare. Whereas good yields were reported with a relatively low loading of vinyl benzyl amine (5 %) [33], at relatively higher loading (30 %), low yields of isolated polymer were achieved [31]. Furthermore, a



Scheme 1 Synthesis of polymers used in this study

free nucleophilic amine might not be compatible with initiators used in RAFT polymerizations, and not easy to analyze by SEC. A very recent report has dealt with the controlled polymerization phthalimide-protected vinyl benzyl amine [34]. We focused on the use of 4-[(*t*-butoxycarbonyl)amino]methyl]styrene **1** (Scheme 1).

The polymerization of monomer **1**, by itself or in combination with styrene, has rarely been reported [35]. Although a small percentage of pendant UPy units would be needed, we have performed experiments for the incorporation of **1** at various loadings on the polymer backbone. We found that increasing amounts of comonomer **1** drastically lowered the achievable molecular weight of the resulting copolymer (see Table S1 in Supporting information), giving oligomeric samples which were difficult to purify by precipitation. It is likely that this result is the consequence of steric inhibition between neighbouring *t*-butoxycarbonyl groups in the growing polymer chains.

At low loadings of comonomer **1**, the AIBN-induced free radical polymerization gave good yields of polymers **2a** and **2b** (Table 1, Table S1 in Supporting information). RAFT-controlled copolymerization of styrene and monomer **1** was efficient in giving narrow polydispersity polymer samples. Both initiators **3** and **4** were tested, with similar results (Table 1).

Discrepancies were found between the observed and calculated number average molecular weights, experimentally determined by GPC against PS standards. However, for polymers **2a** and **2b**, and for polymers **5**, the observed composition of the copolymer after purification by precipitation, calculated by relative integration of the comonomer peak and the total aromatic signal resonances in the ^{1}H NMR spectra, gave good agreement with the feed ratios.

Polymers **2**, bearing differing ratios of comonomers, and polymers **5**, obtained with differing types and amount of RAFT initiators, were deprotected using trifluoroacetic acid in CH_2Cl_2. Characterization by ^{1}H NMR and ^{13}C NMR showed the complete disappearance of the resonances of the *t*-butoxycarbonyl protecting groups (Figs. S1–S3). The fully deprotected polymers were then subjected to post-modification using an excess of isocyanate **6** in hot DMF, following by quenching of the excess isocyanate with butyl amine, and washing with EtOH with sonication, to completely remove monomeric UPy units which could act as chain stopper in the supramolecular polymerization. The functionalized polymers were obtained in essentially quantitative yields.

Whereas sample **7b** was only soluble in hot DMSO, samples with a lower percentage of UPy units (5 %, **7a** and polymers **8**) were slightly soluble in $CHCl_3$, soluble in cold DMF and DMSO, not soluble in THF or AcOEt. ^1H and ^{13}C NMR spectroscopies revealed that efficient functionalization had occurred, with resonances, to be attributed uniquely to the pendant UPy units, effectively present as broad signals in the purified polymers (Fig. 2, Fig. S4 in Supporting information).

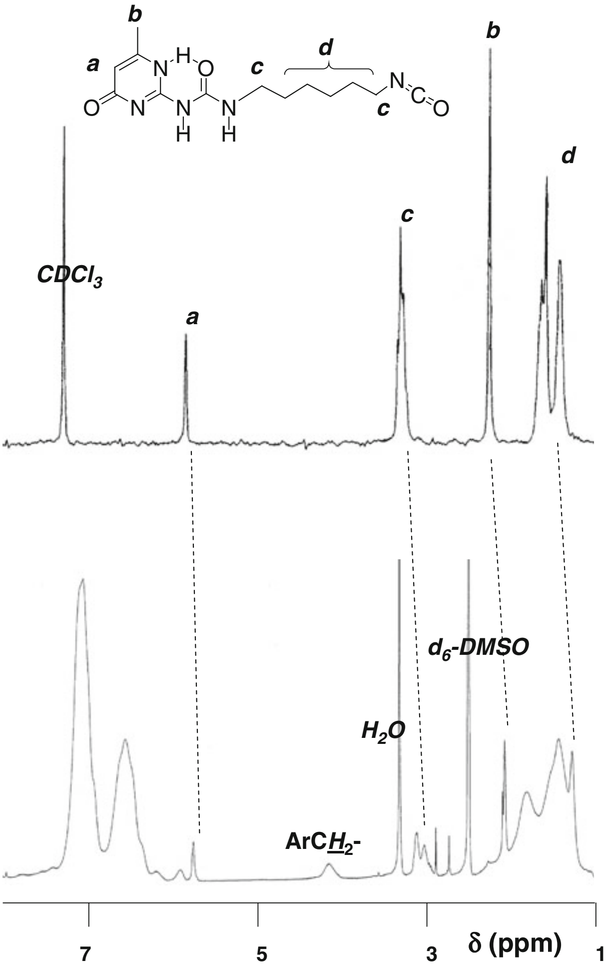


Fig. 2 ^1H NMR spectra (300 MHz, $CDCl_3$) of compound **6** (*top*) and polymer **8c** (*bottom*)

Molecular characterization and aggregation behaviour

The rather small degrees of polymerizations achieved (between 20 and 60), and the low loadings of functionalization for polymers **8**, which are required to maintain solubility in organic solvents, result in a very limited number of UPy unit per polymer chain (1–3 on average). The molecular dilution of effective hydrogen bonding units per chain is likely to facilitate aggregation between the chains. Representative chromatograms of samples **8** are shown in Fig. 3, directly measured by the online MALS detector. We did not observe significant differences between SEC-MALS measurement runs in pure $CHCl_3$ and in $CHCl_3 + 0.3\ \%\ CH_3COOH$ solvents. The presence of acetic acid slightly improves the quality of the detectors signal.

The two samples are composed by two main peaks, labelled **1** and **2** in Fig. 3. Peak **1** is formed by macromolecules with a low degree of association (a few units). On the basis of comparison of single injections of precursors **2** under the same experimental conditions peak **1** is not the single chain polymer unit. This peak is present in high quantity (>90 %, calcd area based on DRI signal). The peak molecular weight M_p varies on the basis of the samples and on the solution concentration from 4,000 and 15,000 g/mol. Peak **2** is formed by clusters with a high aggregation number (Figs. S5–S6). This peak is present in low quantity (2–6 %, calcd area based on DRI signal). The main characterization parameters are shown in Table 2.

The behaviour is similar for all samples **8**, and the aggregation number goes from 22 (**8a** and **8c**) to 26 (**8b** and **8d**). The relative percentages for peak **2** material are 4.7 % (**8a**), 4.6 % (**8b**), 2.0 % (**8c**) and 2.5 % (**8d**). The aggregation tendency is as expected function of the concentration; by increasing the concentration of the injected

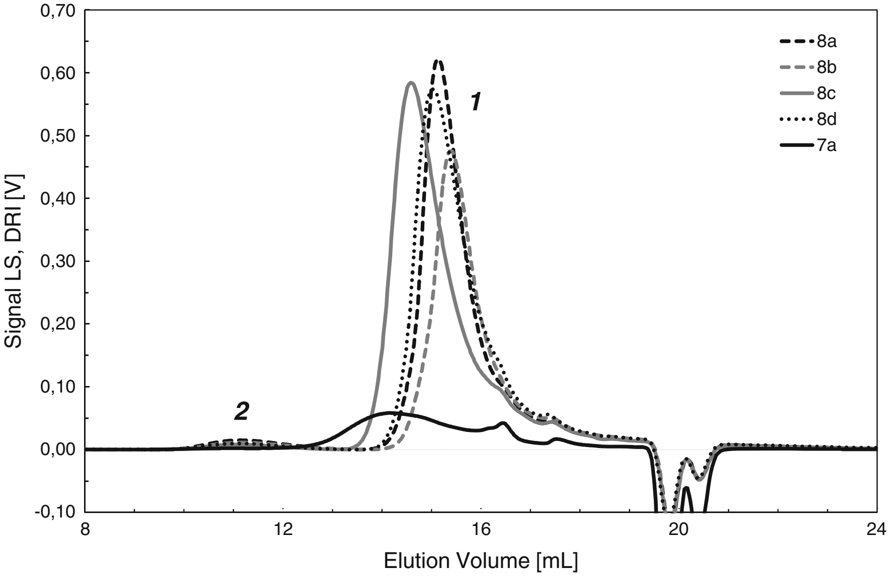


Fig. 3 Chromatograms for polymers **7** and **8**

Table 2 Characterization parameters for peaks **1** and **2** observed in the SEC-MALS chromatograms of polymers **7a** and **8**

Polymer	M_p	M_p	M_n	M_w	M_w/M_n	R_g	N_{Ag}
7a	45,500	–	5,330	29,530	5.5	5.6	8
8a	11,080	246,360	168,030	247,580	1.5	21.0	22
8b	10,200	262,000	156,330	236,040	1.5	21.4	26
8c	13,820	307,740	201,120	276,600	1.4	23.4	22 (27)[a]
8d	10,400	267,940	166,970	246,300	1.5	20.4	26 (62)[a]

M_p peak molecular weight, M_n number average molecular weight, M_w weight average molecular weight, M_w/M_n polydispersity index, R_g radius of gyration (size), N_{Ag} aggregation number

Sample concentration for injection: ca. 0.01 M

[a] Sample concentration for injection: ca. 0.05 M

samples, the aggregation numbers, as expected, increase (27 for **8c** and 62 for **8d**). The dimensions of aggregate clusters were measured by elastic light scattering (MALS), and these aggregate dimensions ($R_g \approx$ 20–24 nm) are noteworthy when compared with the starting units (about 2–3 nm or less). Control experiments with **7a**, obtained by uncontrolled free radical polymerization, showed generally a lower solubility, a very low recovered mass and a negligible amount of peak **2**.

AFM characterization

The visualization of the polymer nanoparticles was possible by performing AFM scans only on drop-cast samples from extremely dilute (10^{-8} mg/mL) nanoparticle solutions from $CHCl_3$ (Fig. S7 in Supporting information). In accordance to Meijer's systems (see for instance Ref. 14), the deposition from solutions at higher concentration brings to very large aggregates (sometimes even bigger than 1 μm), which make difficult if not impossible the observation of the nanoparticles.

Well-defined polymer nanoparticles are easily obtained after solvent evaporation, which appear even homogenously distributed along the whole explored area. The particle diameters range between 50 and 120 nm, whereas the determined height is about 10 nm. The observed size distribution may be attributed to the presence of macromolecules with different degrees of aggregation and/or to the polymer MWD. The estimated spherical radii of the particles, calculated as suggested by Berda et al. [14], are in fair agreement with the estimated R_g obtained from the light scattering measurements in $CHCl_3$ solutions. In particular, estimated spherical radii ranging between 15 and 26 nm may be calculated. Control AFM experiments with polymer **5a**, carried out in similar experimental conditions of polymer **8a**, substantially reveal two families of polymer particles. The first one includes some isolated nanoparticles with diameters of the order of 50–120 nm and height of ~10 nm, as in the case of sample **8a**. A second group comes from a fast aggregation occurring during solvent evaporation, which results in larger and disordered aggregates with dimension in the order of 500 nm and height of 30–60 nm (Fig. S8 in Supporting information).

Conclusions

We have synthesized and characterized a series of PS-based UPy-containing systems which behave as nanoparticles in solution and when deposited on surfaces. The PS precursors are obtained by RAFT-mediated polymerization using styrene and a protected vinylbenzyl amine, to give polymers with narrow distributions and degrees of polymerization between 20 and 60. Rather than a late-stage photochemical deprotection to obtain the self-recognizing UPy units, our approach develops the post-modification of the polymer backbones with preformed, suitable UPy units. Results from light scattering and AFM confirm that the polymer chains effectively aggregate in well-defined nanoparticles, which are not composed from single polymer chains, but rather from well-defined aggregates of several chains. This remarkable difference from the results reported by Meijer's group can be the consequence of: (a) a lower flexibility of the UPy units, due to the presence of a six carbon spacing units linking them to the polymer backbone, when compared with much longer carbon atom spacing units used before [12–14]; (b) the lower loading of UPy units incorporated into the backbone (5 vs. 20–30 % in previously reported systems [12–14]). We believe that our results will aid a deeper understanding of the behaviour of self-aggregating polymers in the stimulating, emerging field of well-defined, organic and polymer-based nanoparticles, certainly useful for a variety of applications at the nanoscale.

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