

# A Novel Polymer Matrix Capable of Crosslinking and Decrosslinking Upon Thermal Irradiation<sup>a</sup>

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## Abstract

A series of copolymer containing sulfonyl and carboxyl units were synthesized and used in combination with a bisvinyl ether monomer in the form of thin film. It was found that the polymer matrix became completely insoluble in aqueous solution after baked at low temperature around 100 °C and then turned to be highly soluble in aqueous solution, even in neutral water, when exposed to high temperature above 200 °C. Systematic investigations by using DSC, TG and FTS and a homemade apparatus for monitoring film thickness change in dissolving revealed that the insolubilization at low temperature was enabled by thermally induced crosslinking between vinyl group of the bisvinyl ether monomer and carboxyl group of the copolymer and the solubilization at high temperature was the result of acid-catalyzed decrosslinking. The sulfonyl group of the copolymer acted as a thermal acid generator. Preliminary imaging experiments showed that this polymer matrix could be possibly applied in thermal laser imaging.

## Introduction

There has been found a wide application of affinity switchable polymer in Deep-UV microlithography and Computer-to-Plate imaging over recent years [1-3]. In common, this kind of polymer undergoes affinity change, say, from being hydrophilic to being hydrophobic, when exposed to physical or chemical stimulus. Previously, we reported thermal properties of copolymers containing different sulfonyl units, such as, metal p-styrenesulfonate, isopropyl p-styrenesulfonate, cyclohexyl p-styrenesulfonate, methyl vinyl sulfonate, butyl vinyl sulfonate and cyclohexyl vinyl sulfonate, and found that these copolymers were found of excellent switchability from being insoluble to completely soluble in neutral water, because of the thermally generated sulfonic acid upon heating treatment [4]. Further, they had a relatively poor thermo-stability below 80 °C for 48h.

In this paper, we found that a new series of polymers containing n-butyl p-styrenesulfonate and n-butyl vinyl sulfonate unit were stable below 80 °C, but readily undergone acid releasing about 200 °C. These copolymers were excellent polymeric thermal acid generators and could be used as polymer binder with bisvinyl ether, which was unstable when strong acid such as sulfonyl acid existed. Their feasibility and effectiveness in combined use with 2,2-bis(4-(2-vinyloxy)phenyl)propane(BPA-DEVE) were fully investigated. This polymer system undergone not only changes in composition, releasing sulfonyl and carbonyl acids, but also changes in structural dimension from networked to linear, upon subject to high temperature above 200 °C. These changes worked

jointly, building high contrast in affinity change between thermally exposed and non-exposed areas of the polymer coating.

## Experimental

### 1. Reagents and Instrumentals

Sodium p-styrenesulfonate (Wako Pure Chemical Industries. Ltd.(JPN)) and sodium isethionate (ACROS ORGANICS(USA)) were commercial products, and other reagents were purchased and used as received. Most reagents were purified and dehydrated before used.

IR spectra were measured with SHIMADZU FTIR-8400 spectrophotometer, DSC spectra were recorded with NETZSCH DSC 200PC, TG spectra were recorded with NETZSCH TG209, <sup>1</sup>H NMR spectra were recorded with ARIA EMAN FX-300 spectrometer. Film thickness was recorded with Taylor Hobson FTS-S3c.

### 2. Monomer Preparation

Monomer 1 (M1): n-butyl p-styrenesulfonate was prepared according to a literature [1].

Monomer 2 (M2): n-butyl vinyl sulfonate was prepared according to literatures [5-6].

Monomer 3 (M3): methyl methacrylate (MMA) was purified by washing with aqueous alkali, drying and distilling. Distilled fraction at 100°C was collected and used as purified monomer.

Monomer 4 (M4): methacrylic acid (MAA) was purified by distilling under reduced pressure.

### 3. Polymer Preparation

Purified monomers were weighed and dissolved in 1,4-dioxane, and then 2mol% (relative to the monomer content) AIBN, the initiator, was added. The mixture was heated to 70 °C and then kept in that temperature for 6 hrs, while being stirred under the flow of N<sub>2</sub>. The solution was poured into large quantity of petroleum ether and the fabric precipitation was fully washed and dried in vacuum at 40 °C for 4 hrs. IR spectra were used to trace the characteristic absorption of the sulfonate unit, and DSC and TG spectra were used to investigate its thermo-decomposition. Changes of the sulfonate unit before and after heating treatment were traced by the corresponding changes in IR spectra. Actual unit fractions of sulfonyl and methyl methacrylate in the polymer were determined by <sup>1</sup>H-NMR, and that of methacrylic acid was obtained by acid-base titration [7]. Number- and weight-average molecule weights (Mn and Mw) of copolymers were determined by a SHIMADZU LC-10AvP GPC system equipped with polystyrene gel columns (GPC-805) at 30 °C in THF at a flow rate

of 1.0ml/min.

#### 4. Polymer Film Preparation and Baking Treatment

Weighed amount of polymer was completely dissolved in THF for making film without bisvinyl ether or weighed amount of polymer and a minute dye having strong absorbency at 780 nm where the other two components did not absorb were completely dissolved in THF for making films with weighed amount of bisvinyl ether BPA-DEVE. The solutions so made were applied onto an aluminum substrate or a glass substrate and then dried in an open oven at 70 °C for 30 min. The resulted films were about 1 m thick.

Polymer films were placed in a homemade heating apparatus for baking treatments and the temperature was controlled at the precision of about  $\pm 1$  °C between above room temperature and 270 °C. Pre-baking was done at 120 °C for 10 min and post-baking treatment at 230 °C for 10 min. After pre- and post-baking treatments, polymer films on glass substrate were set up in the sample holder of a homemade apparatus for in situ film thickness monitoring during development. And polymer films on aluminum substrate were immersed and held in stirred neutral water (PH=7) for 1min for development. Visual changes of the film during the development were carefully monitored and thickness of film left on the substrate after the development was recorded.

#### 5. In Situ Film Thickness Monitoring During Development

An apparatus was made, which was able to trace in situ film thickness change during development. In fact, the apparatus was a special sample chamber attachment to a commercial UV-Vis spectral photometer. In this paper, SHIMADZU UV-2101PC was used as the photometer. The sample chamber attachment consisted of a sample-fixing guide, developing solution let-in and out pipes and two quartz windows, which allowed light beam to pass through. The let-in and out pipes were connected with a solution supplying pump and a waste tank, respectively, to make fresh developing solution circulating constantly in the chamber. A dye, which had strong absorbency at 780 nm, was dissolved in polymer matrix and used as film thickness indicator. During measurement, the photometer was set in ABS~t mode and  $ABS/(\epsilon \times C)$  was plotted against t, where  $\epsilon$  and C were molar extinction coefficient and concentration of the indicator, respectively. According to Beer-Lamber law,  $ABS/(\epsilon \times C) = L$ , and this allowed us to make

## Results and Discussion

### 1. Copolymers of Different Sulfonyl Units and Their Thermal Stability

Free radical copolymerization of M1 or M2 and M3, M4 was carried out and a series of copolymers were obtained (Table 1).

The data in Table 1 indicated that copolymers SS with n-butyl p-styrenesulfonate unit (M1) were thermally more stable and of larger molecular weight than copolymers VS with n-butyl vinyl sulfonate unit (M2). With increasing feeding ratio of sulfonyl monomers, more n-butyl p-styrenesulfonate unit was observed in the copolymer, but the content of n-butyl vinyl sulfonate unit did not increase accordingly. In fact, the ratio of n-butyl vinyl sulfonate unit in the copolymer remained low and almost unchanged, regardless of the increase of its corresponding monomer upon polymerization. Copolymer SS were, therefore, chosen as the polymer in combination with BPA-DEVE for further investigation.

### 2. Sulfonyl Unit Concentration and Aqueous Solubility

#### Polymer Matrix without Bisvinyl Ether

Sulfonic acid, one of the products of the polymer with sulfonyl unit upon thermo-decomposition, was critically important in determining aqueous solubility of the polymer matrix and its concentration was controlled by sulfonate unit in the polymer. Copolymers SS with different concentrations of n-butyl p-styrenesulfonate were prepared and their solubility in neutral water were tested. Post baking temperature was fixed at 230 °C, slightly higher than the thermal acid generation temperature of the copolymer, which fell in the range of about 215-218 °C. Figure 1 showed normalized residual film thickness of copolymer SS after developed in neutral water as a function of sulfonate unit concentration against post-baking time.

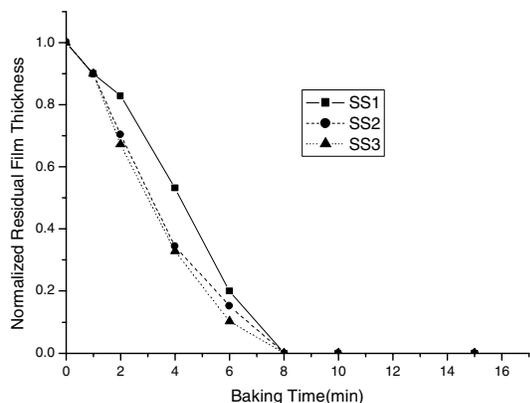
Film thickness decreased with increasing post-baking time and reached zero after being baked for 8 min, indicating that all the three SS polymers were soluble in neutral water. Longer baking time would induce more sulfonyl units to be decomposed and generate more sulfonic acid to facilitate the dissolving process of polymer. The steeper slopes of SS2 and 3 over SS1 were believed to have come from the contribution of higher sulfonyl unit concentrations of SS2 and 3.

Table 1 Base Data of Copolymers

#	Feeding ratio (mol)				Effective ratio (mol) M1(2):M2:M3	Peak temperature of decomposition (°C)	W <sub>n</sub>	W <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	Yield (%)
	M1	M2	M3	M4						
SS1	1	-	1	1	38.5%:35.5%:26%	218.4	17323	26152	1.50967	40
SS2	2	-	1	1	60%:22%:18.3%	216.2	24795	35387	1.42716	39
SS3	4	-	1	1	/	215.9	33210	50031	1.50615	37
VS1	-	2	1	1	28.2%:33%:38.9%	199.1	3988	10465	2.62393	45
VS2	-	4	1	1	29.8%:32.2%:37.9%	198.6	2547	5520	2.16736	42

Note: "/" means the ratio of M1>70% and the ratio of M3<10%, not be measured. "-" means no added.

direct in situ assessment of film thickness during development.



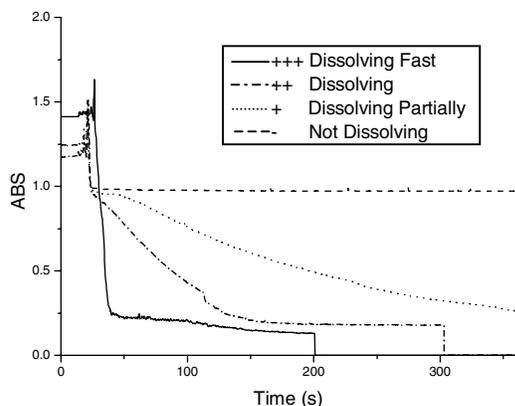
**Figure 1** Normalized residual film thickness of copolymer SS with different sulfonate unit concentrations

### Polymer Matrix with Bisvinyl Ether

It is known that bisvinyl ether compound reacts readily with polymers of phenol or carbonyl groups at about 100 °C, producing acetal structures between the vinyl group and phenol or carbonyl group. The acetal structures cross-link the polymer into three dimensional networks, while shield phenol or carbonyl groups of the polymer, reducing aqueous solubility of the polymer. This was what happened inside polymer films with bisvinyl ether compound during pre-baking.

In post-baking, the sulfonate unit undergone thermolysis, generating sulfonic acids, which in turn accelerated the acetal bonding to decompose and released the shielded carbonyl groups. The released sulfonic acid and carbonyl groups worked jointly to promote aqueous solubility of the polymer. This would lead to a high contrast in aqueous solubility between the pre- and post-baked polymer matrixes. These changes during pre- and post-baking processes could be were also successfully traced by IR spectra [8].

Fig.2 showed four typical dissolving curves of polymer matrix during development, which could be divided into four categories, i.e., Dissolving Fast, Dissolving, Dissolving Partially and Not Dissolving. Slope of the curve was equal to dissolving rate of the polymer. Dissolving rates of different polymer matrixes were taken and provided in Table 2.



**Figure 2** Four typical dissolving curves of polymer matrix

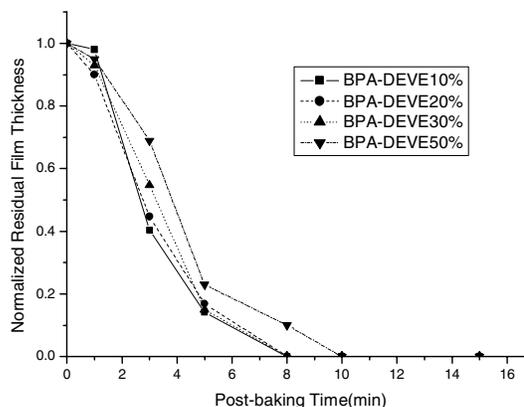
**Table 2** Dissolving Rates of Different Polymer Matrixes

Copolymer	Treatment	THF	Neutral water PH=7
SS1	Drying	+++	-
	Pre-baking	-	-
	Post-baking	-	-
SS2	Drying	+++	-
	Pre-baking	+	-
	Post-baking	++	+
SS3	Drying	+++	-
	Pre-baking	+	-
	Post-baking	++	++

Note: BPA-DEVE=30mol%/MAAmol in copolymer SS. Pre-baking was done at 120°C for 10min and post-baking at 230°C for 10min.

The results in Table 2 indicated that polymer matrixes before baking treatments were Dissolving Fast in THF and Not Dissolving in neutral water, respectively, and became Not Dissolving in either solution after pre-baking. Solubility change in THF was believed to have been brought about by the acetal bonding formed during pre-baking. Effects of post-baking on solubility were different and polymer specific. Polymers of lower sulfonyl unit concentration, such as SS1, remained Not Dissolving, but polymers with higher sulfonyl unit concentration, such as SS3, became Dissolving in both THF and neutral water. Dissolving in THF was mainly contributed by the cleavage of the acetal bonding (decross-linking), but Dissolving in neutral water came jointly from both contributions of the decross-linking and the release of hydrophilic groups. Copolymer SS3 had the highest sulfonyl unit concentration, over 70mol% and would generate more sulfonic acid and at the same time, more effective cleavage of the acetal bonding.

Figure 3 showed the concentration effects of bisvinyl ether on residual film thickness of copolymer SS3 after development in neutral water. Four different films were made, in which 10, 20, 30 and 50mol% of BPA-DEVE relative to that of MAA unit in the copolymer were added, respectively. The films were pre- and post-baked at 120 °C for 10min and 230 °C for different time, respectively, before put into stirred neutral water for development. After development, film thickness was measured and plotted against post-baking time.



**Figure 3** Film thickness change of copolymer SS3 matrix with different concentration of BPA-DEVE

Film thickness decreased with increasing post-baking time and film with 50mol% BPA-DEVE became completely dissolved after post-baked for 10 min, while the other three with less BPA-DEVE became completely dissolved after post-baked for 8 min. Film with 10mol% BPA-DEVE had the steepest slope, though not that different with that of 20mol% BPA-DEVE, indicating the highest rate of dissolving in neutral water. This concentration dependence of aqueous solubility on BPA-DEVE would presumably come from incomplete cleavage of the acetal bonding, but still required more work before convincing explanation would be found.

## Conclusion

A series of copolymer containing sulfonyl and carboxyl units were synthesized and used in combination with a vinyl ether monomer in the form of thin film. It was found that the polymer matrix became completely insoluble in aqueous solution after baked at low temperature around 120 °C and then turned to be highly soluble in aqueous solution, even in neutral water, when exposed to high temperature above 200 °C. The high contrast of this polymer matrix in aqueous solubility was brought about by both contributions of decross-linking and release of acidic groups. Preliminary imaging experiments showed that this polymer matrix could be possibly applied in thermal laser imaging.

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