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Polymer nanoparticles via intramolecular crosslinking of sulfonyl azide functionalized polymers

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ABSTRACT

A new approach to prepare polymeric nanoparticles via intramolecular collapse of single chain of sulfonyl azide functionalized polymers is proposed. Upon heating, the sulfonyl azide functionalized linear copolymers lose nitrogen and form nitrene. This nitrene reacts with C–H bond of the backbone in dilute solution and leads to the efficient intramolecular crosslinking and formation of nanoparticles where the diameter of nanoparticles can be controlled by both the molecular weight and the content of sulfonyl azide groups. A significant reduction in the hydrodynamic volume is observed on going from the starting random coil of linear chains to the corresponding nanoparticles. The morphology and the dimension of nanoparticles are characterized by using transmission electron microscope (TEM), atomic force microscopy (AFM), as well as dynamic laser scattering (DLS).

1. Introduction

Nanoparticles are nanometre-scale aggregates of atoms. Their size gives them unusual optical, electronic, and magnetic properties caused by quantum-mechanical and Coulomb-charging effects, which have many potential applications [1–4]. The preparation of polymeric nanoparticles with a controlled size and pre-determined arrangement of functional groups has become an attractive research topic in recent years [5–7]. This interest is driven by the use of these tailor-made, functional nanoparticles in a variety of applications in the fields of microelectronics [8–10], drug delivery [11–13], polymer processing [14], etc. To address this need, a diverse range of strategies have been developed to increase the scope and availability of these systems including microemulsion techniques [15–17], discrete polymer synthesis of spherical molecules such as dendrimers [18,19], the self-assembly of block copolymers into micelles followed by chemical crosslinking [20,21], as well as supramolecular strategies to collapse nanoparticles [22]. Nanoparticles above 20 nm in size are easier to make but control of their structure is more difficult. In direct contrast, smaller nanoparticles, such as dendrimers, allow access to the potentially more interesting sub-20 nm regime and are structurally well defined, though significantly more difficult to prepare. To achieve the goal of developing a facile synthetic procedure for preparing well defined, sub-20 nm nanoparticles, intramolecular chain collapse strategies have been developed.

By intramolecular crosslinking of functionalized linear polymer chains under dilute solution, a wide range of nanoparticles can be prepared with the chain collapse strategy relying heavily on the reactivity and orthogonality of the crosslinking functionality. Up to date, this technique has made use of free-radical crosslinking of vinyl functionalization [23–25], the thermal crosslinking of benzocyclobutene (BCB) [26,18] or BCB precursors using a continuous addition technique [28], alternative *o*-qinodimethane precursors [29], the room-temperature crosslinking of isocyanate linear copolymers with diamine in dilute solution [30], click chemistry [31], and photo-crosslinking of cinnamoyl groups [32], which has been shown to form particles in the range of 5–20 nm. In present study, the linear copolymers containing the crosslinkable sulfonyl azide groups are synthesized. It is well-known that the sulfonyl azide groups can lose nitrogen and form nitrene when raised to sufficiently high temperature. The nitrene quickly reacts with C–H bond of the backbone in diluted solution which leads to the efficient intramolecular crosslinking and formation of nanoparticles of single chain.

2. Experimental

2.1. Materials

Styrene (St) and methyl methacrylate (MMA) were purchased from Shanghai Chemical Reagent Co and distilled under reduced pressure before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. The chain transfer agent, s-ethoxycarbonyl phenylmethyl dithiobenzoate (ECPDB), was prepared using

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a literature procedure [33]. Tetrahydrofuran (THF) and chloroform from Shanghai Chemical Reagent Co were dried by sodium, using benzophenone as indicator. All other chemicals were purchased from Shanghai Chemical Reagent Co and used without further purification.

2.1.1. Synthesis of 4-styrenesulfonyl azide (SSAz) **3**

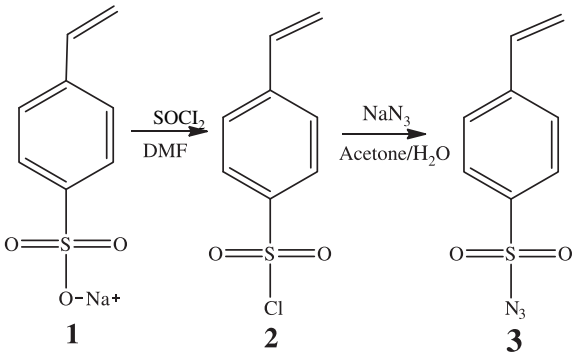
The method for the synthesis of SSAz is shown in Scheme 1. Na-4-styrenesulfonate **1** (14.7 g, 72.6 mmol) was suspended in DMF (75 mL) under nitrogen and cooled to 0 °C. Afterwards thionyl chloride (32 mL, 441 mmol) was added dropwise within 10 min. The reaction mixture was stirred at 0 °C for 30 min and subsequently at room temperature for 1 h, during which a homogenous solution was obtained. The solution was poured onto ice (380 g). The resulting aqueous layer was extracted with diethyl ether (3 × 80 mL). After removing the solvent in the collected organic layers, the resulted styrene sulfonyl chloride **2** (2.27 g, 11.2 mmol) was dissolved in acetone (35 mL) and an aliquot volume of water (35 mL) was added. The turbid reaction mixture was cooled to 0 °C and NaN_3 (802 mg, 12.33 mmol) was added in small portions. After the reaction mixture was stirred for 1.5 h at 0 °C, the acetone was removed in vacuum (30 °C, 150 mbar) and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated at 30 °C. The resulting oil **3** (2.19 g, 10.5 mmol, 94%) was dried in vacuum and used in the polymerization reaction without further purification. FTIR (KBr, ν/cm^{-1}): 3092(C–H), 2934(–CH_2), 2127(–N_3), 1631(–C=C–), 1566, 1493, 1451(–C=C), 1161(–S=O), 758, 652(benzyl). ^{1}H NMR ($CDCl_3$, δ/ppm): 7.91 (2H, C-*Har*), 7.61 (2H, C-*Har*), 6.78 (1H, –*CH*=CH_2), 5.95 (1H, –CH=CH*Hcis*), 5.52 (1H, –CH=CH *Htrans*).

2.1.2. Synthesis of poly(styrene-co-(4-styrenesulfonyl azide)) ***5***

In a typical run of the polymerization process, a mixture of styrene **4** (4.68 g, 45.0 mmol), 4-styrenesulfonyl azide **3** (1.05 g, 5.0 mmol), ECPDB (15.80 mg, 0.05 mmol), and AIBN (4.11 mg, 0.025 mmol) in DMF were added to the reaction mixture. After three times freeze and thaw cycles, the tube was sealed under nitrogen and heated for 5 h at 60 °C. The resulting polymer solution was diluted with 3 mL THF, then precipitated into a large excess of ethanol for three times. Then the copolymer was dried in vacuum and used without further purification. ^{1}H NMR ($CDCl_3$, δ/ppm): 7.26–6.57 (m, ArH), 2.56 (brs, CH), 1.83–1.26 (m, CH, CH_2); FTIR (KBr, ν/cm^{-1}): 2127 (–N_3), 1171, 1081(Ar–SO_2^-).

2.1.3. Synthesis of poly((methyl methacrylate)-co-(4-styrenesulfonyl azide)) **7**

In a typical run of the polymerization process, a mixture of methyl methacrylate **6** (1.80 g, 18 mmol), 4-styrenesulfonyl azide **3** (0.418 g, 2 mmol), ECPDB (6.32 mg, 0.02 mmol), and AIBN (1.64 mg, 0.01 mmol) in DMF were added to the reaction mixture. After three times freeze and thaw cycles, the tube was sealed under nitrogen and heated for 5 h at 60 °C. The resulting polymer solution was diluted with 3 mL THF, then precipitated into a large excess of ethanol for three times. Then the copolymer was dried in vacuum and used without further purification. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.76–6.85 (m, ArH), 3.58 (bt, CH_3), 1.84 (bs, CH_3), 1.82–1.25 (m, CH, CH_2); FTIR (KBr, ν/cm^{-1}): 2127 (–N_3), 1730 (–C=O), 1149, 1071(Ar–SO_2^-).



Scheme 1. Synthesis of 4-styrenesulfonyl azide.

2.2. Collapse reaction of the copolymers in dilute solution

In a 100 mL three-necked flask equipped with an internal thermometer, 25 mL of benzyl ether was heated at 190 °C under nitrogen. 0.1 g sulfonyl azide-functionalized linear polymer **5** (Mw = 46 902, PDI = 1.54) was dissolved in benzyl ether (12 mL) and added dropwise via a peristaltic pump at ca. 12 mL/h with vigorous stirring. After addition the reaction mixture was heated for an additional 1.5 h, the solvent was distilled under reduced pressure, and the remaining crude product was dissolved in THF and precipitated into ethanol. Finally, the nanoparticle **8** was obtained as a brown solid. The nanoparticle **9** was prepared from polymer **7** with the same method.

2.3. Characterization methods

^{1}H nuclear magnetic resonance measurements were carried out at room temperature using a Bruker AMX 300 spectrometer. $CDCl_3$ was used as the solvent.

FTIR analysis of the samples was carried out by a thermo Bruker EQUINOXSS/HYPERION2000 spectrometer. KBr pellet method was employed.

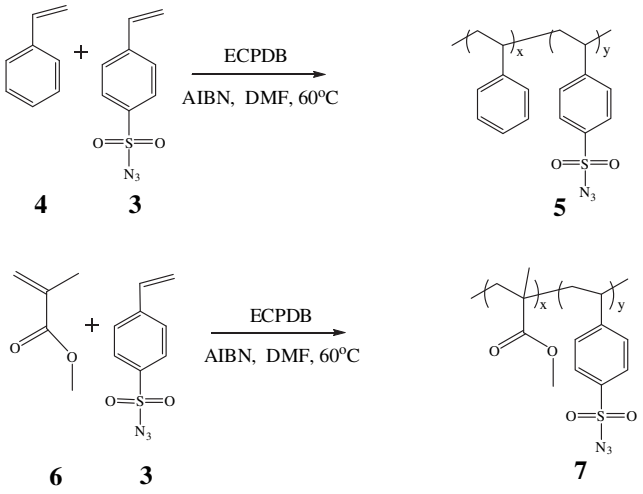
Gel permeation chromatography (GPC) was performed in tetrahydrofuran on a Waters Alliance HPLC system. The molecular weight of the polymers was calculated relative to linear polystyrene standards.

Transmission electron microscopy (TEM) was performed with a transmission electron microscope (TEM, Hitachi H-600), operating with an acceleration voltage of 200 kV. The TEM samples were prepared by placing one drop of the diluted dispersion of the nanoparticles on a 200 mesh carbon coated copper grid and left in air to dry.

The height and distribution of the nanoparticles were also determined by tapping-mode atomic force microscopy (AFM) (SPA-300HV, Seiko Instruments Inc.) under ambient condition in air. The standard silicon tips were used. The average particle size of the nanoparticles was also determined on a commercial dynamic light scattering (DLS) (Malvern Autosizer 4700). Differential scanning calorimetry (DSC) of the polymers was performed on MDSC-Q100 (TA).

3. Results and discussion

Synthetically, the preparation of single-chain polymeric nanoparticles through thermally activated methods involves two steps. The first step involves the incorporation of thermally activated crosslinkable groups into linear polymer backbones. The second strategy is collapsing via intramolecular crosslinking in ultradilute solution. The advantages of BCB as the thermally activated crosslinkable group are its stability to radical polymerization and high reactivity under crosslinking condition [26,27]. However, the disadvantage of BCB, which has a crosslinking temperature as high as 250 °C, precludes the presence of sensitive groups and reduces the application of the nanoparticles. To overcome these challenges, we investigate 4-styrenesulfonyl azide **3** with the ability to be



Scheme 2. Synthesis of poly(styrene-co-(4-styrenesulfonyl azide)) **5** and poly((methyl methacrylate)-co-(4-styrenesulfonyl azide)) **7**.

incorporated as a comonomer into the backbone of the linear polymer and similar crosslinking characteristics at 180–200 °C.

The synthetic strategy involves copolymerization of 4-styren esulfonyl azide **3** with a variety of vinyl monomers, such as styrene, methyl methacrylate, as shown in Scheme 2, to give the desired polymers with sulfonyl azide functionality incorporated along the backbone. To prepare the sulfonyl azide functionalized copolymers with well-controlled molecular weight, polydispersity, and contents of sulfonyl azide groups in the copolymers, we performed a typical RAFT-mediated free radical polymerization, with ECPDB as the chain transfer agent. The reaction temperature of polymerization is at 60 °C with AIBN as the initiator, because the decomposition of the azide group only takes place at much higher temperatures [34]. The SSAz-functionalized copolymer **5** can be readily characterized by FTIR which shows the characteristic peak of sulfonyl azide groups for the azide group at 2127 cm^{-1} and the S=O group at 1160 cm^{-1}.

Since the seminal work of Breslow et al. in 1960s, it is well-known that sulfonyl azide groups cleave off nitrogen and form a nitrene when raised to sufficiently high temperature. The nitrene has a high tendency to insert into almost CH-bonds and in some cases even OH-bonds [35–37]. After successful incorporation of the sulfonyl azide group into linear copolymers, differential scanning calorimetry (DSC) results of styrene/SSAz (90/10) copolymer indicate that the decomposition temperature of azide groups in the linear copolymer is around 160–220 °C and the temperature for the maximum peak of exothermic is at 194.52 °C. Fig. 1 shows the decomposition and binding mechanism of sulfonyl azide groups. Upon heating, the sulfonyl azide groups lose nitrogen and form nitrene. The further reaction for the nitrene has five possibilities, (1) the polymer with nitrene abstracts the hydrogen in CH-bond of another polymer chain and recombines with it; (2) the polymer with nitrene inserts the CH-bond of another polymer chain; (3) the polymer with nitrene recombines with itself or another polymer chain with nitrene; (4) the polymer with nitrene inserts the groups of sulfonyl azide of polymer chain to form the azo dimmers in highly concentrated solution. (5) the polymer with nitrene abstracts the hydrogen in CH-bond of its own chain and recombines with it, then the intramolecular crosslinking structure is formed. In dilute solution, the fifth reaction is quite easier than the other four reactions. Thus, the nanoparticles based on the intramolecular collapse of the single chain can be achieved via the continuous addition strategy of the copolymer in dilution solution. In the traditional strategy, the concentration of polymer solution needs to be on the ultra-dilute reaction conditions (ca. 10^{-5}–10^{-6} M) to ensure the collapse and intramolecular coupling of single-polymer chains to give nanoparticles. According to Hawkers' work [26], following a continuous addition strategy and this coupling event, the traditional conditions of ultrahigh dilution need only be met for the reactive intermediates and not for the polymers themselves, which allows their concentration to increase to very high levels (0.1–1.0 M) without intermolecular crosslinking reactions leading to gelation or coupling of individual nanoparticles. We also adopt the continuous addition strategy, and the concentration of polymer solution is controlled in 0.1–1.0 M to avoid the intermolecular crosslinking. A temperature of 190 °C for the intramolecular chain collapse process in benzyl ether can be used. In this approach, a concentrated solution of the starting linear polymer **5**, was continuously added via peristaltic pump to the solvent. After the addition of the polymer **5**, the reaction continued for 1.5 h and the solvent was removed, the nanoparticle **8** was isolated using normal precipitation techniques (Scheme 3).

Evidence of the conformational change from the random coil of the linear polymer to the nanoparticle via intramolecular collapse is obtained from an apparent molecular weight decrease of the copolymer, as shown in Table 1. Comparison of GPC results for the collapsed nanoparticles versus the starting linear polymer is an efficient diagnostic technology for demonstrating the volume change of a random coil of the polymer caused by an intramolecular crosslinking of the single chain. A significant feature is the reduction in hydrodynamic volume of the random coil of the linear polymer via the intramolecular collapse to give the final nanoparticles. As shown in Table 1 for styrene based copolymers containing 5, 10, and 15 mol % of sulfonyl azide-functionalized repeat

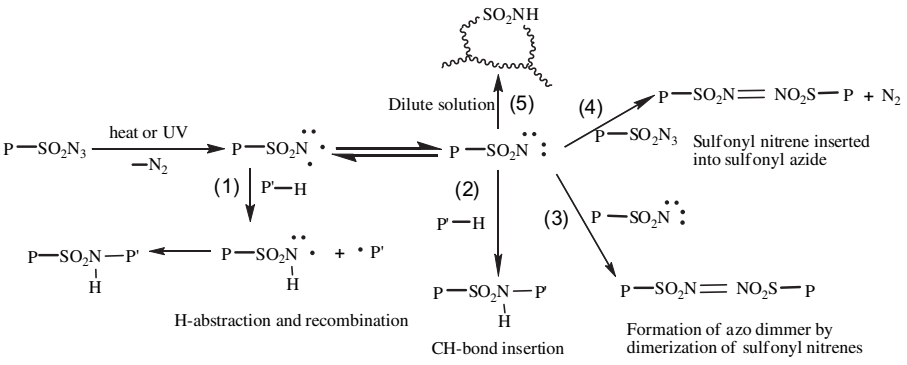
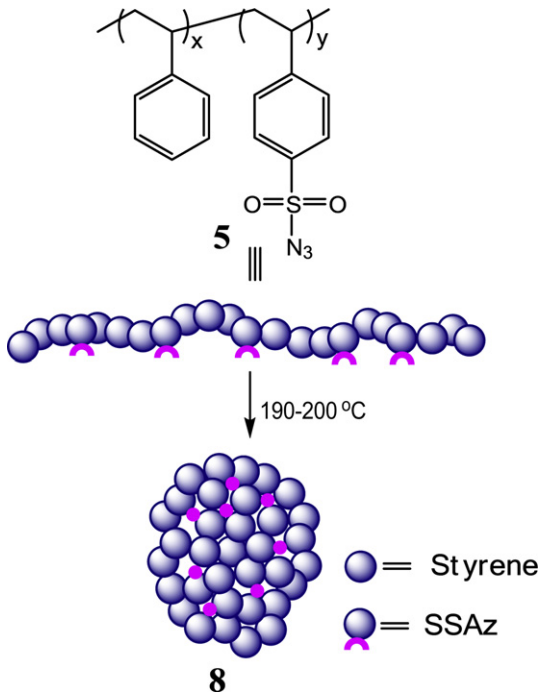


Fig. 1. The decomposition and binding mechanism of sulfonyl azide groups.



Scheme 3. Diagram of the preparation of nanoparticle **8** via the intramolecular collapse of linear polymer **5**.

units, a remarkable increase in molecular weight is observed when the relative percentage of sulfonyl azide groups increases. After crosslinking, the increased retention time corresponds to a reduction in hydrodynamic volume of the nanoparticle with increasing intramolecular crosslink density. For example, the original linear polymer **5** (styrene/SSAz = 85/15) has a molecular weight *Mw* = 46 902 (PDI = 1.54). However, upon reaction the chain decreases in size to give a nanoparticle with an apparent molecular weight *Mw* = 24 885 (PDI = 1.52) (Fig. 2). For the same molecular weight of the starting linear polymer **5**, a systematic decrease in the hydrodynamic volume of the nanoparticles is observed on increasing the content of sulfonyl azide groups from 15% to 20%. It is consistent with an increase in the level of intramolecular crosslinking and a globular structure. It is also clear that no significant intermolecular crosslinking is observed, and the GPC trace with a slightly lower polydispersity than the linear precursor.

The data in Table 1 also demonstrate the inherent versatility of this approach in controlling the size of the nanoparticle. The size and density of crosslinking of the nanoparticle can be controlled by the level of sulfonyl azide groups and the molecular weight of the starting linear polymer. The change of the size of the nanoparticles can be reflected via the change of the hydrodynamic volume of the starting linear polymer and the nanoparticles. For example,

Table 1
Comparison of the equivalent molecular weights and PDI for the starting linear polymers **5**, **7**, and the final nanoparticles **8**, **9**

Copolymers	SSAz%	Linear copolymers		Nanoparticles	
		Mw	PDI	*Mw*	PDI
SSAz-St	5	10 340	1.38	8536	1.40
SSAz-St	10	21 880	1.59	12 239	1.61
SSAz-St	15	46 902	1.54	24 885	1.52
SSAz-St	20	47 105	1.46	20 604	1.53
SSAz-MMA	5	9138	1.43	7446	1.44
SSAz-MMA	10	25 457	1.41	15 599	1.54

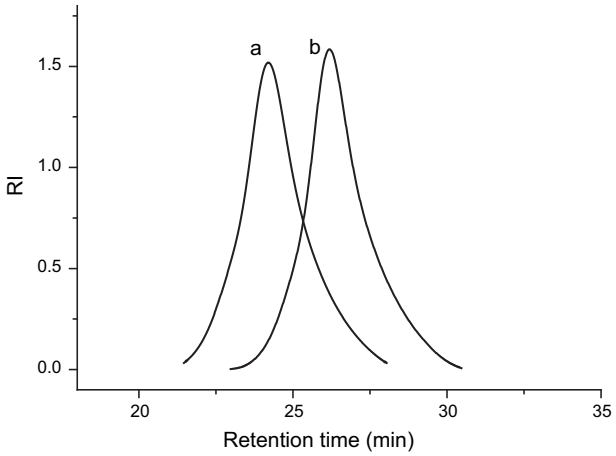


Fig. 2. GPC traces for, (a) linear polymer **5** (*Mw* = 46 902, PDI = 1.54), (b) nanoparticle **8** (*Mw* = 24 885, PDI = 1.52).

a polystyrene derivative with 5% sulfonyl azide gives a nanoparticle, whose hydrodynamic volume diminishes to 17% of the starting linear polymer because of the intramolecular crosslinking. The copolymer with 10% sulfonyl azide gives a nanoparticle, whose hydrodynamic volume diminishes to 45% of the starting linear polymer. However, the polystyrene derivative with 20% sulfonyl azide gives a nanoparticle with the hydrodynamic volume diminishing to 56% of the starting linear polymer. The hydrodynamic volume decreases with increasing density of crosslinking. The hydrodynamic volume decreases with increasing level of sulfonyl azide, thus the size of the nanoparticle also decreases with increasing density of crosslinking. The data of dynamic light scattering (DLS) also confirm the conclusion. The polystyrene derivative with 15% sulfonyl azide gives a nanoparticle with the average diameter of 16.5 nm. Increasing the molecular weight and incorporating 20% sulfonyl azide gives a nanoparticle with the average diameter of 15 nm (Fig. 3). A consequence of this is that the size of the nanoparticle can be controlled by the structure and the functionality of the starting linear polymer.

Furthermore, the confirmation of the structural change is obtained from FTIR results. Comparison of FTIR spectra for the starting linear polymer **5** and the nanoparticle **8**, which show the disappearance of the azide (2127 cm^{-1}) after reacting 1.5 h at

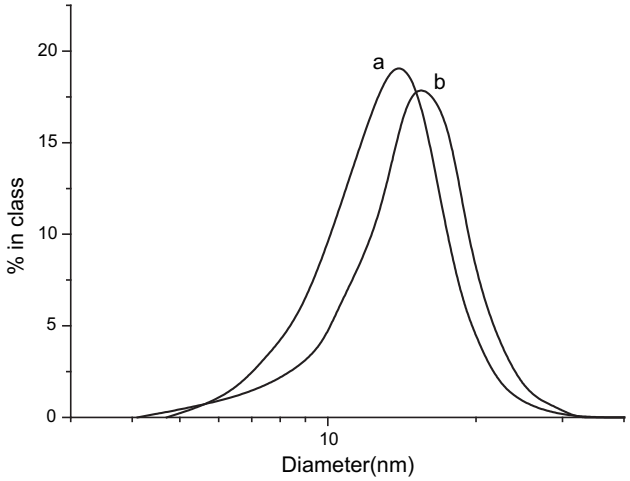


Fig. 3. Size distribution for nanoparticle **8**, (a) 20% SSAz, and (b) 15% SSAz.

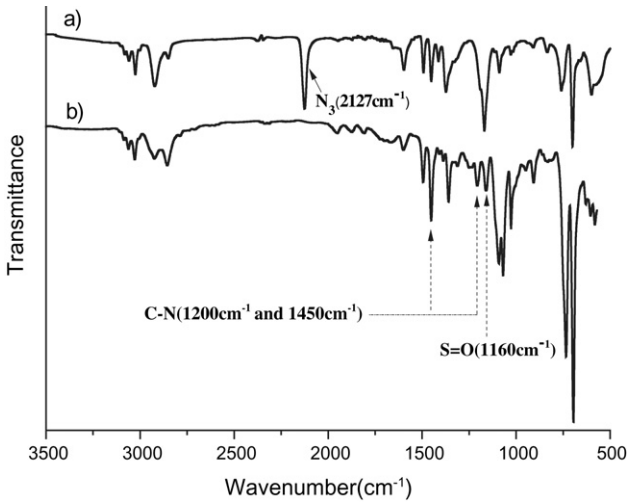


Fig. 4. FTIR spectra of polymer **5** (a) and nanoparticle **8** (b).

190 °C and the formation of the C—N bonds (Fig. 4). A new peak appears at 1200 cm^{-1} for stretching vibration of groups of C—N bond. Furthermore, the peak intensity of polymer **5** at 1450 cm^{-1} is stronger than the nanoparticles **8** because of the appearance of bending vibration of C—N bond. The peak at1160 cm^{-1} is the groups of —S═O. Meanwhile, the peaks of other groups have no significant change, which indicates the similar structure and composition between the linear polymer and the nanoparticle.

RAFT-mediated living free radical polymerization can also be used for the synthesis of a variety of linear copolymers with other vinyl monomers. As show in Table 1, starting linear polymers based on methyl methacrylate (MMA) **6** can be employed as the precursor polymer with no change in the efficiency of the intramolecular collapse process. For example, the copolymerization of MMA/SSAz (90/10) results in the well-defined random copolymer **7** with a molecular weight Mw = 25 457 (PDI = 1.41). Addition of a concentrated solution of **7** to benzyl ether at 190 °C to give nanoparticle **9** with an apparent molecular weight Mw = 15 599 (PDI = 1.54). From these data it can be concluded that a similar volume reduction and crosslinking density are observed for the styrenic and methacrylate based materials, illustrating the high efficiency of the sulfonyl azide-based intramolecular crosslinking reaction.

The dimension of the nanoparticles was measured by AFM (Fig. 5) and TEM (Fig. 6). In Fig. 4 the nanoparticle **8** (15 mol% SSAz) gives effective particle diameter of 14 ± 0.2 nm, which is in basic agreement with the size determined by TEM (15 ± 0.5 nm). Dynamic light scattering (DLS) was also performed in THF solution of the nanoparticles on the functionalized polymers and their respective collapsed products. The results also support a change in effective diameter from 25 nm as an extended coil to 16 nm in particle size for the 15 KDa copolymers. Performing the light scattering measurements in chloroform and toluene gives similar results.

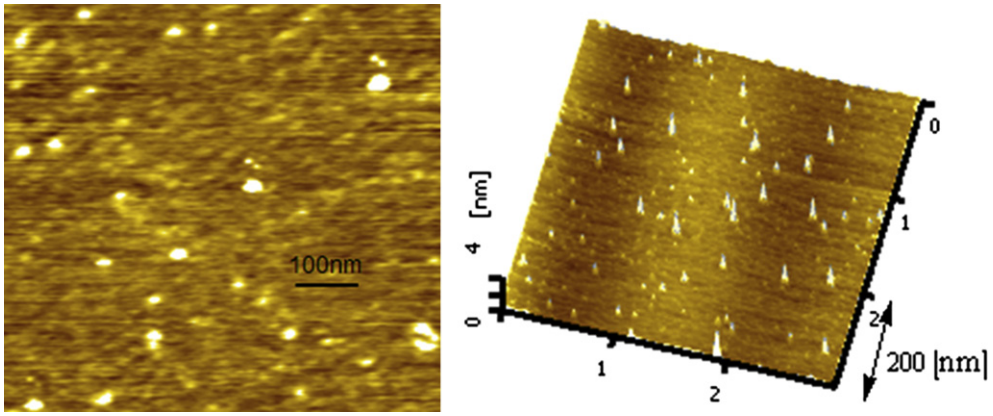


Fig. 5. Representative tapping-mode AFM image of nanoparticle **8**, samples were prepared by drop deposition onto freshly cleaved mica and allowed to dry under ambient condition.

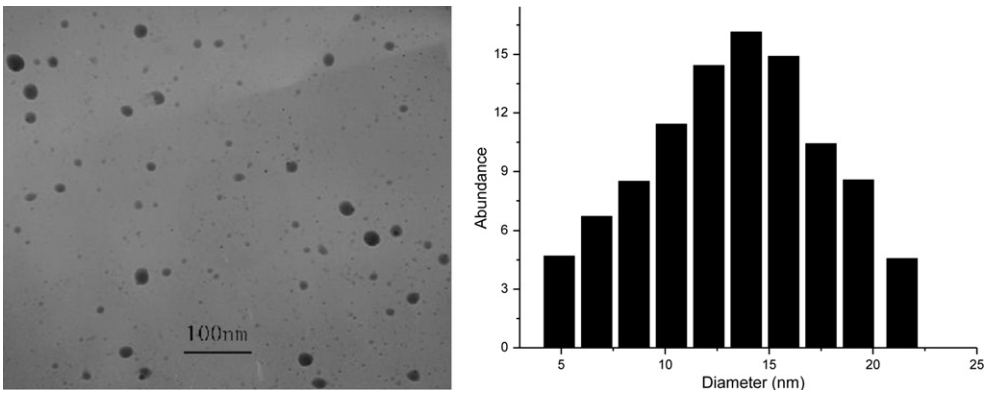


Fig. 6. TEM micrograph of polymeric nanoparticle **8**, average diameters are shown with the corresponding distribution and a representative image.

4. Conclusions

In summary, we have demonstrated the sulfonyl azide functionalized linear copolymer can provide efficient intramolecular crosslinking of the polymer and form single-chain nanoparticles. By using the continuous addition strategy, intermolecular crosslinking can be effectively eliminated even at high concentration. The novel crosslinking unit can react with a variety of vinyl monomers and the temperature for the crosslinking reaction is lower than BCB. The dimension of nanoparticles can be controlled in 5–20 nm by varying the molecular weight and molar percentage of sulfonyl azide groups for the starting linear copolymers.

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