Synthesis of Nano-Latex Particles of Optically Active Helical Substituted Polyacetylenes via Catalytic Microemulsion Polymerization in Aqueous Systems

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ABSTRACT: This article reports on the first catalytic microemulsion polymerizations of substituted acetylenes in aqueous medium, providing nanoscale particles exhibiting optical activities and consisting of helical polymers. Three types of substituted acetylenes—one achiral *N*-propargylamide, two chiral *N*-propargylsulfamides, and chiral *N*-propaygylurea—were polymerized in the presence of hydrophobic Rh-based catalyst and with SDS as emulsifier and DMF as coemulsifier. Such microemulsion polymerizations led to nanoscale particles (70–110 nm in diameter) of polymers adopting helical conformations. The particles derived from the chiral monomers showed large specific rotations and intense circular dichroism (CD) signals. The obtained polymer dispersions demonstrated high stability. The thus-prepared polymers after removing the emulsifier and coemulsifier showed much stronger CD signals, and the helices were found to have higher thermal stability when compared with the corresponding polymers synthesized via catalytic polymerizations in organic solvents. The microemulsion polymerizations enable the polymers to form predominantly one-handed helical structures. The possible mechanisms were proposed for the formation of optically active polymer particles, for the formation of predominantly one-handed helices, and for the increased thermal stability of the helices formed in the polymers.

Introduction

Conjugated polymers have been widely used in solar cells, photovoltaic devices, and organic light-emitting diodes.[1] Despite the enormous advances since the pioneering work on polyacetylene by Heeger, MacDiarmid, Shirakawa, and colleagues,[2] a majority of conjugated polymers still suffer from various intractable disadvantages, particularly the critical drawbacks of insufficient solubility and processability. Even though a limited success has been accomplished by for instance introducing substitutents[3] and grafting conjugated polymers to other polymers,[4] the desired properties of the targeted polymers are often weakened, and certain additional synthetic processes are generally required.

The preparation of conjugated polymers in the form of emulsion seems to be a viable alternative, as it not only circumvents the problems mentioned above but also renders aqueous dispersions environmentally benign. For some conjugated polymers other than polyacetylenes, e.g., polypyrrole, polythiophene, and polyaniline, their particles can be easily synthesized by oxidation–polymerization of the corresponding monomers in aqueous solution.[5] However, as far as monomers of acetylene and its derivatives are concerned, they have historically been catalytically polymerized.[6] Furthermore, most of the early transition catalysts (e.g., Ti- and Zr-based catalysts) are particularly ineffective in aqueous solution due to their high sensitivity toward water.[7] Accordingly, even though the concept of preparing and processing polyacetylene particle dispersions was put forward much early by Vincent et al.,[8] nearly all the dispersions at that time were prepared in organic solvents but not in aqueous medium. Nowadays, the development of late transition catalysts has rendered such polymerizations in water possible.[9] Nuyken and Buchmeiser et al.[10] and Mecking et al.[11] have recently synthesized polymer particles via catalyzed polymerizations in aqueous media. Moreover, in view of the importance and wide applicability of polymerization in aqueous media as clearly demonstrated by radical-initiated emulsion and dispersion polymerizations,[12] catalytic polymerizations in aqueous medium are drawing ever-increasing attention,[13] and the preparation of conjugated polymer latex is full of significance and interest.[14] However, to the best of our knowledge, nanometer-sized emulsion latex composed of ordered helical polymers and possessing a chiroptical activity have not yet been reported on. Such a novel type of latex would undoubtedly combine the desirable properties of polymer particles and those of polymers adopting ordered helical structures.

Design and synthesis of polymers with well-defined structures has always been one of the most active fields in polymer science.[15] By biomimicking the intriguing helical structures of naturally occurring biomacromolecules, e.g., proteins and DNA, a number of artificially helical polymers have been obtained.[16] We have recently synthesized a serious of helical substituted polyacetylenes: poly(*N*-propargylsulfamides),[17] poly(*N*-propargylureas),[18] and poly(*N*-propargylamides).[19] These interesting helical polymers possess significant potentials to be used in asymmetric synthesis, chiral recognition and resolution, polarizer devices, etc. However, these helical polymers unfortunately exhibited low solubilities, thus severely hampering any investigations with regard to their applications.

In the present report, we successfully polymerized four substituted acetylenes including two chiral *N*-propargylsulfamide monomers (monomers **1** and **2**), one chiral *N*-propargylurea (monomer **3**), and one achiral *N*-propargylamide (monomer **4**), as presented in Scheme 1, via catalytic microemulsion polymerization in aqueous medium. Particularly, the obtained nanolatex particles showed high optical activities; the polymers constituting the particles adopted ordered helical structures just as anticipated, and moreover, the thermal stability of the helices was largely improved as compared to the corresponding polymers synthesized in organic solvents. Therefore, the present study not only developed a straightforward route to prepare latex

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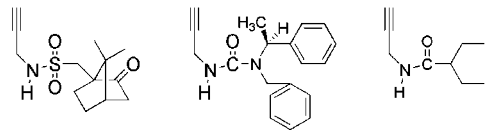
Scheme 1. Chemical Structures of Investigated Monomers



Monomer **1** (*S*)
Monomer **2** (*R*)
Monomer **3** (*R*)
Monomer **4**

particles composed of helical polymers but also opened a facile, novel approach to improve the thermal stability of the helical structures adopted by the polymers, which had ever been an intractable task and only realized to a limited degree by introducing bulky pendent groups onto the polymer backbones.[19c,d]

Results and Discussion

On the basis of our previous studies[17−19] and referring to the investigations from others,[20] rhodium (Rh)-based catalysts are obviously advantageous over other catalysts in terms of preparing acetylene-based polymers with high stereoregularity. Furthermore, Rh-based catalysts have been proved still effective and highly efficient in initiating the polymerization of acetylene monomers in water.[21] Yashima and co-workers[21a] have successfully polymerized acid-functionalized alkynes in aqueous solution with three different Rh-based complexes: $[Rh(cod)_2BF_4]$ (cod = 1,5-cyclooctadiene), $[Rh(nbd)_2]ClO_4$ (nbd = norbornadiene), and $Rh(cod)(tos)(H_2O)$ (tos = tosylate). These three complexes are reported to be water-soluble. Accordingly, oil-soluble $[(nbd)Rh^+B^-(C_6H_5)_4]$ and water-soluble $[Rh(cod)_2BF_4]$ Rh catalysts were both examined herein, but only the former was found to be highly effective under the conditions in the present research. Thereby, the former was employed in all the subsequent polymerizations in aqueous emulsion.

Sodium dodecyl sulfate (SDS) and dimethylformamide (DMF) were used as emulsifier and coemulsifier, respectively, to form the monomer micelles in water. The investigated monomers are presented in Scheme 1. A certain amount of SDS was first dissolved in water, to which a monomer/DMF solution was added to form the monomer microemulsion. Subsequently, the catalyst/DMF solution was added dropwise to the system above, and the monomers underwent polymerization at 30 °C. No precipitation of monomer or catalyst was observed. The change in appearance of the polymerization system demonstrated the occurrence of emulsion polymerization. Initially, the reaction system was colorless and transparent; shortly after adding the catalyst, monomers underwent polymerization, which can be confirmed by the color change of the reaction system, i.e., from a colorless solution to an emulsion with slight fluorescence. As the polymerization proceeded further, the emulsion exhibited a unique appearance, as illustrated in Figure 1.

Polymerizations of all the four monomers proceeded smoothly. After 3 h of polymerization, the conversion percentage for all the monomers exceeded 85%, demonstrating that the Rh-based catalyst was indeed highly effective in initiating the polymerizations. Compared with the polymers previously obtained in organic solvents,[17a,18,19d] the present polymers showed higher average molecular weight (M_n) and narrower molecular weight distribution (M_w/M_n). The relevant data are presented in Table 1. The stereoregularity of the polymer main chains was determined by measuring the ^{1}H NMR spectra; however, the involved signals were too broad to provide exact data even at high temperatures. This is similar to the results for the polymers synthesized in organic solvents.[17a,18,19d] Raman spectra were further measured on the resulting polymers, and all of the materials were found to possess high cis contents (≥98%).

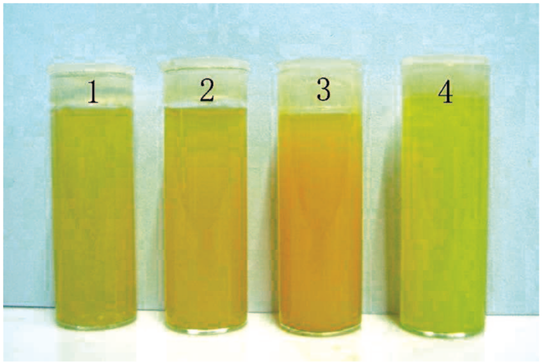


Figure 1. Emulsions of polymers **1**−**4** with different colors.

Table 1. Characteristic Data Concerning the Microemulsion Polymerization of Monomer 1[a]

monomer **1**/SDS [mol/mol]	molecular weight M_n[b]	M_w/M_n[b]	particle diameter[c] [nm]	appearance
1/1[d]				precipitation
1/2[d]				precipitation
1/3	16 800	1.21	103.1	emulsion
1/4	16 000	1.25	101.9	emulsion
1/5	16 450	1.22	102.2	emulsion
1/6	16 900	1.22	45.2	emulsion

[a] Monomer concentration, 5×10^{-2} M; catalyst concentration, 1×10^{-3} M; DMF:H_2O, 2:18 v/v (mL); temperature, 30 °C; polymerization time, 3 h. [b] Determined by GPC (polystyrenes as standards; THF as the eluent). [c] Obtained according to TEM. [d] A homogeneous emulsion could not be obtained.

Table 2. Characteristic Data Concerning the Microemulsion Polymerization of Monomers 2−4[a]

monomer	molecular weight M_n[b]	M_w/M_n[b]	particle diameter[c] (nm)	appearance
2	16 400	1.28	103.1	stable emulsion
3	14 400	1.28	70.7	
4	27 700	1.61	106.3	

[a] Monomer concentration, 5×10^{-2} M; catalyst concentration, 1×10^{-3} M; DMF:H_2O, 2:18 v/v (mL); temperature, 30 °C; polymerization time, 3 h. [b] Determined by GPC (polystyrenes as standards; for **2** and **4**, THF as the eluent; for **3**, $CHCl_3$ as the eluent). [c] Obtained according to TEM.

The content of SDS had a large influence on the stability of the resulting emulsions, on the particles' diameters, and on the size distribution of the particles (Tables 1 and 2). Taking monomer **1** as an example, a monomer/SDS ratio of 1/1 and 1/2 (mol/mol) led to the polymerization taking place but no homogeneous emulsion being obtained. In other words, an obvious precipitation was found in the resulting emulsions. When the monomer/SDS ratio was changed to 1/3, 1/4, 1/5, and 1/6, stable nanosized particle dispersions were formed. For polymers **1**−**4**, the average size of the particles was approximately 102, 103, 71, and 106 nm (with monomer/SDS = 1/5, mol/mol), and typical TEM images of the four polymer emulsions are presented in Figure 2. The so-obtained emulsions were relatively stable as very little change was observed in the emulsions after they having been stored at ambient temperature for 1 month, and for some emulsions they remained stable even for 6 months and above.

The emulsions of polymer **1** were subjected to CD and UV−vis spectroscopy measurement to investigate the optical activity of the resulting latex particles. Hardly any differences in UV absorption could be seen in the presence vs absence of SDS (Figure 3A), while the CD signal, on the other hand, demonstrated a slight blue shift in the presence of SDS (Figure 3B). After polymerization, obvious changes could be observed in UV−vis absorptions (Figure 3C) and CD signals (Figure 3D),

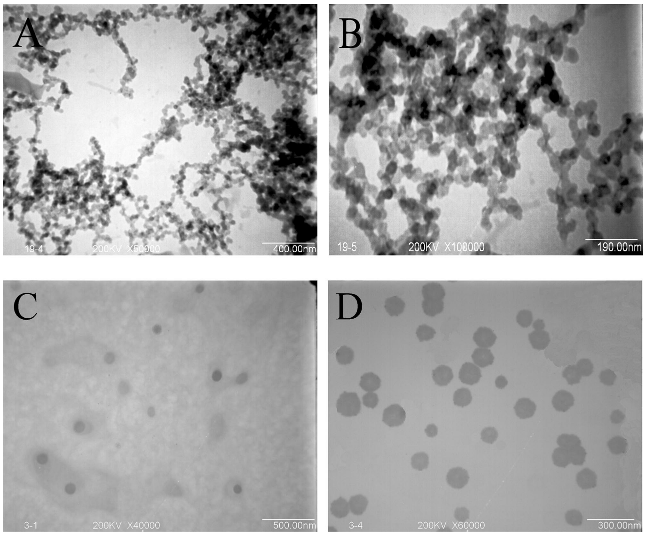


Figure 2. TEM image of the emulsion of polymer **1** (A: monomer **1**/SDS = 1/5, mol; B: monomer **2**/SDS = 1/6, mol; C and D: monomer **3** and **4**/SDS = 1/5, mol).

both of which appeared around 325 nm. In comparison to the corresponding polymer **1** whose maximum UV absorption and CD signal appeared around 410 nm (cf. ref 27 and Figure 4), considerable blue shifts from about 410 to 325 nm were observed; in particular, much stronger CD signals with the same sign were apparent from Figure 3D, as opposed to Figure 3B. The blue shifts were attributed to the highly packed polymer chains and their reduced effective conjugation length inside the latices. The stronger CD signals were the results of an "amplification effect" frequently observed in artificially helical polymers.[22] In aggregates of chiral polymers considerable blue shifts and larger CD signals have been observed as opposed to those for molecularly dispersed systems.[23] Additionally, "small size effects"[24] frequently seen in the nanometer range should also be partly responsible for the blue shifts. According to our earlier studies on the same type of helical polymers,[17−19] the high CD signal intensity in Figure 3D strongly indicated that the particles possessed high chiroptical properties resulting from the ordered helical structures of the polymer chains. Specific optical rotations ($[\alpha]_D$) listed in Table 3 also provided a significant support for this conclusion.

According to our earlier investigations,[17,18] chiral polymers **1**−**3** can form helices under suited conditions, and moreover, the helices have predominantly one-handed screw sense. The three polymers thus perform optical activity, based on their CD spectra. Accordingly, the secondary structures of the polymers prepared via the present microemulsion polymerizations were investigated by UV−vis absorption and CD spectroscopies. After excluding the residual monomer, emulsifier, and coemulsifier by centrifugal separation, the polymer particles were collected and dissolved in a suited organic solvent to measure CD and UV absorption spectra. It is proved that all the three chiral polymers (polymers **1**−**3**) can form stable helical conformations and possessed optical activities. Figure 4 gives the CD spectra of polymer **1** as a representative.

Figure 4 demonstrates that the intensities of the UV−vis absorptions of the present polymers exhibited a slight difference, but the temperature sensitivity of the UV absorption bands decreased largely, when compared with those of the corresponding polymers prepared through solution polymerization.[17] CD signals showed more considerable differences. Stronger CD signals were observed in the present polymers. More interesting, the CD signals changed little when the temperature was elevated from 20 to 90 °C. Referring to our earlier investigations,[17−19] CD signals of polymer **1** at about 410 nm reflect the helical structure adopted by the polymer main chains. The slight change upon increasing temperature clearly demonstrated the high thermal stability of the helices. For polymer **1** synthesized in organic solvent, it lost its helical conformation by approximately 1/3 when the temperature increased from −50 to 50 °C,[17a] while in Figure 4, even when the temperature was elevated up to 90 °C, the intensity of the CD signals changed little, apparently demonstrating the polymers prepared via emulsion polymerization form thermally stable helices. The variations in the CD intensities in Figure 4 are assumed to be originated in the different particle sizes and the different packing degrees of the polymer chains inside the lattices.

Like polymer **1**, helices were also observed in polymers **2** and **3**, and the obtained CD signals were also much stronger than those observed in the corresponding polymers prepared via solution polymerization in organic solvents.[17,18] Regarding polymer **4**, it formed helices with higher thermal stability than the corresponding one synthesized in organic solvent,[19d] but both of them could not demonstrate optical activity due to the same amount of right- and left-handed helices. It is accordingly reasonable to conclude that microemulsion polymerization allow the resulting polymers to form thermally stable helices. The possible reason for this will be stated below. In addition, considering the unique colors of the resulting polymer emulsions mentioned above, it is indicated that the latex particles comprise polymer molecules in ordered helical structures.

Referring to the microemulsion polymerizations initiated by free radicals in aqueous media[25] and considering the insolubility of the present solid monomers and catalyst in water, monomer-swollen micelles should be the principal loci for polymerization. In the present microemulsion polymerizations catalyzed by Rh catalyst, a possible mechanism for the particles formation involves three major steps: the formation of monomer/SDS/DMF micelles, the penetration of catalyst into the micelles, and the polymerization of monomers inside the micelles. Since both the substituted acetylene monomers and the Rh-based catalyst were hydrophobic, they cannot exist stably in water medium by themselves. During the first step, monomer molecules were surrounded by SDS/DMF molecules, and stable micelles were generated. When the catalyst/DMF solution was added, catalyst molecules could not remain in the DMF solution but penetrated into the afore-formed micelles from the DMF solution. Then under the catalysis of the catalyst, monomers underwent polymerization inside the micelles. Along with the polymerization, the micelles grew larger and more SDS was required to keep the particles stable. This process is entirely different from that one proposed by Mecking et al.[11a] In their research, catalyst formed miniemulsion droplets first, into which acetylene molecules distributed and then polymerization occurred therein. The relevant mechanism for the formation of optically active nano-latex particles in the present research is schematically shown in Scheme 2, in which polymerizations A and B lead to latex particles consisting of optically active helical polymers (polymers **1**−**3** in the present investigations) due to the formation of predominantly one-handed helical strucutres, while polymerization C results in latex particles consisting of helical polymers but without optical activity (polymer **4**), due to the equal amounts of right- and left-handed helices formed by the polymer main chains.

Inside the resulting micelles in the present polymerizations, only monomer and catalyst were present. Therefore, the polymerization can be taken as a "microscale bulk polymerization". Without the influence of solvents and/or other factors, the monomers were prone to polymerize in the same pattern. Accordingly, fewer turning points were formed in the polymer chains synthesized by the emulsion polymerization than those

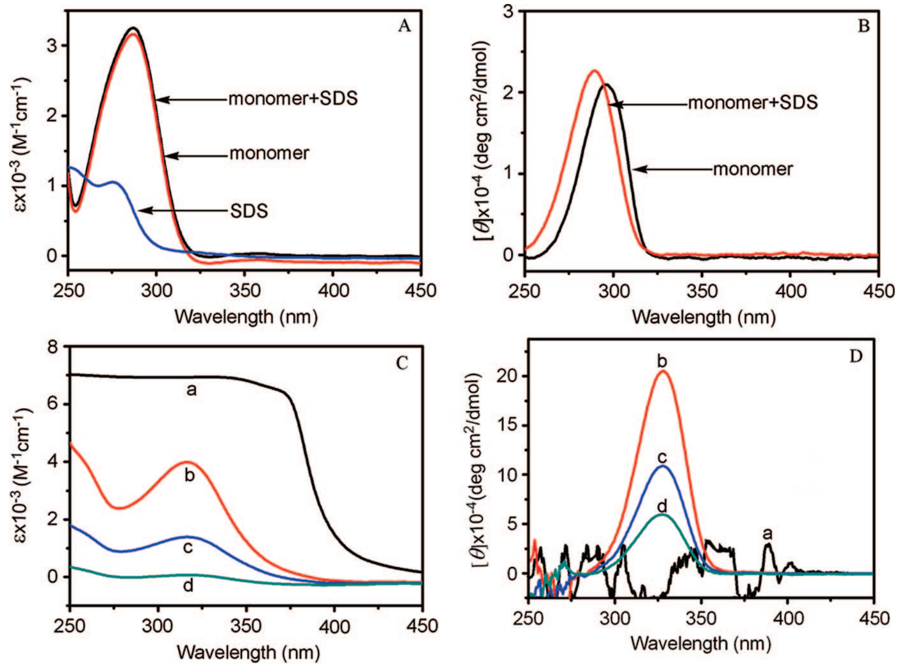


Figure 3. UV−vis and CD spectrum of monomer **1** (A and B: with $CHCl_3$ as solvent; monomer concentration, 0.04 M), monomer **1**/SDS emulsion before (A and B: monomer concentration, 0.04 M; SDS/monomer, 5/1, mol/mol) and after (C and D) polymerization. In (C) and (D), the original emulsion was diluted with water by emulsion/water (v/v): a, 1/0; b, 1/10; c, 1/20; and d, 1/40. The spectra were recorded at 25 °C.

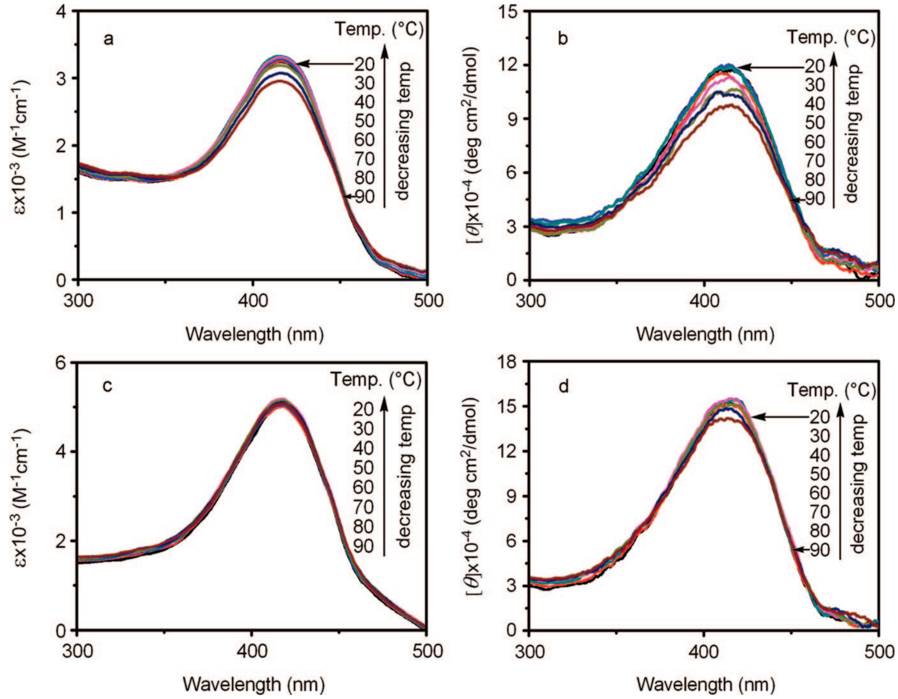


Figure 4. UV−vis and CD spectra of polymer **1** obtained via microemulsion polymerization with varied monomer/SDS ratios: a and b, 1/3; c and d, 1/5 (mol/mol). For detailed polymerization conditions, refer to Table 1.

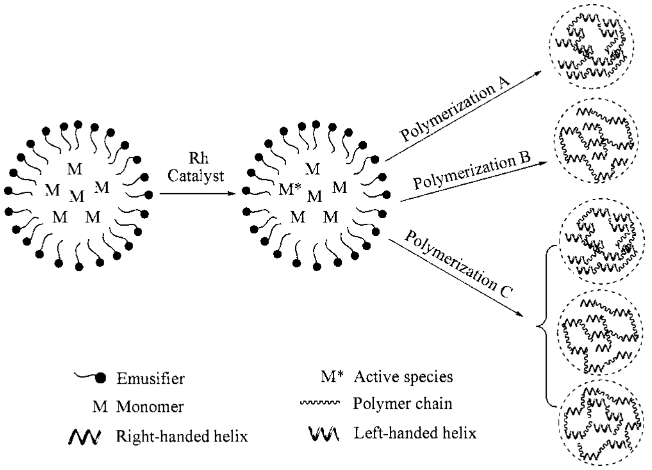
Table 3. Specific Optical Rotations ($[\alpha]_D$, deg) of Monomer 1, of the Monomer 1/SDS System before and after Polymerization, and of Polymer 1

microemulsion polymerization[a]				
monomer	microemulsion before polymerization	emulsion after polymerization	polymer	ref polymer (by solution polymerization)[b]
−31	−28	+1026	+2899	+1500

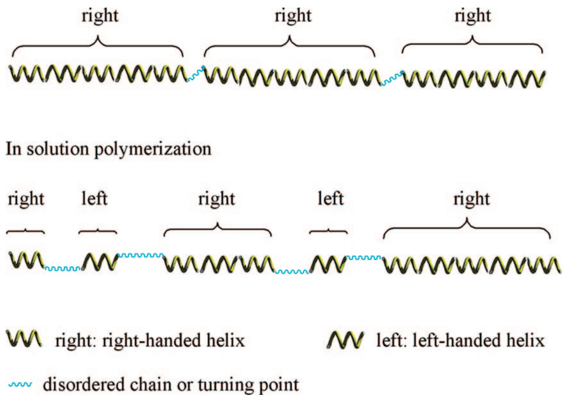
[a] Microemulsion polymerization: monomer/SDS = 1/5 (mol); $[\alpha]_D$ of the emulsion before and after polymerization was measured in water with the same concentration, and $[\alpha]_D$ of the monomer and polymer was measured in toluene, with $c = 0.080{-}0.1$ g/dL. [b] Polymerization of monomer **1** in toluene for comparison.

by typical solution polymerizations, as depicted in Scheme 3. The term “turning points” in Scheme 3 refer to some special chain segments, before and after which the chain segments have different secondary structures, i.e., right-handed helix, left-

Scheme 2. Proposed Mechanism for the Formation of Latex Particles with Optically Active Helical Polymers (Polymerization A and B) or Helical Polymers (Polymerization C)



Scheme 3. Proposed Mechanism for the Higher of Helical Contents and Much Stable Thermal Properties about Helical Polymers via Emulsion Polymerization Compared with Solution Polymerization



handed helix, and/or disordered polymer chain segments. In microemulsion polymerization, the polymer chains have fewer such turning points when compared to the corresponding polymers obtained via solution polymerization, and thereby the polymer chains of the former tend to take the same helical handedness while forming helical structures. Similarly, the fewer turning points enable the polymer chains to be less sensitive to heating. The lower content of turning points and/or disordered structures are assumed to be most likely responsible for the high CD signal intensity in the polymers and the high thermal stability of the formed helices, which have been discussed in detail above. This also illustrates the effect of micellar "nanoreactors"[26] existing in microemulsion polymerization systems.

Conclusion

We have succeeded in preparing stable emulsions of substituted polyacetylenes via catalytic microemulsion polymerization in water; more importantly, the nano-latex particles consisted of polymers adopting ordered helical structures. Compared with the polymers synthesized in organic solvent, the polymers synthesized via microemulsion polymerization showed a higher preference of one-handed screw sense in forming helical structures, and the helices were much more stable against thermal. We have elaborated the first synthetic protocol that allows the preparation of conjugated polymer particles consisting of polymer chains taking stable helical conformations. The present investigations are not only important in solving the problems of low solubility and low processability of monosubstituted polyacetylenes but also offer a novel and facile approach to improve the thermal stability of the helical structures adopted by polyacetylene main chains. We are strongly convinced that the novel particles composed of helical polymers are of very considerable potential applications, and the findings presented herein are opening up a new field of polyacetylenes. Extended experiments focusing on controlling the particle size and chiroptical property of the new class of materials are currently underway.

Experimental Section

Materials. The solvents were distilled under reduced pressure under a N_2 atmosphere in advance. Deionized water was used for the polymerization. 1*S*-(+)-10-Camphorsulfonyl chloride, 1*R*-(−)-10-camphorsulfonyl chloride, (*R*)-(+)-*N*-benzylmethylbenzylamine, 2-ethyl-*n*-butyric acid, propargylamine, bis(trichloromethyl)carbonate, sodium dodecyl sulfate (SDS), and Rh-based catalyst $[Rh(cod)_2BF_4$: cod = cyclooctadiene], all purchased from Aldrich, were used as received without further purification. $(nbd)RhB(C_6H_5)_4$ was prepared according to a procedure reported elsewhere.[27]

Measurements. ^{1}H NMR measurements were performed on a Bruker AV600 spectrometer, and IR spectra were recorded with a NICOLET NEXUS 670 infrared spectrometer. Circular dichroism (CD) and UV−vis absorption experiments were conducted on a Jasco 810 spectropolarimeter. The molecular weights and molecular weight polydispersities of the polymers were determined by GPC (Shodex KF-850 column) calibrated by using polystyrenes. Emulsion particle and particle size distribution data were recorded on a laser particle size analyzer (ZETA SIZER Nano series, zen3600). 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.

Synthesis of Monomers and Polymer Emulsions. Monomers were synthesized according to previous reports: monomers **1** and **2**,[17] monomer **3**,[18] and monomer **4**.[19d]

Taking monomer **1** as an example, the typical polymerization procedure was the following: a 50 mL glass reactor equipped with a reflux condenser, a stirrer, an N_2 inlet, and a dropping funnel was first deoxygenated by purging with N_2 for 30 min. Predetermined amounts of SDS (1.44 g, 0.25 M) and deionized water (~18 mL) were added to the reactor. The water had been deoxygenated for 30 min in advance. The aqueous solution was stirred with a stirring rate of 350 rpm for 15 min at 30 °C to ensure the complete dissolution of SDS dissolve completely, after which the solution of monomer **1** (0.269 g, 50 mM)/DMF (1 mL) was dropwise added to the SDS aqueous solution. The solution mixture was subsequently stirred for 10 min (350 rpm), and the catalyst (0.006 g, 0.6 mM)/DMF (1 mL) solution was dropwise added to the monomer system. The drip speed was ~40 drops/min. After all of the catalyst solution had been added, the stirring speed was reduced to ca. 300 rpm/min, and the polymerization was performed under N_2 at 30 °C.

In order to acquire pure polymer particles, SDS was repeatedly excluded by centrifugation, and a rotary evaporator was used to remove the water that was present in the emulsion. Subsequently, $CHCl_3$ was charged to the residual product, and stirring was performed at room temperature for 10 min. This process was repeated at least three times. The $CHCl_3$ polymer solution was dried and concentrated to give the target polymer.

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