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Applications of telechelic polymers as compatibilizers and stabilizers in polymer blends and inorganic/organic nanohybrids[☆]

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Abstract

We report new application fields of telechelic polymers synthesized via chain-end functionalizations of living polymers readily prepared from anionic polymerizations using lithium naphthalenide. The molecular weights of functionalized polymers were controlled in the range of 2000–50,000 g/mol. The functionalization yields were over 98 mol% on the basis of the results by ^{1}H NMR analysis. Among several telechelic polymers, dilithium α,ω-disulfonated polystyrene could be used as an efficient compatibilizer to control the morphologies of the polystyrene/nylon 6 or the polystyrene/poly(ethylene terephthalate) blend systems through the ionic-dipole interaction mechanism. All telechelic polymers carrying hydoxylate, carboxylate, sulfonate, and thiol groups were successfully used as the polymer stabilizers for preparation of nano-sized cadmium sulfide (CdS) semiconductor in the range of 5–30 nm.

Keywords: Anionic polymerization; Telechelic polymers; Compatibilizers

1. Introduction

Recently, functionalized polymers have received a great attention in academic as well as industrial field because of its variety of applications [1–3]. One of the important applications of functional polymers is that those can be used as the compatibilizers to control the morphology and the phase size affecting the physical property of the polymer blends. The morphology control of the polymer blends may be achieved by the reduction of the interfacial tension between different polymeric materials using proper compatibilizers [4]. In this respect, functionalized polymers are expected to be useful to control the interfacial tension of the polymer blends between non-polar polymers and polymers having the polar groups such as the amide or ester groups. Chain-end functionalizations of living polymers prepared via anionic polymerization can provide the best methodology to obtain a variety of telechelic polymers [5,6]. Specifically, the authors have reported the efficient route to synthesize dilithium α,ω-disulfonated polystyrene [7].

Ligand-capped metal and semiconductor nanoparticles have been utilized in a variety of important application fields [8–11]. Functional polymers including polyelectrolyte or block copolymers have been well-known to be used as the excellent capping or stabilizing materials in the nanotechnology field [8–11]. In this respect, chain-end functionalized polymers may be applied for the preparation of nano-sized transition metals or semiconductor particles.

In this communication, the results for successful applications of telechelic polymers as polymer compatibilizers or stabilizers both in the polymer blend systems and in the nanotechnology field to prepare semiconductor cadmium sulfide (CdS) nanocomposites are reported.

[☆] Supplementary data associated with this article can be found in the online version of this paper.

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2. Experimental section

2.1. Materials

All the experiments to synthesize terminally functionalized polymers were carried out under a high vacuum. Styrene (KANTO Chem. Co., reagent grade) was purified as described in the literature [12]. Benzene (Dong Yang Chem. Co., reagent grade) and tetrahydrofuran (THF; Dong Yang Chem. Co., reagent grade) were also purified by following the procedures as described in the literature [12]. Degassed methanol (Dong Yang Chem. Co., reagent grade) ampoules were made in the high vacuum line prior to use. *n*-Butyllithium (*n*-BuLi; Aldrich Chem. Co., 1.6 M in hexane) was used as an initiator without further purification after the titration following the Gilman's color testing procedures using dibromobenzene [13]. Lithium naphthalenide was prepared by following the procedures described in the literature [7]. Ethylene oxide (DaeHan Gas Co., 99%) and ethylene sulfide (Aldrich Chem. Co., 98%) were purified by following the modified procedures described in the literature [6,14,15]. 1,1-Diphenylethylene (1,1-DPE; Aldrich Chem. Co., 97%) was stirred over Na–K alloy with degassing, followed by vacuum distillation into calibrated ampoules and dilution with benzene. 1,3-Propanesultone (Aldrich Chem. Co., 99%) was dried and degassed on the vacuum line, followed by dilution with benzene or THF. Carbon dioxide (CO_2; ShinYang Gas Products, 99.99%) was used without further purification.

2.2. Synthesis of telechelic polymers

All the reactions were performed in all-glass, sealed reactors, using break-seals and standard high vacuum techniques [12]. Anionic polymerization of styrene using lithium naphthalenide as a difunctional anionic catalyst was carried out in benzene/THF (20/1, v/v) at 25 °C for 24 h. After completion of polymerization, the known concentration of five aliquots of the α,ω-dilithiopolystyrene were taken; one of them was terminated with degassed methanol to produce homopolystyrene. The other aliquots were used for the preparation of telechelic polymers by reaction with the specific terminating agents following the modified procedures described in the literatures, respectively [14–16]. All the substances were precipitated in excess volume of methanol, followed by hydrolyzing and drying in vacuum at 25 °C for at least 48 h.

2.3. Use in polymer blends

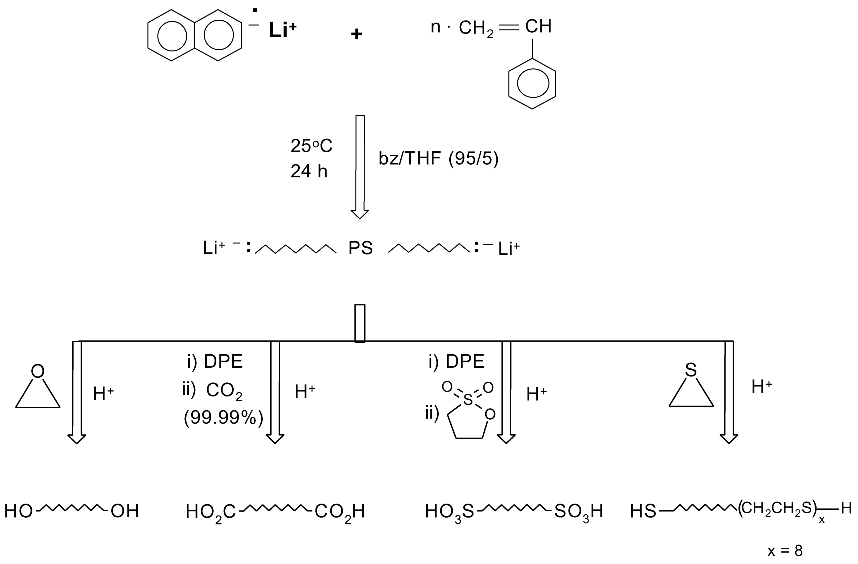
Dilithium α,ω-disulfonated polystyrene was used as a compatibilizer in the polymer blend systems between polystyrene (GPPS: HanNam Chem. Co.; $M_w = 290,000$) and nylon 6 (KOLON Co., $M_w = 51,000$) or poly(ethylene terephthalate) (PET: KOLON Co., $M_w = 52,000$). Melt blending of the mixture of polystyrene (60 part), nylon 6 (40 part), and α,ω-dilithium polystyrene disulfonate polystyrene (α,ω-sPS; 2 part) with $M_n = 8000$ was performed at 240 °C using an internal mixer (Brabender with mixing head W50E) with a 26 rpm of speed. The phase change of the above blend system was observed with mixing time. Analogously, melt blending of the mixture of PET/GPPS/α,ω-sPS was also performed at 255 °C.

2.4. Preparation of nanocluster CdS

Specifically, dilithium α,ω-difunctionalized polystyrenes in the range of molecular weight of 2500–3300 as synthesized in Scheme 1 were first hydrolyzed by the reaction with 1.0 N HCl/THF at room temperature for 24 h, followed by drying them at 50 °C for at least 48 h. 0.1 g of each telechelic polymer was dissolved in 10 ml of the mixture of toluene/methanol (80/20, v/v) using a 25 ml of vial. 1.0 g of cadmium acetate dihydrate ($CdAc_2 \cdot 2H_2O$: Aldrich Chem. Co., 98%) was also dissolved in 10 ml of the mixture of toluene/methanol. 1.7 ml of the Cd salt solution was delivered into the polymer solution vial, followed by adding 40 ml of H_2S using a syringe and covering each vial with stirring for 24 h.

2.5. Characterization

Size exclusion chromatographic (SEC) analysis of homopolystyrene was performed at a flow rate of 1.0 ml/min in THF at 30 °C using the Waters HPLC component system with five Ultrastyrygel® columns (10^6, two 10^5, 10^4, and 10^3 Å) after calibration with standard polystyrene samples (Polymer Lab.). SEC analysis of dilithium α,ω-difunctionalized polystyrenes was carried out by using a ternary solvent as the eluent as described in the literatures [6,7]. The ternary solvent consisted of a mixture of 10/1 (v/v) of THF-dimethylformamide (DMF; Fischer Scientific Co., reagent grade; without further purification) containing 2 g/l of $LiNO_3$ after calibration with standard samples. ^1H NMR spectroscopic analysis of the polymer samples was performed using a Varian Gemini-200 spectrometer with $CDCl_3$ as solvent. The morphology change of the polymer blends was observed through scanning electron microscopic analysis (Hitachi S-510 at 10–15 kV) after the PS phase from the freeze-fractured polymer blends was extracted by using toluene or after the PA 6 minor phase was extracted by allowing the freeze-fractured specimens to sit in formic acid at room temperature for 1 h. The normalized force was measured by the rheometric dynamic spectrometer (RDS; Rheometrics, Inc). The size of the CdS nanoclusters was analyzed by using transmission electron (TEM, Philips CM).



Scheme 1.

3. Results and discussion

3.1. Synthesis of telechelic polystyrenes

Chain-end functionalizations of polymeric organolithium compounds using a variety of electrophiles leading to the production of the corresponding telechelic polymers have been well described in the literatures [2,5]. Practically, the synthesis of telechelic polystyrenes was performed by chain-end functionalizations of α,ω-dilithiopolystyrene first synthesized by lithium naphthalenide as shown in Scheme 1. All the number average molecular weights were in the range of 2000–50,000 g/mol. The functionalization yields ($f > 1.96$) were over 98 mol% based on ^{1}H NMR spectroscopic analysis. Fig. 1 shows a comparison of size exclusion

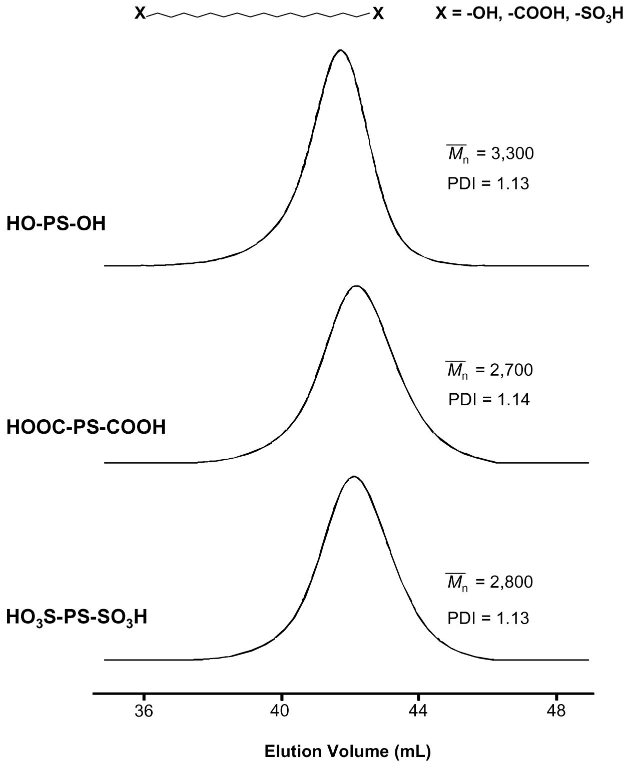


Fig. 1. Size exclusion chromatograms of α,ω-difunctionalized polystyrenes using a ternary solvent as the eluent consisting of THF–DMF (10/1, v/v) containing 2 g/l of $LiNO_3$.

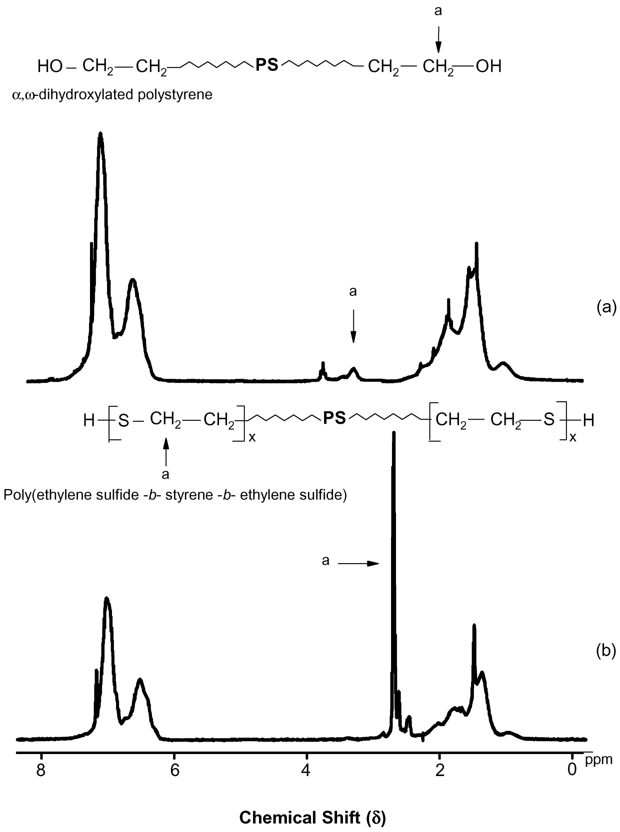
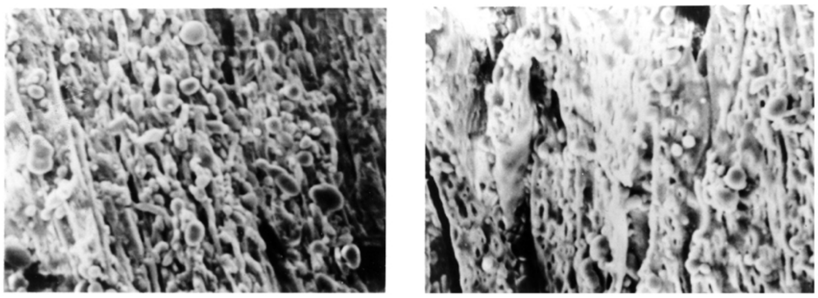
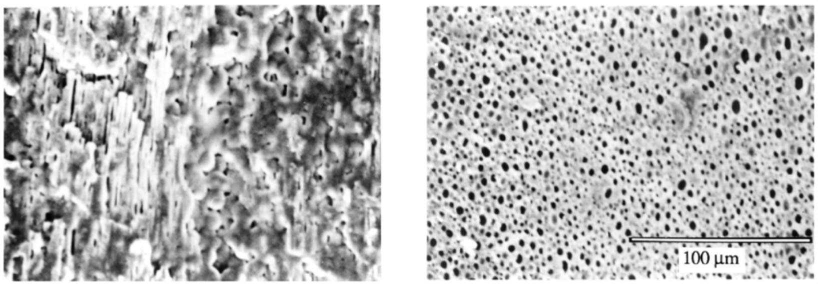


Fig. 2. ^{1}H NMR spectra of α,ω-dihydroxypolystyrene and poly(ethylene sulfide-*b*-styrene-*b*-ethylene sulfide).



(a) after 2 min (b) after 5 min



(c) after 10 min (d) after 20 min

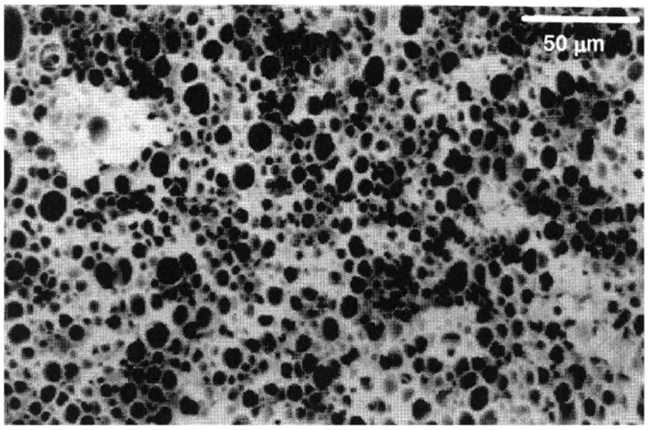
Fig. 3. The change of morphology of the PS/Nylon 6/α,ω-sPS (60/40/2, wt%) blend with mixing time in an internal mixer (all photographs have the same magnitude as that of the (d) case).

chromatograms of telechelic polystyrenes exhibiting the single molecular weight distributions. On the basis of this result, the functionalized polymers seemed to be successfully synthesized in this experiment.

Fig. 2 represents the typical ^{1}H NMR spectra of α,ω-dihydroxylated polystyrene and poly(ethylene sulfide-*b*-styrene-*b*-ethylene sulfide) synthesized from the crossover reaction of α,ω-dilithiopolystyrene with ethylene oxide and ethylene sulfide, respectively. The mechanism on the poly(ethylene sulfide) chain formation in alkyllithium-initiated polymerization of ethylene sulfide has been well described in the literature [15]. With this regard, the production of dilithium α,ω-dithiolated poly(ethylene sulfide-*b*-styrene-*b*-ethylene sulfide) from the reaction of α,ω-dilithiopolystyrene with ethylene sulfide was unavoidable in this experimental condition. Concerning the chemical shift at 2.7 ppm assigned to the protons on the methylene carbons adjacent the sulfur atom ($-\mathrm{C}H_2-\mathrm{S}-$), the production of the triblock copolymer could be confirmed. However, the other telechelic polymers carrying dihydroxylate, dicarboxylate, and disulfonate groups can be prepared quantitatively.

3.2. Polymer blends

Functionalized polymers can be used as the compatibilizers to reduce the interfacial tension of the polymer blends between polar polymer and non-polar polymer via an ionic-dipole interaction mechanism. In this respect, dilithium α,ω-disulfonated polystyrene (α,ω-sPS) is expected to be used as a polymer compatibilizer in the polystyrene/nylon 6 or the polystyrene/poly(ethylene terephthalate) system. Practically, melt blending of polystyrene (60 parts) and nylon 6 (40 parts) using α,ω-sPS compatibilizer ($M_n = 8000$; 2 parts) was performed at 240 °C. The photographs shown in Fig. 3 present the morphology change of the polymer blend with mixing time. The morphologies from the early mixing stage to 10 min indicated that this blend consisted of the dispersed nylon 6 domains and the polystyrene main matrix even using the α,ω-sPS as shown in Fig. 3(a)–(c). The occurrence of the phase inversion as shown in Fig. 3(d) was observed clearly in a limited mixing range (over 20–30 min) leading to the formation of disperse phase of polystyrene in the main matrix of nylon 6. This means that a large amount of polystyrene (60 parts) was rather dispersed into the small amount of nylon 6 (40 parts). Interestingly, when the mixing time at 240 °C was over 25 min, the morphology could not be controlled even in this blending system. This morphology change must arise from an inverse micellization by the α,ω-sPS carrying the strong polar sulfonate group under a specific condition. As shown in Fig. 4, the normalized



PS/PA6/α,ω-SPS (60/40/2)

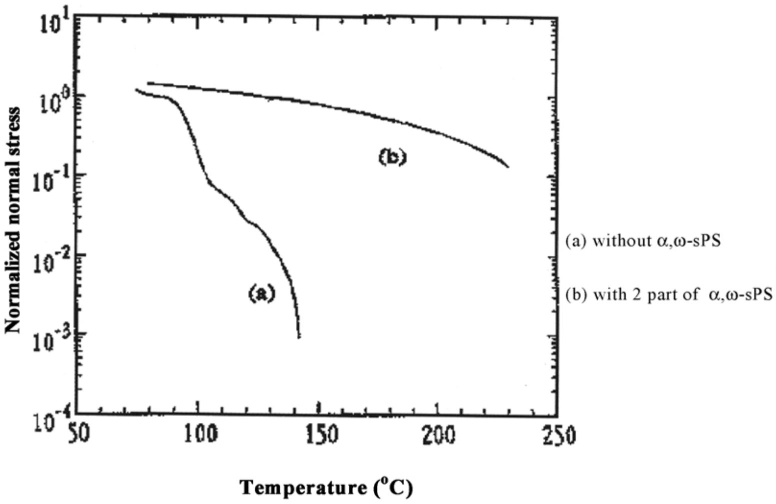


Fig. 4. The morphology of the PS/nylon 6/α,ω-sPS (60/40/2, wt%) blend controlled for 20 min of mixing time and the comparison of heat distortion temperature of the PS/nylon 6 (60/40, wt%) with α,ω-sPS and the corresponding blend without α,ω-sPS.

force by the RDS measurement of the blend system with α,ω-sPS presenting the interesting morphology (upper) seems to be analogous to that of the corresponding plain nylon 6. However, the normalized stress change against temperature of the plain blend system without α,ω-sPS shows totally different force change as shown in Fig. 4 (below). Analogous results were observed from melt-blending of the polystyrene/PET/α,ω-sPS system except for the mixing time. Telechelic polymer carrying a strong polar group such as the sulfonate group must be an efficient compatibilizer for controlling the morphologies of the blending systems between non-polar and polar polymers via ionic-dipole interaction mechanism. Therefore, it can be concluded that the physical properties of the polymer blend systems may be improved synergistically depending upon processing conditions such as the change of mixing time and the concentration of the specific compatibilizers used.

3.3. Preparation of CdS nanocomposites

Functional polymers were found to be used as the effective stabilizers for preparation of transition metal and semiconductor nanoclusters [8–11]. In this respect, telechelic polystyrenes as functionalized polymers synthesized in Scheme 1 are expected to be used as the polymeric stabilizer to prepare semiconductor cadmium sulfide (CdS)/polymer nanocomposites. Practically, Fig. 5 represents the change of chromophores of the telechelic polymer-stabilized CdS nanocomposites prepared in the mixture of toluene/methanol (80/20, v/v). Poly(ethylene

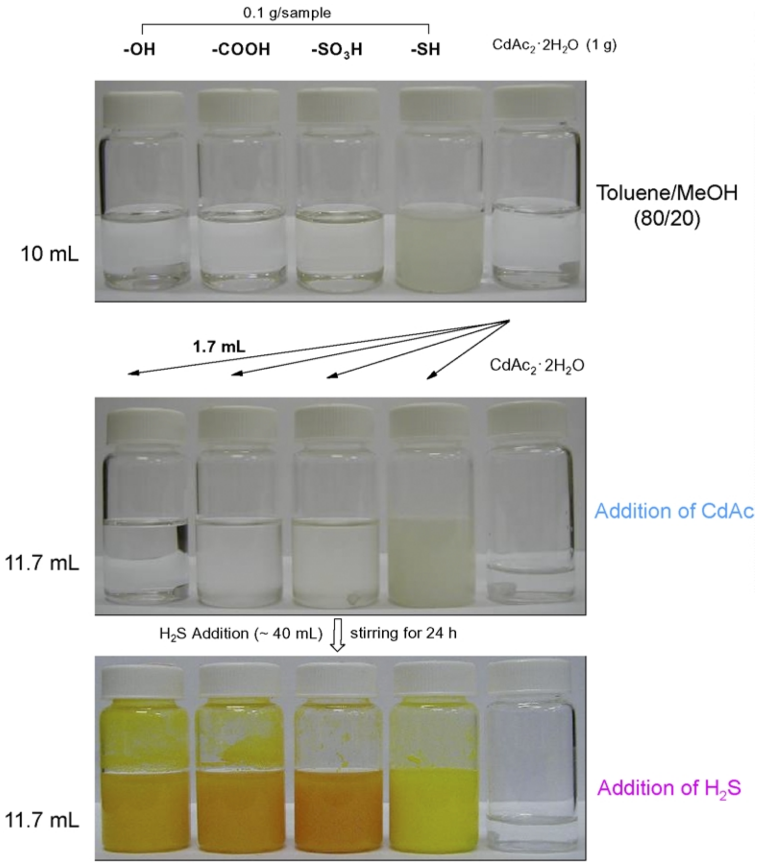


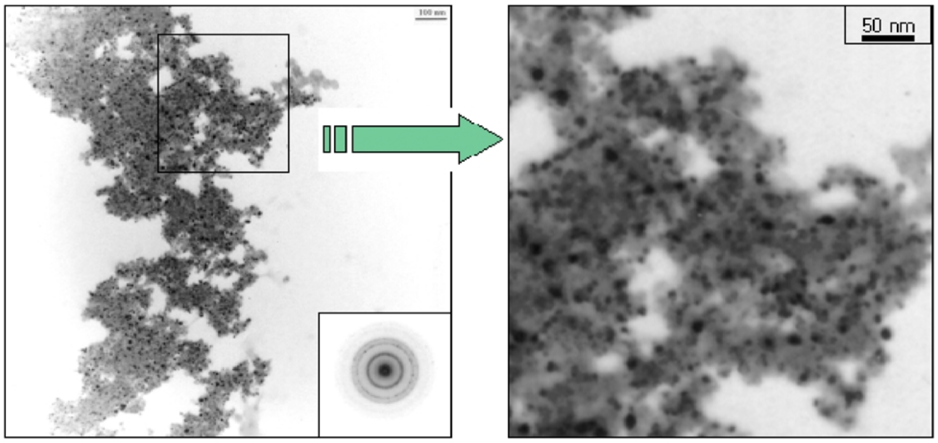
Fig. 5. The color change of the mixture solutions of telechelic polymers and cadmium acetate dihydrate with adding H_2S in the mixture solvent of toluene/methanol (80/20, v/v) at room temperature.

sulfide-*b*-styrene-*b*-ethylene sulfide) as synthesized in Scheme 1 was also found to be used as a polymer stabilizer for the preparation of nano-sized cadmium sulfide (CdS) clusters. Each polar group on telechelic polymers to stabilize the CdS nanoclusters may contribute to the ligand effects to the CdS surface like the core-shell structure resulting in the generation of different chromophores. The formed CdS nanocomposites are expected to have almost the same size and shape each other as shown in Fig. 6 (see the subset; electron diffraction pattern). Unfortunately, the CdS nanocomposites purified and dried could not be re-dissolved in organic solvents. The X-ray diffraction patterns of these nanocomposites are not obtained in this experiment. On the basis of our preliminary results, not only telechelic polystyrene carrying the sulfonate group can be used as the efficient compatibilizer in the polymer blend systems between polar polymers, but also most telechelic polymers can be utilized as the polymeric stabilizers for the preparation of nano-sized transition metals or metal salts exhibiting a ‘quantum size’ effect.

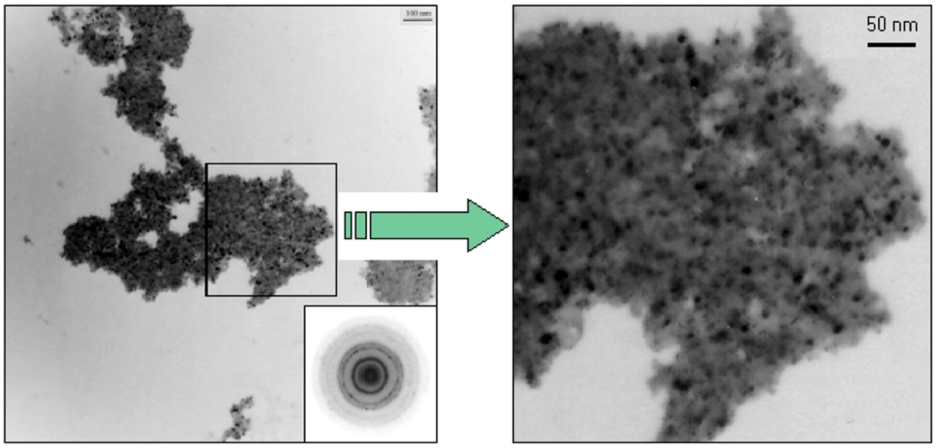
4. Conclusion

Several telechelic polystyrenes carrying hydroxylate, carboxylate, sulfonate, and thiol groups have been successfully synthesized by chain-end functionalizations of the α,ω-dilitiopolystyrene. One of them, dilithium α,ω-disulfonated polystyrene (α,ω-sPS), was successfully used as a powerful compatibilizer in melt-blending of polystyrene with engineering plastics such as nylon 6 or PET acting as a surfactant to control the interfacial tension between two polymers leading to the improvement of the physical properties. The other telechelic polystyrenes were found to be inefficient to control the morphology of the same blend systems of polystyrene and nylon 6 or PET unlike α,ω-sPS. This implies that both the melt blending technique and the concentration of α,ω-sPS as the compatibilizer must be involved in the morphology changes affecting the physical properties of the polystyrene and nylon 6 or PET blends.

Telechelic polymers can be utilized in the nanotechnology field. They were successfully used as the polymer stabilizers for the preparation of semiconductor cadmium sulfide (CdS) nanoparticles in the size range of 5–30 nm. The polymer matrices were insoluble in organic solvents arising from a crosslinking agent effect of the CdS nanoparticle in the telechelic polymer matrices. Any way, it is clear that the telechelic polymers can be utilized as the polymeric sstabilizers in the nanoscience field. Further



(a) dihydroxylate PS/CdS



(b) disulfonate PS/CdS

Fig. 6. TEM photographs of the telechelic polymer-stabilized CdS nanocomposites: (a) in α,ω-dihydroxylated PS; (b) in α,ω-disulfonated PS.

studies are essential for optimization of the useful applications of chain-end functionalized polymers.

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