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Novel Category of Optically Active Core/Shell Nanoparticles: The Core Consisting of a Helical-Substituted Polyacetylene and the Shell Consisting of a Vinyl Polymer

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ABSTRACT: This article reports on a novel methodology for preparing a new class of core/shell nanoparticles. The nanoparticles consist of a unique core (composed of an optically active helical-substituted polyacetylene) and a shell (composed of a vinyl polymer) and thus exhibit optical activities. Such nanoparticles were synthesized by combining aqueous catalytic microemulsion polymerization and free radical polymerization in one specific system. The shells could be further cross-linked for improving the properties of particles. The investigations are of high importance not only in polymer chemistry due to the combination of catalytic polymerization and free radical polymerization in one system but also in materials due to the integration of "chirality" and "nano" concepts in one single material.

Introduction

Over the past decade, core/shell structured nanoparticles (NPs) have attracted a great deal of interest because they allow a fine control over the composition, morphology, and property of nanomaterials. Combining several materials into an NP is an effective way to develop systems possessing desirable physical and chemical properties.[1] These integrated properties are generally not performed by the single-component counterparts.[2] The starting material for the core and shell in a core/shell NP can be a metallic,[2,3] ceramic,[4] or polymeric[5] material. Core/shell NPs offer interesting prospects in a broad spectrum of applications for instance in electrical and optical materials,[6] catalysis,[7] biomaterials,[8] and magnetic materials.[1b] The present article reports for the first time a unique type of core/shell NPs, in which the core is made up of a helical-substituted polyacetylene, whereas the shell is constituted by a vinyl polymer. Apart from the interesting structures, this class of NPs exhibits large optical activities and thus is expected to find some applications not achieved by usual core/shell NPs. In addition, the versatile and facile methodology involved herein deserves to be highlighted and would allow us to prepare series of novel core/shell NPs particularly incorporating chirality and nanoconcepts in one system.

Conjugated polymers have been extensively explored over the last decades because of their excellent chemical and physical properties originating from the unique π-conjugated structures.[9] However, many conjugated polymers are considered as instable, rigid, fragile, and intractable materials with limited solubility and processability due to the conjugated backbones. These disadvantages substantially limit their industrial applications. One of the promising approaches for solving these problems is to blend the rigid conjugated polymers with flexible polymers, for example, in the form of core/shell-structured NPs.[10] For some other conjugated polymers, for example, polyaniline,[11] polypyrrole,[12] and polythiophene,[13] many reports can be found in literature devoted to their core/shell NPs, but for polyacetylene and the derivatives, only a few reports on their NPs can be found.[14] Mecking et al. made breakthroughs in preparing polymer emulsions based on acetylene monomers.[14] We[15] reported optically active NPs consisting of helical-substituted polyacetylenes in our previous work. However, the preparation of core/shell NPs based on acetylene and the derivatives is still a big challenge, and such investigations have not yet been found in literature. In the present article, we report for the first time a category of core/shell NPs: the cores consist of an optically active helical polymer, and the shells consist of a vinyl polymer. Following the same idea, many more core/shell NPs with tailored properties will be prepared.

Experimental Section

Materials. Solvents were distilled under reduced pressure. Freshly deionized water was used for the polymerizations. Propargylamine and 1*S*-(+)-10-camphorsulfonyl chloride were purchased from Aldrich and used as received without further purification. (nbd)$Rh^+B^-(C_6H_5)_4$ (nbd = norbornadiene) was prepared as reported.[19] Vinyl monomers, BA, MMA, and St were obtained from Aldrich and purified by distillation before use. AIBN (azobisisobutyronitrile), obtained from Aldrich, was purified by recrystallization in advance. Triton X-100 (polyethylene glycol *tert*-octylphenyl ether) and TMPTA (trimethylolpropanetriacrylate) were bought from Aldrich and directly used.

Measurements. Circular dichroism (CD) and UV−vis absorption experiments were conducted on a Jasco 810 spectropolarimeter. The molecular weights and molecular weight polydispersities were determined by GPC (Shodex KF-850 column) calibrated by using polystyrenes with THF as eluent. Transmission electron microscopy (TEM) was performed on the polymer emulsions with a Hitachi H-800 electron microscope. Before carrying out the TEM experiments, the polymer emulsions were first diluted. Cis content of the substituted polyacetylenes was determined by Raman spectroscopy. Specific rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp as the light source at room temperature (the emulsion without dilution).

Synthesis of Core/Shell Nanoparticles. The substituted acetylene monomer (*N*-propargyl-(1*S*)- camphor-10-sulfamide: SA)

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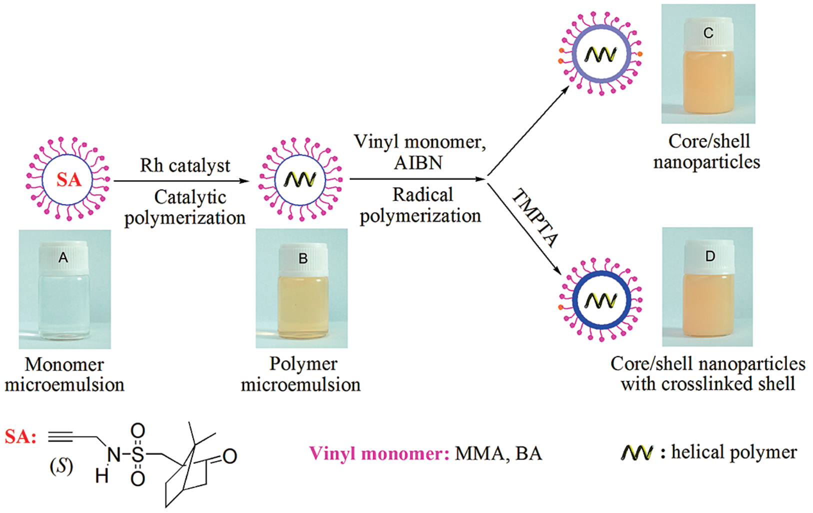

Figure 1. Schematic representation of the strategy for the preparation of core/shell NPs consisting of substituted polyacetylene core and vinyl polymer shell. (The shell is non-cross-linked or cross-linked with TMPTA.) (A) The monomer SA emulsion, (B) the emulsion of PSA, and the emulsions of core/shell NPs with (C) non-cross-linked and (D) cross-linked shell.

was synthesized according to previous reports.[15,17] The aqueous catalytic microemulsion polymerization of SA was previously reported in detail.[15] The major procedure is as follows. Predetermined amounts of Triton X-100 (2.88 g, 4.5 mmol) and deionized water (~17 mL) were added to a reactor. The aqueous solution was stirred with a stirring rate of 350 rpm for 15 min at 30 °C, after which the solution of SA (0.1 g, 0.37 mmol)/DMF (6.5 mL) was added dropwise to the solution above. The solution mixture was subsequently stirred for 10 min, in which the catalyst (0.0039 g, 7.6 μmol)/DMF (6.5 mL) solution was added dropwise. The polymerization of SA was performed under N_2 at 30 °C.

With the polymer emulsion prepared above as the seeded emulsion, a predetermined amount of vinyl monomer was added to the emulsion and stirred for 30 °C at room temperature. Then, the emulsion system was heated to 60 °C, during which a predetermined amount of AIBN (AIBN/vinyl monomer = 1 wt %) was dropwise added to the system. The radical polymerization of the vinyl monomer proceeded for 4 h at 60 °C. For the preparation of nanoparticles with cross-linked shells, a given amount of TMPTA was added together with the vinyl monomer. The other processes were the same as those for the preparation of core/shell particles with non-cross-linked shells.

To acquire pure substituted polyacetylene from the pure PSA emulsion, a rotary evaporator was used to remove the water present in the emulsion. The residual product was dissolved in $CHCl_3$ to exclude Triton X-100 and then filtered; finally, the pure substituted polyacetylene was acquired by rotary evaporation again. In the case of core/shell NPs without cross-linked shells, the emulsion was first subjected to centrifugation (Centrifuge, GL-22MS, max speed, 22 000 r/min); then, a small amount of acetone was added to the precipitate to dissolve the PMMA. This process was repeated at least three times, and the PMMA/acetone solution was collected. After evaporation, PMMA was obtained. Meanwhile, the residual substituted polyacetylene (PSA) was obtained.

Results and Discussion

Strategy for the Preparation of Core/Shell NPs. In our previous investigations,[15] a series of stable polymer emulsions was obtained by catalytic microemulsion polymerization of substituted acetylene monomers in aqueous systems. The nanoparticles were found to be 100 nm and below in diameter. The polymers forming the NPs took helical conformations; therefore, the NPs exhibited large optical activities.[15]

We herein further prepared core/shell NPs, for which the relevant concept is schematically depicted in Figure 1. Two entirely diverse polymerization mechanisms were subsequentially involved: the helical-substituted polyacetylene (core) was first preformed via aqueous catalytic microemulsion polymerization, whereas the shell was formed via a free radical polymerization of vinyl monomers. Following this strategy, we successfully prepared the expected core/shell NPs.

In the present research, the investigated substituted acetylene monomer is *N*-propargyl-(1*S*)-camphor-10-sulfamide (SA). SA first formed monomer micelles in the presence of a surfactant Triton X-100. Then, SA underwent aqueous catalytic microemulsion polymerization with a Rh-based catalyst $[(nbd)Rh^+B^-(C_6H_5)_4]$ providing stable latex particles of the polymer of SA (PSA). The involved aqueous catalytic microemulsion polymerizations were previously investigated in detail.[15] In the subsequent step, a vinyl monomer, butyl acrylate (BA), methyl methacrylate (MMA), or styrene (St), and an initiator (AIBN) of a predetermined amounts were added in the above latex system. Free radical polymerizations of the vinyl monomers took place upon being heated to 60 °C and provided core/shell NPs, as discussed below.

Morphology of Core/Shell Nanoparticles. In the free radical polymerization of the vinyl monomers, the hydrophobic monomers should be dispersed inside the preformed PSA core particles stabilized by the Triton X-100 surfactant molecules. Nevertheless, the higher hydrophilicity of the vinyl monomers (BA and MMA) made them distributed around the core particles constituted by the PSA chains, as schematically displayed in Figure 1. Therefore, the formed vinyl polymers ended up as a shell on the surface of the core particles after the completion of polymerization. This assumption was clearly confirmed by the TEM images of the obtained NPs, as presented in Figure 2. The average diameter of the initial PSA nanoparticles was ~90 nm (Figure 2A). When BA was employed as the vinyl monomer, core/shell NPs indeed could be obtained but aggregation occurred, as observed in Figure 2B. This can be explained by the low glass-transition temperature (T_g) of the shell-forming material PBA (polymer of BA; T_g, −48.5 °C), which could result in a tacky behavior among the particles. Moreover, the core/shell structures could not be distinguished very clearly.

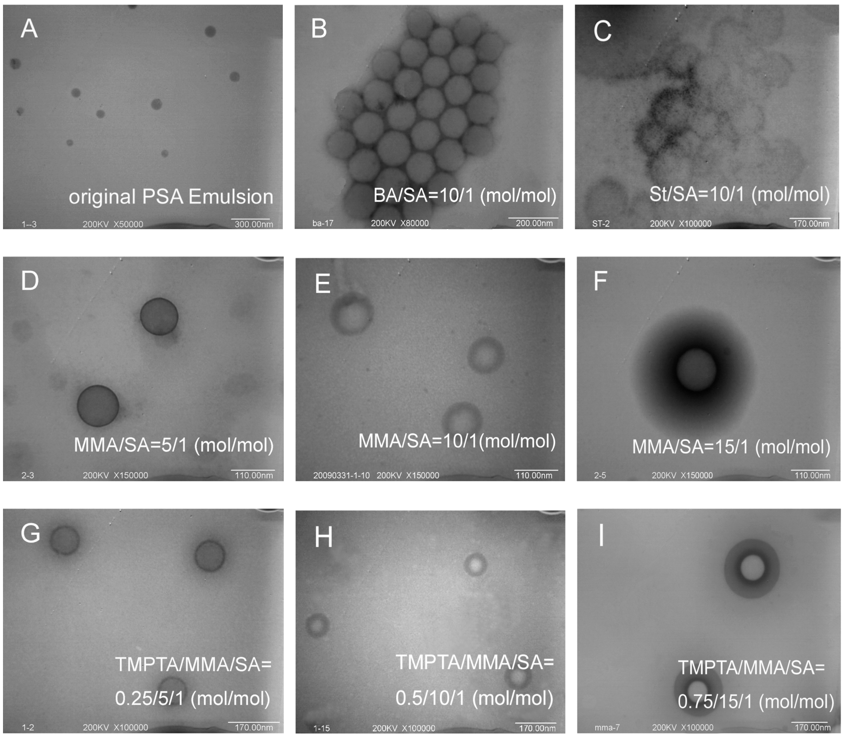

Figure 2. TEM images of (A) the pure PSA NPs, (B) the core/shell NPs of BA/SA system, (C) the core/shell NPs of St/SA system, and the core/shell NPs of MMA/SA systems (D−F) without and (G−I) with TMPTA.

Table 1. Parameters of the PSA Particles and the Core/Shell NPs with and without Crosslinked Shells Obtained in MMA/SA Systems

particles	MMA/SA (mol/mol)	diameter (thickness) (nm)[a]		optical activity	
		core	shell	$[\theta]$ (mdeg)[b]	$[\alpha]_D$ (deg)[c]
PSA	0/1	89.7 (particle)		27.8	847
core/shell: non-cross-linked	5/1	92.3	5.4	22.1	620
	10/1	90.3	39.8	19.8	615
	15/1	94.4	102.3	17.6	606
core/shell: cross-linked	5/1	93.7	6.7	22.3	646
	10/1	89.7	39.1	19.7	628
	15/1	95.6	100.3	15.6	611

[a] Determined according to TEM images. [b] According to the CD spectra in Figure 3. [c] Measured by polarimeter under the same concentration conditions.

Therefore, we tried styrene (St) as the vinyl monomer because the polymer of St (PS) has a much higher T_g (~100 °C) than PBA, but no stable emulsion could be formed, and considerable precipitation took place in this system. One typical TEM image of the resulting emulsion is presented in Figure 2C. Higher hydrophobicity of PS than that of the preformed PSA led to such a result that PS entered inside the preformed PSA core rather than staying at the surface of the core. The precipitate was found to be mainly composed of PSA, offering evidence of our assumption above.

Methyl methacylate (MMA) was found to be an ideal monomer because the polymer of MMA (PMMA) has a higher T_g (~105 °C) than PBA, and besides, it has higher hydrophilicity than PS. The prepared MMA/PSA core/shell emulsions were quite stable for at least 6 months, well exemplified by the photograph in Figure 1C (MMA/SA = 1/10, mol/mol), where the pictures of the SA emulsion before polymerization (Figure 1A) and the PSA emulsion (Figure 1B) are also presented for comparison. (The pictures of the core/shell particle emulsions for MMA/SA = 5/1 and 15/1 are presented in Figure S1 in Supporting Information.) An increase in the MMA concentration led to a slight decrease in the transparency of the emulsions, most likely due to the particles growing larger. (See below.) The related TEM images are presented in Figure 2D−F, in which the MMA/SA ratio was 5/1, 10/1, and 15/1 (mol/mol), respectively. The shells can be clearly distinguished from the cores in all core/shell NPs. It is further indicated that the shell thickness of the core/shell NPs could be easily controlled by tuning the amount of the vinyl monomer. The relevant data are listed in Table 1.

Characterization of the Polymerizations. The shell and the core materials of the NPs were isolated and separately collected by their different solubility to investigate the characteristics of and to gain deep insight into the core and the shell materials. In the MMA/SA NPs systems, both the SA and MMA monomer conversion were 92% and above. For the specific system with MMA/SA 10/1 (mol/mol), the number-average molecular weight (M_n) and its polydispersity (M_w/M_n) of PMMA were 4500 and 1.50, respectively. The core of the NPs, that is, the PSA, was investigated to explore the effects of the subsequent free radical polymerization and the existence of vinyl polymer chains on the helical PSA. It was found that the preformed PSA was hardly affected by the following radical polymerizations. The investigations on the molecular weight and cis content provided support for this conclusion. The M_n and its polydispersity (M_w/M_n) and the cis content of the original PSA

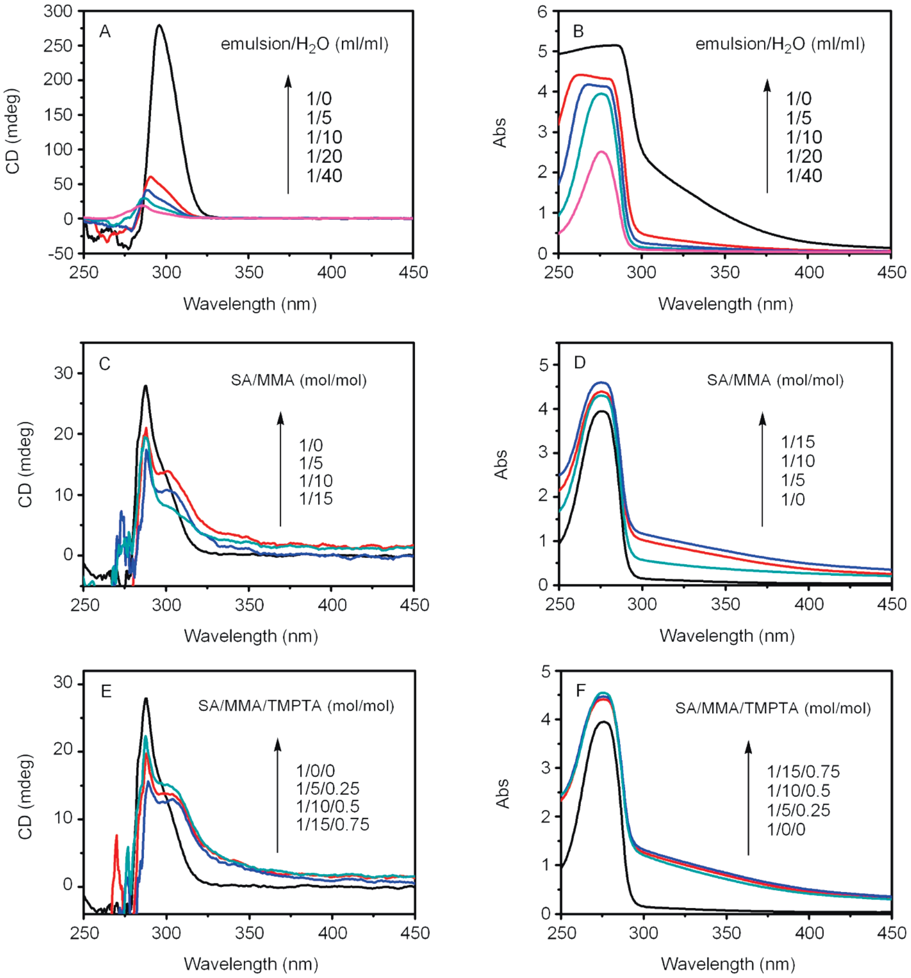

Figure 3. CD and UV spectra of (A,B) the pure PSA and the core/shell NPs with (C,D) non-cross-linked (E,F) and cross-linked shells. All spectra were recorded at room temperature.

were 9900, 1.31, and 98%, respectively, whereas they were 10 000, 1.68, and 99%, respectively, for the PSA taken from the core of the core/shell NPs (MMA/SA 10/1 in mol/mol). This demonstrated clearly that the subsequent free radical polymerizations had little influence on the preformed polyacetylene chains, even though the latter had C=C bonds in backbones. Similar situations can be found in the literature, for example, by Tang et al.[16]

Optical Activities of Core/Shell Emulsions. The typical CD and UV−vis absorption spectra of PSA and the core/shell NP emulsions are presented in Figure 3. Our previous investigations demonstrated that PSA could adopt helical structures both in solution[17] and in emulsion,[15] according to CD and UV−vis absorption spectroscopies.[18] The obtained spectra are displayed in Figure 3A,B for the pristine PSA emulsion. In the preceding investigation, SDS (sodium dodecyl sulfate) was employed as the surfactant to conduct the microemulsion polymerization of SA. In the course of our experiments, a nonionic surfactant, Triton X-100, was found to be more suitable for preparing stable emulsions. Therefore, Triton X-100 was utilized as the surfactant instead of SDS. In Figure 3A,B, both CD signals and UV absorptions can be clearly observed around 320 nm. When compared with the CD and UV−vis absorption spectra of the PSA emulsions prepared with SDS (Figure S2 in Supporting Information), the corresponding spectra of the core/shell particle emulsions prepared with Triton X-100 (Figure 3A,B) demonstrated little difference in terms of the profiles of the spectra, the intensities of CD effects, and the strengths of UV absorptions. Accordingly, the PSA used in Figure 3A,B was also considered taking helical structures with a preferential helicity.

It should be pointed out that in Figure 3A,B, the polymer emulsions should be diluted with water to certain times (namely, emulsion/H_2O 1/5, 10, 20, and 40, mL/mL) to provide a clear profile for UV absorption spectra. In the following investigations, the CD and UV spectra were recorded with the emulsion diluted with water (emulsion/water 1/20, mL/mL). More CD and UV absorption spectra are illustrated in Figure 3C,D. In Figure 3C, the four spectra correspond with the pure PSA particle and the three emulsions of core/shell NPs with varied MMA/SA ratios, that is, 5/1, 10/1, and 15/1 (mol/mol), respectively. More complex CD signals around 285 nm slightly weakened with an increase in the MMA concentration because of the gradually larger scattering effects caused by the thick shells, for which the appearance of the emulsions in Figure 1 offered support. A minor shoulder signal band appeared around 300 nm in the core/shell NPs. The reason for this result is not yet clear. The core/shell NPs still possessed large optical activities, as demonstrated by Figure 3 and the data in Table 1. The UV absorption at about 280 nm increased with the increase in MMA concentration. This should be attributed to the UV absorption of PMMA around the wavelength of 280 nm. It is further implied that by using MMA as the vinyl monomer with a suitable concentration, core/shell NPs with intense optical activities could be prepared.

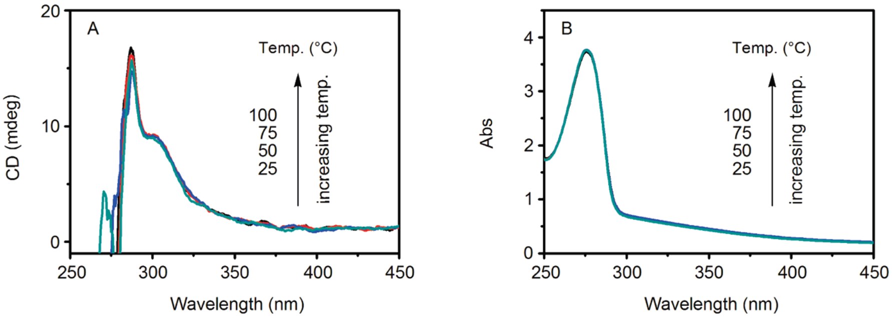

Figure 4. CD and UV spectra of the core/shell NPs with cross-linked MMA shells at various temperatures. Emulsion/water 1/20, mL/mL; SA/MMA 1/10, mol/mol; TMPTA/MMA 1/20, mol/mol.

Nanoparticles with Cross-Linked Shells. With the intriguing core/shell NPs in hand, the cross-linked shells with considerable rigidity, strength, and stability were successfully achieved by using TMPTA as a comonomer and a cross-linking agent simultaneously in the free radical polymerization step. The obtained core/shell particle emulsions were also quite stable, as evidenced by the picture in Figure 1D (TMPTA/MMA = 1/20 in mol/mol; the pictures for the emulsions of other TMPTA concentrations are presented in Figure S3 in Supporting Information). The TEM images are displayed in Figure 2G−I. The particles with cross-linked shells showed little difference from the non-cross-linked shells in core/shell NPs morphologies. Meanwhile, the size of the core and the thickness of the shells for the two cases differ negligibly, as shown by the data in Table 1. This is also true in CD and UV−vis spectra presented in Figure 3E,F. A comparison between the CD spectra in Figure 3E,C and the UV absorptions between Figure 3F,D led to a similar conclusion; that is, cross-linked shells and non-cross-linked shells scarcely affected the helical polymers constituting the cores.

For the PSA synthesized by traditional solution polymerization, it lost its helical structures by approximately 1/3, indicated by the dramatic decrease in the intense of CD effects upon increasing temperature of the polymer from −50 to 50 °C.[17a] On the contrary, for the present core/shell NPs emulsions, the CD and UV−vis spectra (Figure 4) exhibited little difference, even when the temperature was elevated from 25 to 100 °C. This indicates the high stability in the secondary structures of the substituted polyacetylene constituting the core of the NPs. Meanwhile, the NPs emulsions showed little difference after heating. The M_n and its M_w/M_n of PSA in NPs heated to different temperatures for 20 min were also examined. M_n and its M_w/M_n were found to be 10 800 and 1.71 (50 °C); 11 000, 1.76 (75 °C); and 11 000, 1.81 (100 °C), respectively, whereas they are 10 000 (M_n) and 1.68 (M_w/M_n) for the PSA in the core/shell NPs emulsion before heating. Accordingly, it is indicated that little degradation occurred to PSA inside the core of NPs. It is thus demonstrated that PMMA constituting the shell provided a protection for the PSA inside the NPs.

Conclusions

We have prepared a novel category of core/shell-structured NPs. Combining subsequential aqueous catalytic microemulsion polymerization and free radical polymerization in one aqueous system, nanoparticles consisting of intriguing cores and shells were obtained. The cores comprise helical polyacetyelens, whereas the shells consist of vinyl polymers cross-linked or not. Because of the interesting helical structures of the substituted polyacetylenes in the core, the whole nanoparticle exhibited large optical activities, and the shells built herein can remarkably increase the thermal stability of the secondary structures of PSA inside the core. We are convinced that by the same effective and flexible strategy, a series of novel nanoparticles could be prepared next. Such type of nanoparticles is of great importance not only from the viewpoint of scientific research because of the helical polymers in the core and the combination of different polymerization mechanisms in one polymerization system but also from the potential applications in particular originating from NPs chiropticities.

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Supporting Information Available: Photographs for the core/shell NP emulsions of varied MMA/SA ratios with and without TMPTA and UV−vis and CD spectra of PSA emulsion with SDS as the surfactant. This material is available free of charge via the Internet at http://pubs.acs.org.

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