NOTES

Kinetic Study on the Radical Polymerization of Sodium Isoprenesulfonate in Water

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Water-soluble polymers are important in a wide variety of industrial applications including mineral and petroleum recovery, fluid modification, controlled drug release, personal care formulations, industrial water treatment, and wastewater treatment.¹ There are several important sulfonate-containing water-soluble polymers, such as poly(vinylsulfonic acid) (PVSA) and its salts, and poly(*p*-styrenesulfonic acid) (PSSA) and its salt.² Extensive development has been also conducted on acrylic sulfonate-containing monomers, such as 2-sulfoethylmethacrylate (SEM) and 2-acrylamido-2-methylpropanesulfonate (AMS).²

Recently, JSR Corporation has developed a novel sulfonate-containing diene monomer, sodium isoprenesulfonate (IPS) synthesized from isoprene and sulfur trioxide (Figure 1).^{3,4} This new class of water-soluble monomers has excellent polymerization ability and corresponding water-soluble polymers have been proven useful for a variety industrial applications, *e.g.*, as an anionic surfactant for coal water slurry.^{5,6} Ono *et al.* have investigated the polymerization of IPS initiated by potassium persulfate (KPS) in water and concluded that 1,4-polymerization and 3,4-polymerization proceed at approximately the same ratio, and that weight-average molecular weights of polymers range from 2.9×10^4

to 11.2×10^4 g mol⁻¹ according to the GPC measurement using sodium polystyrene sulfonate standards (Figure 2).⁴ This paper describes the kinetic results of radical polymerization of IPS in water, such as rate of polymerization (R_p) and activation energy of polymerization (E_a), where sodium persulfate (SPS) was used as initiator.

EXPERIMENTAL

Materials

IPS was supplied as water solution (41.6 wt%) by JSR Corporation. SPS was purchased from Wako Pure Chemical Industries, Ltd. and used as received. Ion-free water was used.

Typical Procedure of Polymerization

98.75 g of 25.3 wt% IPS in water was added to a 300 mL three-necked reaction flask with a mechanical stirrer under nitrogen flow, and then heated by hot-water bath. 1.25 g of 20 wt% SPS in water was added at 40°C. Eventually, monomer concentration was 25 wt% (1.67 mol L⁻¹). A small amount of the reaction mixture was withdrawn from the reaction mixture every 10 min up to 1 h, and every 30–60 min from 1 h up to 4 h. These

Figure 1. Synthesis of Sodium Isoprenesulfonate (IPS).

Figure 2. Radical polymerization of Sodium Isoprenesulfonate in Water.

samples were weighted and immediately diluted with water in 250 mL volumetric flask to a concentration of 20–40 mg L⁻¹ and analyzed by UV spectrophotometry.

Techniques

UV spectra were recorded on a Hitachi U-3300 UV spectrophotometer. Conversions of monomer to homopolymer were determined as decrease of the conjugated diene peak of IPS monomer (235 nm) vs. a calibration curve prepared using seven IPS water solutions with different concentrations.

RESULTS AND DISCUSSION

IPS was polymerized in water at various concentration and temperatures using SPS as an initiator (Figure 2). At this point, it is appropriate to briefly discuss the experimental procedure used to determine conversion and R_p . One of the most practical methods to measure the conversion from monomers to polymers is the gravimetric method, that is, isolating the polymer from the reaction mixture by either precipitation of the polymer by addition of a non-solvent or by distillation of monomer.⁷ However, these methods present difficulties, since both IPS and the corresponding homopolymers show similar solubility and are solids. Conversions can also be experimentally followed by measuring change in any property that differ for the monomer and polymer, such as density, refractive index, or the spectral absorption.⁷ It has been noticed that IPS in water has a strong adsorption at 235 nm in the UV spectrum, while the corresponding homopolymers, where unreacted IPS was removed by dialysis, do not absorb at 230 nm or above. Thus, conversions were easily and accurately determined by decrease in the conjugated diene peak of IPS.

Figure 3. Time-conversion curves in the polymerization of IPS with SPS in water at different temperatures ([IPS] = 1.67 mol L⁻¹, [SPS] = 1.13 × 10⁻² mol L⁻¹).

Figure 3 shows time-conversion plots observed at 40, 50, 60, and 70°C at initial concentrations of IPS and SPS of 25.0 wt% (1.67 mol L⁻¹) and 1.00 wt% (1.13 × 10⁻² mol L⁻¹) respectively. Higher conversions were reached as polymerization time and/or temperature increased. The highest conversion reached 82% at 70°C after 4 h. R_p was determined from the initial slope of steep rise of conversion curves and is summarized in Table I. As the weight % (wt%) unit is generally used in the chemical industry, all reactants were weighed by wt%, and calculation was carried out using molar units. From the Arrhenius plots shown in Figure 4, overall E_a of polymerization was calculated to 25.6 kJ mol⁻¹. This is higher than the reported values for the polymerization of acrylonitrile in water (17.2 kJ mol⁻¹) and methacrylamide in water (15.5 kJ mol⁻¹),⁸ and lower than the value for the polymerization of sodium p-styrenesulfonate in water initiated potassium persulfate (46.1 kJ mol⁻¹).⁹ The temperature dependence of R_p of IPS may be lower than that of

Table I. Rate of polymerization (R_p) of IPS^a with SPS^b in water at various conditions

Temp °C	[IPS] wt% (mol L ⁻¹) ^c	[SPS] wt% (10 ⁻² mol L ⁻¹) ^c	10 ⁴ R_p mol L ⁻¹ s
40	25.0(1.67)	1.00(1.13)	1.74
50	25.0(1.67)	1.00(1.13)	1.98
60	25.0(1.67)	1.00(1.13)	3.07
70	25.0(1.67)	1.00(1.13)	3.92
50	6.25(0.40)	1.00(1.13)	0.28
50	12.5(0.81)	1.00(1.13)	0.75
50	25.0(1.67)	1.00(1.13)	1.98
50	40.0(2.79)	1.00(1.13)	5.22
50	25.0(1.67)	0.25(0.28)	1.19
50	25.0(1.67)	0.50(0.56)	1.52
50	25.0(1.67)	1.00(1.13)	1.98
50	25.0(1.67)	2.00(2.29)	3.31

^aSodium isoprenesulfonate. ^bSodium persulfate. ^cConcentrations are practically based on wt%, then converted to mol L⁻¹ for calculation.

Figure 4. Arrhenius plots of R_p in the polymerization of IPS with SPS in water at different temperatures ([IPS] = 1.67 mol L⁻¹, [SPS] = 1.13 × 10⁻² mol L⁻¹).

sodium *p*-styrenesulfonate, and thus the control of R_p is mildly achieved.

R_p was determined in various IPS and SPS concentrations at 50°C in a similar manner as above (Table I). Figure 5 presents the effects of IPS concentration on R_p at 50°C when the initial concentration was fixed at 1.00 wt% (1.13 × 10⁻² mol L⁻¹). R_p was proportional to the 1.48 power of monomer concentration indicating much higher dependence of R_p on the monomer concentration than the first-order dependence usually observed in radical polymerization. Although the viscosity of the polymerization was not investigated in this paper, we speculated that the higher dependence of R_p on the monomer concentration results in retardation of termination due to the viscosity effect. This causes acceleration of polymerization which has been reported

Figure 5. Relationship between polymerization rate (R_p) and IPS concentration at 50°C in water ([SPS] = 1.13 × 10⁻² mol L⁻¹). **Figure 6.** Relationship between polymerization rate (R_p) and SPS concentration at 50°C in water ([IPS] = 1.67 mol L⁻¹).

in various radical polymerization systems.^{10–12} Figure 6 shows the effects of SPS concentration on R_p at 50°C when the initial IPS concentration was fixed at 25.0 wt% (1.67 mol L⁻¹). R_p increased in proportion to the 0.47 power of the initiator concentration, indicating that the present polymerization involves usual bimolecular termination between propagating polymer radicals.¹³ Detailed studies on solution viscosity, molecular weight, stereochemistry, pH-dependence and copolymerization will be published elsewhere.

SUMMARY

Polymerization of sodium IPS was kinetically investigated in water using SPS as initiator. The conversion of monomer to homopolymer was determined from decrease in the conjugated diene peak of IPS monomer as measured by UV spectrometry. E_a of polymerization was 25.6 kJ mol⁻¹. R_p was expressed by $R_p = k[\text{SPS}]^{0.47}[\text{IPS}]^{1.48}$, indicating that the polymerization of IPS involves usual bimolecular termination between

propagating polymer radicals, and that deviation from the first-order dependence may possibly be attributed to viscosity. These new kinetic data are considered useful for further investigation.

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