# Interaction of Sodium Dodecyl Sulfate with Polyelectrolyte Complex from Diazoresin and Poly(sodium styrene sulfonate) in Aqueous Solution

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ABSTRACT: Polyelectrolyte complex diazoresin-poly(sodium styrene sulfonate) (DR-PSS) from diazoresin (DR) as cationic polyelctrolyte and poly(sodium styrene sulfonate) (PSS) as anionic polyelectrolyte does not dissolve in water or organic solvent because of its electrostatic crosslinking structure. It was found that the complex dissolves considerably aqueous solution of sodium dodecyl sulfate (SDS) and confirmed that the DR-PSS—SDS system possesses extraordinary thermostability as well as high photosensitivity and can be used directly to produce a photoimaging coating. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1817–1821, 1998

**Key words:** polyelectrolyte complex; diazoresin; poly(sodium styrene sulfonate); sodium dodecyl sulfate

### INTRODUCTION

The interactions of polyelectrolyte (PE) with surfactant were studied extensively and have attracted more and more attention recently $^{1-12}$ ; however, the studies on the interaction of polyelctrolyte complex (PEC) with surfactant or related works are very limited. Kataoka et al.<sup>13</sup> reported a polyelectrolyte complex from poly-(ethylene glycol)-polylysine and oligonucleotide forms micelles spontaneously and revealed that the micelle with the size of 60 nm have a considerable narrow size distribution and core-shell structure. Osada and coworkers<sup>14-17</sup> studied the interaction of cationic surfactants with negativecharged polyelectrolyte gels and confirmed that the binding of *n*-alkylpyridium chloride with poly-[2-(acrylamido)-2-methylpropylene sulfonic acid] (PAMPS) is cooperative, whereas the binding of tertraphenylphosphonium chloride with PAMPS is not cooperative.

The complexes formed from cationic and anionic polyelectrolytes usually don't dissolve in water or any organic solvents and were considered as a kind of crosslinking material via ionic bonds. Only a specific solvent system, known as shielding solvent composed of water–organic solvent– inorganic salt, can dissolve the PEC.<sup>18,19</sup>

In a previous article, we reported a that kind of polyelectrolyte complexes based on diazoresin as polycation will dissolve in  $H_2O$ -dimethylformaldehyde (DMF)-LiCl (wt ratio 2 : 4 : 1) and revealed that under irradiation of ultraviolet (UV) light, the complex becomes indissolve since the crosslinking structure of the complex changes from ionic to covalent.<sup>20</sup>

In this article, we report the interaction of diazoresin-poly(sodium styrene sulfonate) (DR-PSS) with SDS in an aqueous solution and found that the DR-PSS will dissolve in SDS aqueous solution considerably. Furthermore, we confirmed that the thermostability of DR-PSS in SDS aque-

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ous solution is much higher than that of DR in 2-methoxyethanol or diazonium salt in water. The photosensitive properties of DR-PSS—SDS aqueous solution was also reported.

## **EXPERIMENTAL PART**

#### **Materials and Instruments**

Diphenylamine-4-diazonium chloride  $(\frac{1}{2} \operatorname{Zncl}_2 \operatorname{complex})$  was purified from reprecipitation of its ethanol solution by ether. SDS was recrystallized from ethanol. PSS (Aldrich,  $M_n = 7000$  g/mol) was used as received. The diazoresin was prepared from polycondensation of diphenylamine-4-diazonium salt with formaldehyde according to Cao et al.<sup>20</sup> Ultraviolet–visible (UV–vis) spectra and differential scanning calorimetry (DSC) were recorded on a Shimadzu UV-1200 and a Shimadzu DSC-50, respectively.

### Preparation of DR-PSS

Under stirring, 7.66 g (containing 0.02 mol diazonium group) of diazoresin dissolved in 200 mL of water as polycation was mixed with 4.16 g (containing 0.02 mol sulfonate group) of PSS solution (100 mL). The DR–PSS was formed instantaneously as a gel-like precipitate and filtered. Yield was 7.04 g (90%).

### Preparation of DR-PSS-SDS Aqueous Solution

Five grams of DR–PSS (newly prepared, containing 79 wt % water) was added into 16 mL of 0.15M SDS aqueous solution with stirring to dissolve. The solution containing about 5 wt % DR–PSS was used to form the photoimaging coating.

### Photochemical Decomposition of DR-PSS in SDS Aqueous Solution

The DR–PSS—SDS aqueous solution exhibits strong absorption at 380 nm, which is characteristic of diazonium group of DR–PSS. The photodecomposition of DR–PSS was monitored by a UV–vis spectrophotometric method to measure the absorbance of the solution at 380 nm after every irradiation for a given time (usually 10 s). The decomposition (mol %) was calculated from the following equation:

Decomposition (mol %)

$$= (A_0 - A_t)/A_0 \times 100\% \quad (1)$$

where  $A_t$  and  $A_0$  represent the absorbance at the time = t and time = 0.

# The Thermal Decomposition of DR-PSS—SDS Aqueous Solution

The thermal decomposition of DR–PSS—SDS is also monitored spectrophotometrically. The solution of DR–PSS—SDS was heated at  $70 \pm 0.1$  °C in a thermostat for given time, then the absorbance of the solution at 380 nm was determined. From the decreasing of absorbance, the decomposition (mol %) of DR–PSS was also calculated according to eq. (1).

# Preparation of Image from DR-PSS—SDS Composition

The DR–PSS—SDS aqueous solution (0.15*M* SDS containing ~ 5% DR–PSS) was coated on a printing aluminum plate with a laboratory coating machine and dried in dark to form a coating (1–2  $\mu$ m thickness). A photographic film was covered on the coating and exposed with a 300 medium-pressure mercury lamp at distance of 30 cm for 2 min, then developed [in water or in developer composed of sodium sulfite (5 g), benzyl alcohol (10 mL), nonionic surfactant (OP-10, 5 g), anionic surfactant (SDS, 5 g), and water (250 mL)]. The unexposed areas of the coating were dissolved, and the exposed areas remained. A clear imaging, which is contrary to that of photographic film, was obtained.

# **RESULTS AND DISCUSSION**

### Preparation and Photoreaction of DR-PSS

The formation of DR–PSS is represented as follows:



It should possess an ionic crosslinking structure because every molecule of DR or PSS contains more than two cationic or anionic groups. The most important chemical characteristic of DR–PSS is



Table IThe Solubility of DR-PSSin Different [SDS] and Temperatures

Temperature (°C)	$[\text{SDS}] \\ (\text{mol } L^{-1})$	[DR–PSS] (wt %)
20	0.0 (water)	0.25
20	0.05	1.48
20	0.10	2.96
20	0.15	5.02
40	0.0 (water)	0.38
40	0.05	2.02
40	0.10	3.23
40	0.15	5.25
60	0. 0 (water)	0.48
60	0.05	2.34
60	0.10	3.51
60	0.15	6.44

that under irradiation of UV light, the crosslinking structure of DR–PSS changes from ionic to covalent<sup>20</sup> (see Scheme 1).

The structural change of DR–PSS from ionic to covalent can be verified by the dramatically change of its solubility. After irradiation, the coating film no longer dissolves in water, SDS aqueous solution, or shielding solvent composed of  $H_2O$ –DMF–LiCl (2 : 4 : 1 weight ratio), which can dissociate the ionic bond and dissolve the DR– PSS. Other evidence is that after irradiation (the full surface was irradiated), the weight of the coating film shows almost no loss in developing process. The result shows that the PSS, which dissolves in water or developer easily, certainly does not dissolve after irradiation. The detail structural evidence of DR–PSS after irradiation of UV light will be reported elsewhere.

#### The Solubility of DR-PSS in SDS Aqueous Solution

DR–PSS does not dissolve in water or any organic solvents, but we found that the DR–PSS can dissolve in SDS aqueous solution, as shown in Table I.

The results show that the solubility of DR–PSS in 0.15*M* SDS solution at room temperature is about 5 wt %. It is higher than that in shielding solvent composed of H<sub>2</sub>O–DMF–LiCl (2 : 4 : 1 weight ratio).<sup>20</sup>

The interaction of polyelectrolyte complex based on diazoresin as a cationic chain with SDS has not been found in the literature. We proposed that the complex dissolves in SDS by two steps: at first, the complex is separated into its two components by SDS, which is probably able to associate the ionic bond; then in the second step, the SDS molecules combine further with diazoresin molecules via hydrophobic interaction. The excessive SDS molecules binding on diazoresin; as a result, the diazoresin was dissolved. The interaction process can be illustrated schematically, as shown in Figure 1.

The nonionic surfactant, such as OP-10, Tween-80, does not dissociate the ionic bond of the complex, so the DR–PSS does not dissolve in aqueous solution of nonionic surfactants. The effect of sodium chloride, which is able to dissociate the ionic bond, on the solubility of DR–PSS is very limited (Fig. 2) because the NaCl does not combine with diazoresin. The solubilities of DR–PSS in water, in aqueous solutions of OP-10, Tween-80, and SDS, are shown in Figure 2.

It is shown that the solubility (5.02 wt %) of DR–PSS in 0.15M SDS aqueous solution is much higher than in water (0.25%), OP-10 (0.30%), Tween-80 (0.28%), or Tween-NaCl (0.57%).



Figure 1 The schematic illustration of DR-PSS dissolved in SDS aqueous solution.



**Figure 2** The solubilities of DR–PSS in various solutions (20°C): OP-10, 5.96 wt % OP-10 in water; Tween-80, 8.10 wt % Tween-80 in water; Tween-80 + NaCl, 8.10 wt % Tween-80 in 4.0*M* NaCl solution; SDS, 0.15*M* aqueous solution.

# The Photosensitive Behavior of DR–PSS—SDS Composition

The photodecomposition rate of DR–PSS in SDS solution is very rapid. The absorbance of the solution decreasing with irradiation time is shown in Figure 3.

From Figure 3, we can see that the photochemical decomposition of DR–PSS is very rapid and decomposition is almost complete within 1 min under experimental condition.

# The Thermal Decomposition of DR-PSS—SDS Aqueous Solution

We found that the diazonium group of DR–PSS in SDS aqueous solution exhibits extraordinary thermostability. The  $k_d$ , the rate constant of decomposition, and  $t_{1/2}$ , the half-life period of diazonium-containing compounds in SDS aqueous solution or in 2-methoxyethanol or in water, were determined (Table II). The results show that the thermostability of DR–PSS in SDS aqueous solution ( $t_{1/2} = 122.7$  min at 70°C) is much higher than that of DR in 2-methoxyethanol ( $t_{1/2}$ 



**Figure 3** The photodecomposition of DR–PSS in SDS aqueous solution under irradiation of UV light: [DR–PSS] =  $4 \times 10^{-5}M$  (as  $-N_2^+$  unit); [SDS] = 0.15*M*. Irradiation condition: 80-W medium pressure mercury lamp with a distance of 10 cm. Irradiation time (s): (1) 0; (2) 10; (3) 20; (4) 30; (5) 40; (6) 50.

= 30.1 min) or that of diazonium salt in water  $(t_{1/2} = 9.9 \text{ min}).$ 

The extraordinary thermostability of DR–PSS in SDS solution probably can be ascribed to the aggregation of SDS on the complex molecules via hydrophobic interaction. The aggregation of SDS on the polymer chain may protect the diazonium group from attack by nucleophiles.

### The Photoimaging Properties of DR–PSS—SDS Aqueous Solution

The photochemical properties of DR–PSS in SDS aqueous solution are interesting for developing DR–PSS as photoimaging materials. The imaging characteristic of the layer of DR–PSS coated on a printing aluminum plate has been verified. After irradiation with UV light, the exposed areas become insoluble in water or in developer, but the unexposed areas were dissolved, and a clear image was obtained. The substrate in the exposed areas was protected by the resin, which is hydrophobic, and accepted ink easily; but in the unex-

Table II The  $k_d$  and  $t_{1/2}$  of Thermal Decomposition of Diazonium-Containing Compounds in SDS Aqueous Solution or in 2-Methoxyethanol or in Water at 70°C

Solvent System	Diazonium-Containing Compound	$k_d ({ m min}^{-1})$	$t_{1/2} \; ({ m min})$
$ m H_2O$ HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> 0.2M SDS	$\begin{array}{l} {\rm Diazonium\ salt\ }({\rm HSO}_4^- \ {\rm as\ anion}) \\ {\rm Diazoresin\ }({\rm HSO}_4^- \ {\rm as\ anion}) \\ {\rm DR-PSS} \end{array}$	$egin{array}{rcl} 6.64 \  imes \ 10^{-2} \ 2.29 \  imes \ 10^{-2} \ 5.56 \  imes \ 10^{-3} \end{array}$	$9.9 \\ 30.1 \\ 122.7$

posed areas, the aluminum surface is hydrophilic and accepts water only, so the aluminum plate coated with DR–PSS as photosensitive material probably represents a new kind of negative presensitized plate.

#### CONCLUSION

A polyelectrolyte complex from diazoresin (DR) as cationic chain and poly(sodium styrene sulfate) (PSS) as anionic chain was prepared. It was found that the complex, which is insoluble in water or any organic solvent, will dissolve in SDS aqueous solution and that the DR-PSS-SDS aqueous solution exhibits extraordinary thermostability as well as photosensitivity. A proposal to explain the soluble of DR-PSS in water in the presence of SDS has been proposed in which the SDS plays a role of the dissociation agent to separate the complex into its two components, then the excessive SDS combines with diazoresin molecules via hydrophobic interaction and causes the resin to dissolve in water. The extraordinary thermostability of the diazonium group of the resin was explained by the aggregation behaviors of the SDS. The aggregations of SDS molecules around the diazonium groups may protect them from attack by the nucleophiles.

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