Synthesis of Poly[ST-*co*-(COPS-I)] Particles by Soap-Free Emulsion Copolymerization and Its Optical Properties as Photonic Crystals

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ABSTRACT

Synthesis of poly[Styrene(ST)-*co*-Allyloxy-2-hydroxypropane sulfonic acid sodium salt(COPS-I)] microspheres with number average diameters(D_n) within 165~550 nm size range by soap-free emulsion polymerization was successfully carried out and their optical properties under visible light were studied. All the latices showed highly monodispersity and the respective shiny structural colors from their photonic crystals. Refractive indices and the reflectivity increased with COPS-I concentration, might be due to the formation of core-shell morphological latex particles.

1. INTRODUCTION

Monodispersed and highly surface charged particles are particularly interesting to chemists due to their photonic crystalline property.[1] Usually, highly surface charged particles are synthesized by copolymerization of styrene with ionic monomers, [2], [3] such as sodium styrene sulfonate, unsaturated esters with end carboxyl groups, 2-hydroxyethyl methacrylate, acrylamide and acrylate derivatives, and Quaternary cationic monomers. However, not many work were concerned with emulsion copolymerization of styrene with Sodium 1-allyloxy-2-hydroxypropane sulfonate(COPS-I) for the synthesis of highly charged, monodisperse colloidal photonic crystals[4]

We report the synthesis highly monodisperse poly[Styrene(ST)-*co*-Allyloxy-2-hydroxypropane sulfonic acid sodium salt(COPS-I)] microspheres with number average diameters(D_n) within 165~550 nm size ranges by soap-free emulsion polymerization and their optical properties by reflection of visible light. For this purpose, a series of experiments was carried out at various reaction conditions such as ST/COPS-I ratio, polymerization temperature, initiator and monomer concentration.

2. EXPERIMENTAL

2.1. Materials

Styrene (ST, Junsei) was purified prior to use by an inhibitor remover (Sigma-Aldrich, St. Louis, MO, USA). Sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS-I, 40%, Sigma-Aldrich) was used as functional monomer without further purification. Potassium persulfate(KPS, Junsei) was used as initiator without further purification. The deionized water used for polymerization was distilled before use.

2.2 Polymerization procedure

Soap-free emulsion polymerization was conducted in a 250 ml round bottom, four necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and pipette outlet for sampling and constant temperature-control system. The polymerizations were carried out at 70 ^oC and 175 rpm of stirring rate. In a typical procedure, 95 ml of DDI-water, 0~0.4g of COPS-I and 1~3.5g of ST were first introduced into the reactor and stirred under nitrogen atmosphere for 30 min. and the heating was started. When the reactor temperature was reached at 70 ^oC, 0.1~0.5 g of KPS initiator dissolved in 5 ml of DDI-water was then added to the reactor, and the polymerization was allowed to proceed for 6h. The resulting latices were passed with 100 mesh screen.

2.3 Colloidal photonic crystals

Once the poly[ST-*co*-[COPS-I)] latices were cleaned with DDI water several times using centrifugation and microscope slide glass was pre-cleaned with piranha solution (3:1 mixture of concentrated sulfuric acid and aqueous hydrogen peroxide and DDI-water). The microscope slide glass was placed in a glass petri dish with a cover where a cotton wool or cloth fully wet with DDI-water is placed beside the sample to delayed DDI-water evaporation from the colloidal dispersion. The colloidal dispersions were cast on a microscope slide glass, and a controlled drying of the latices for 1~2days resulted in colloidal opaline photonic crystals.

2.4. Characterization

After the polymerization was started, 1~2 ml of the reaction mixture was sampled at appropriate intervals throughout the polymerization for the measurement of the conversion versus polymerization time curves. Once the samples were taken out, two drops of 0.1% hydroquinone solution were added in to the sample solution to stop the reaction. The percent solids and conversion of each sample were determined gravimetrically. The latex particle sizes and the shapes were examined by scanning electron microscopy (SEM, Jeol Jsm 6400). The samples were sputter coated with gold, and examined at 5KV. The particle size of the latices were measured on photographs and the particle size distributions (PSD) were determined from the ratio of number (D_n) and weight (D_w)-average diameters.

For the reflectance measurement of each colloidal crystal, a fiber optic UV-visible spectrometer(Avaspec, Avantes ULS3048) was used which was could with an reflected light microscope(Leica DMLM). Optical images of the photonic crystal films were taken with a digital camera(Samsung VLUU NV24HD) and the built-in flash as lightening.

The refractive indices of poly[ST-*co*-(COPS-I)] materials were obtained by back-calculation from the Bragg's equation using measured λ_{max} and D_n

The molecular weight and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC, waters 515) in tetrahydrofuran (THF) equipped with a differential refractometer detector, using three polystyrene gel columns (100, 500, 10000 in pore size); flow rate, 0.3 ml/min; temperature, 30 ^oC.

Conductivity was measured by using PH/Cond 720(WTW series, Inolab) at room temperature for the fresh-made latices.

3. RESULTS AND DISCUSSION

Soap-free emulsion polymerization of styrene was first studied with varying styrene concentration from 1% to 2.9% as shown in Table 1. All the polymerizations gave almost 100% conversion to polymer with negligible amount of coagulum and highly monodispersed[PSD: 1.001~1.005] latices making self-assembled colloidal crystals with the respective shiny structural colors. Average particle diameters increased within the range of 165~428 nm with increasing styrene concentration from 1 to 2.9%, leading to increase the λ_{max} from 395 to 992 nm. Refractive indices of the polystyrene samples prepared in the study, calculated by the Bragg's equation using λ_{max} and D_n were found to be almost same value(1.57~1.58) as experimental value by Abbe refractometer, irrespective of styrene concentration.

Table 1: Soap-free emulsion copolymerization of ST

Sample	Styrene (*wt%*)	D_n (*nm*)	PSD	λ_{max} (nm)	RI
A	1.0	165.2	1.005	394.9	1.5719
B	1.5	251.2	1.002	582.3	1.5758
C	2.0	345.1	1.003	801.9,456.2	1.5799
D	2.4	409.1	1.002	969.5,542.6,	1.5798
E	2.9	428.3	1.001	991.5.,564.0	1.5794

▌Polymerization condition : 70℃,175 rpm for 6 hrs

Poly[Styrene(ST)-*co*-Sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS-I)] latices with 4 different COPS-I concentrations were also synthesized, based on the 2.9% of styrene as shown in Table 2 and Figure1. All the polymerizations showed the colloidal photonic crystals with the respective shinning structural colors and λ_{max} as shown in Figure 2. Average particle diameter decreased drastically from 428 to 241 nm for the addition of 2% COPS-I and after that, increased to 255~295 nm with increasing COPS-I concentration from 4 to 8%. Rate of polymerization(R_p) decreased with the particle size as shown in Figure 3 and the molecular weight increased(Table 2). It is very likely that the particle nucleation in the system is affected very much by the ion strength in the medium due to the increase of concentration of COPS-I, leading to the changes in R_p and D_n. Refractive indices of the poly[ST-*co*-(COPS-I)] samples, calculated by the Bragg's equation were found to increase with COPS-I concentration from 1.61 to 1.66, along with the reflectivity as shown in Table 2, might be due to the formation of core-shell shaped particles with increase in COPS-I concentration.

Table 2: Effect of COPS-I concentration

COPS-I* (%)	D_n (*nm*)	RI	Reflectance (%)	M_n ($\times 10^4$)	Conductivity (ms/cm)
0	428.3	1.5794	Not measured , 27.6	2.74	2.11
2	241.2	1.6122	73.2	1.89	2.65
4	255.3	1.6264	76.2	2.06	2.75
6	265.2	1.6493	78.4	2.17	2.89
8	294.6	1.6552	81.2, 49.8	2.38	2.94

▌Polymerization condition : 70℃, 175 rpm for 6 hrs, ST 2.9%, * Based on the ST content.

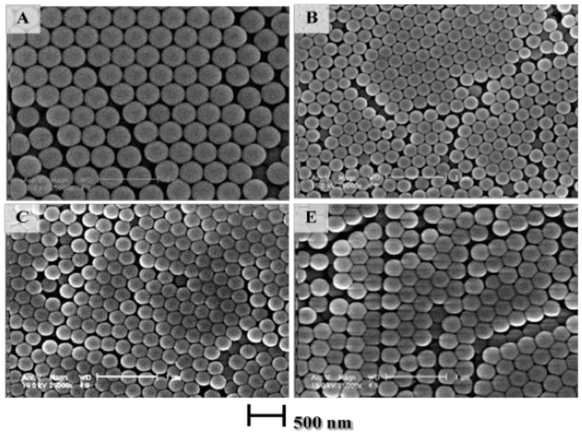

Figure 1: SEM micrographs of poly[ST-*co*-(COPS-I)] latices A: 0, B: 2, C: 4, E: 8 in COPS-I(%)

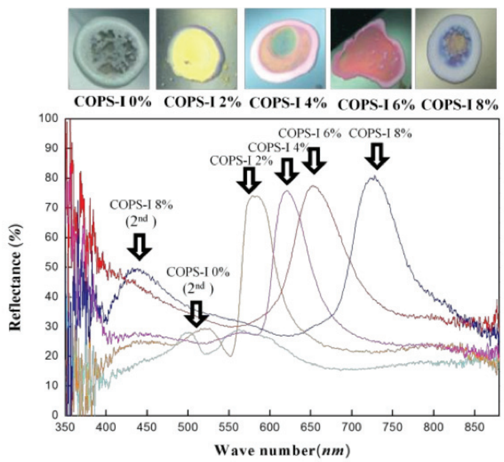

Figure 2: Colors and visible spectra of poly[ST-*co*-(COPS-I)] colloidal photonic crystals

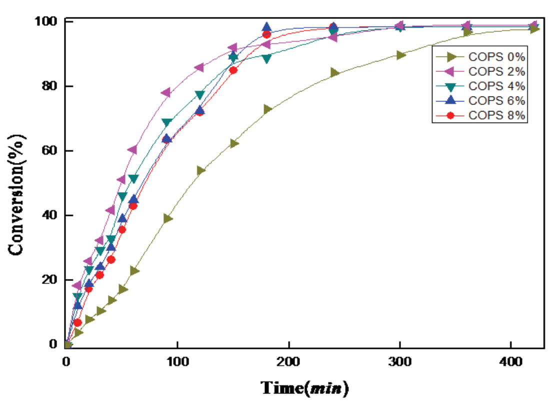

Figure 3: Conversion versus time curves for copolymerization of ST with COPS-I

Table 3 shows the experimental results for the Poly[Styrene(ST)-*co*-Sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS-I)] latices with 4 different potassium persulfate(KPS) initiator concentrations, synthesized based on the 2.9% of styrene and 2% of COPS-I. Highly monodispersed latices showed the respective dazzling structural colors and λ_{max} as shown in Figure 4 & 5. Average particle diameter decreased rapidly from 549 to 241 nm by the addition of KPS from 1.7 to 3.3 wt%, and after that, increased slowly to 260~302 nm with 5.8~6.7 wt% of KPS. Polymerization rate increased by the order of 1.7<6.7<5.8<3.3 wt% of KPS as shown in Figure 6, same as the order of the particle size(D_n) and the molecular weight(M_n). These phenomena may be explained by the effect of increase in ion strength with KPS concentration. The refractive indices of 1.59~1.61 does not have much relationship with KPS content.

Table 3: Effect of KPS concentration

KPS* (*wt%*)	D_n (*nm*)	RI	Reflectance (%)	M_n ($\times 10^4$)	Conductivity (ms/cm)
1.7	549.5	1.5929	Not measured, 29.4	2.42	2.04
3.3	241.2	1.6122	73.2	1.89	2.65
5.8	260.1	1.6089	78.3	1.94	3.55
6.7	302.2	1.5845	69.2	2.19	3.71

▌Polymerization condition : 70℃, 175 rpm for 6 hrs ,ST 2.9%, COPS-I 2%, * Based on the total monomer weight.

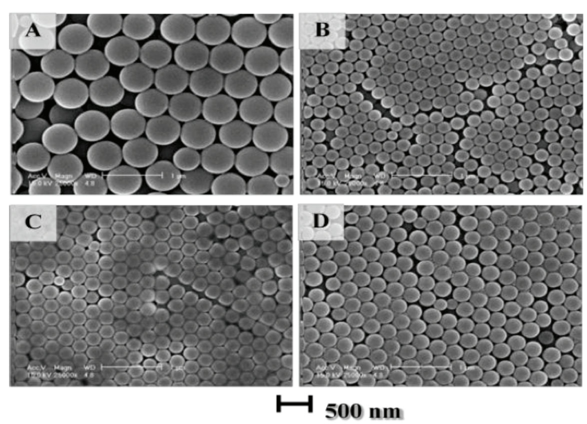

Figure 4: SEM micrographs of poly[ST-*co*-(COPS-I)] latices with change of KPS initiator concentration
A: 1.7, B: 3.3, C: 5.8, D: 6.7% based on the total monomer weight

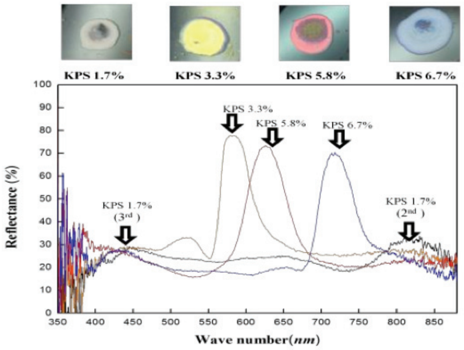

Figure 5: Colors and visible spectra of poly[ST-*co*-(COPS-I)] colloidal photonic crystals with change of KPS initiator concentration

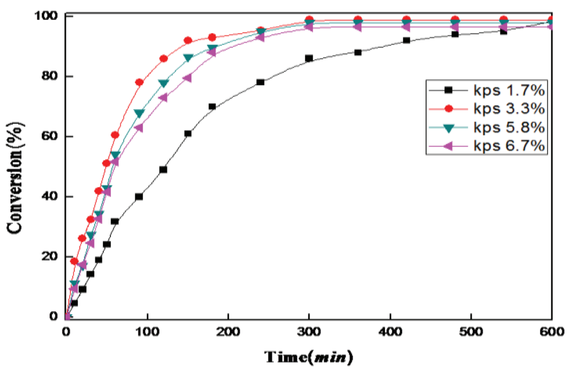

Figure 6: Conversion versus time curves with change of KPS initiator concentration

Table 4: Effect of polymerization temperature

Temp (℃)	D_n (*nm*)	RI	Reflectance (%)	M_n ($\times 10^4$)	Conductivity (ms/cm)
65	508.6	1.6185	Not measured ,38.1	2.46	2.21
70	255.3	1.6264	76.2	2.38	2.75
75	232.5	1.6408	83.2	1.84	3.12
80	195.0	1.6680	85.1	1.81	3.61

Polymerization condition : 175 rpm for 6 hrs, ST 2.9%, COPS-I 4%

Table 4 shows the experimental results for the Poly[Styrene(ST)-co-Sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS-I)] latices with 4 different polymerization temperatures from 65 to 80^{o}C, synthesized based on the 2.9% of styrene and 4% of COPS-I. Highly monodispersed latices showed the respective brilliant structural colors and λ_{max} as shown in Table 4. Average particle diameter and molecular weight decreased with increasing the polymerization temperature, on the other hand, polymerization rate increased. The refractive indices increased gradually with the polymerization temperature from 1.62 to 1.67. The reason for that is not clear at the moment.

4. Conclusion

Soap-free emulsion copolymerization of Styrene(ST) and Allyloxy-2-hydroxypropane sulfonic acid sodium salt(COPSI)] was tried to study on the effect of ST/COPS-I ratio, polymerization temperature, initiator and monomer concentration. The resulting latices were all monodisperse with number average diameters within 165~550 nm size range and could form the colloidal photonic crystals with various structural colors. Their optical properties under visible light were studied. Refractive indices and the reflectivity increased with COPS-I concentration, might be due to the formation of core/shell morphological latex particles.

REFERENCES

[1]. K.C.Lee, *JNN*, **13**, 6286~6292 (2013)

[2]. P.H. Wang, C.T. Pan, *Colloid Polym Sci* **280**, 152~159 (2002)

[3]. A. Pitch, Y. Lu, H.J. Alder, *Colloid Polym Sci* **281**, 907~915 (2003)

[4]. Chad E, A. Asher, *Journal of Colloid and Interface Science* **232**, 76–80 (2000)