

# Synthesis and Properties of Water Soluble Phenolic Resin Bearing Side Groups of Tertiary Amino oxide <sup>a</sup>

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## Abstract

This paper was mainly focused on the synthesis and properties of a novel water-soluble phenolic resin with side groups of tertiary amino oxide. First, 3-(dimethylamino)propanoic acid was synthesized by the addition reaction of dimethylamine with methyl acrylate followed by the hydrolysis of the adduct. Then, 3-(dimethylamino)propanoic acid was oxidized with hydrogen peroxide to yield 3-(dimethylamino)propanoic acid oxide. Finally, epoxy phenolic was reacted with 3-(dimethylamino)propanoic acid oxide to give the water soluble modified phenolic resin. Thermal behaviors and thermo-induced solubility change of the prepared resin were investigated. It was found that the modified epoxy phenolic resin could still dissolve in water after being heated at 120 °C for 10 min, and the solubility remained almost unchanged. But upon being heated at the temperature of 140 °C, the resin became completely insoluble in water. This modified epoxy phenolic resin had excellent film forming property, and its aqueous coating formed uniform films with strong adhesive attraction to substrate. This new resin can be possibly applied in thermal imaging applications.

## Introduction

CTP has been a hot topic in printing industry and highlighted in all international and local industrial shows since DRUPA95. There is no doubt that CTP is the direction that the graphic arts technology evolution is heading and it will become dominant in all professional sectors. CTP plate is believed to be the ultimate destination of prepress technology evolution <sup>[1-3]</sup>. So, a quite number of institutes and companies are engaged in designing and developing CTP plates, among which thermal laser imaging plates seem to be the major direction. However, most of the commercial CTP plates are those that require a procedure for washing away non-image areas with organic solvents or aqueous alkaline solution. And this inevitably causes pollution problems. Environmental considerations and legislation have impelled interest in processless or chemistry-free CTP plates, which reduce or eliminate the need for harmful organic solvents or chemicals. In this paper, a new water-soluble phenolic resin with tertiary amino oxide groups was synthesized and characterized. The thermal behaviors of the new resin were also investigated. In addition, a homemade apparatus for in situ monitoring film thickness change in dissolving were employed to evaluate the thermo-induced solubility change of the polymer films.

## Experimental

### Reagents and Instrumentals

Dimethyl-amine aqueous solution (30%), hydrogen peroxide (30%), methyl acrylate, epoxy phenolic resin (F-44) and organic solvents were obtained from Beijing Chemicals and used without further purification.

FTIR spectra were obtained with a SHIMADZU FTIR-8400 infrared spectrophotometer. Film thickness was recorded with a Taylor Hobson FTS-S3c instrument.

### Preparation of 3-(dimethylamino)propanoic acid oxide

3-(Dimethylamino)propanoic acid oxide was synthesized through three steps. First, methyl 3-(dimethylamino) propanoate was prepared by the addition reaction of dimethylamine with methyl acrylate according to the reported procedure <sup>[4]</sup>. Then, 3-(dimethylamino) propanoate was hydrolyzed to give a white product of 3-(dimethylamino) propanoic acid (mp: 148-149 °C). Finally, 3-(dimethylamino) propanoic acid was oxidized by hydrogen peroxide to obtain 3-(dimethylamino) propanoic acid oxide. In a typical experiment, a solution of 3-(dimethylamino) propanoic acid (11.7 g, 0.1mol) in water (20 ml) was stirred and heated to 70 °C. Then, hydrogen peroxide (11.4 g) was added dropwise to the mixture and completed within 1-1.5 h. After the addition, the mixture was stirred for another 2 h. The mixture was concentrated with a vacuum evaporator to afford a viscous product. The product was used in the next step.

### Modification of epoxy phenolic resin to prepare water-soluble polymer

A mixture of epoxy phenolic resin (5.0 g), 3-(dimethylamino) propanoic acid oxide (2.4 g), N,N-dimethylaniline (2 drops) and N-methyl-2-pyrrolidinone (NMP, 5 ml) was stirred at 70-75 °C for 5 h. After cooling to room temperature, the clean viscous solution was slowly dispensed into 50 ml of acetone with stirring to afford a light yellow precipitate.

### In Situ Evaluation of Film Thickness Change During Development

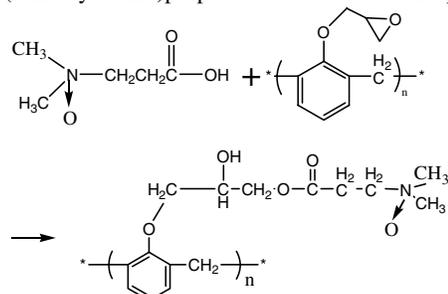
A homemade apparatus was employed to trace in situ film thickness change during development. The apparatus was a special sample chamber attachment to a commercial UV-Vis. spectral photometer. In this paper, SHIMADZU UV-2101PC was used as the photometer. The sample chamber attachment consisted of a sample 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 that had strong absorbency at longer wavelength where the polymer did not absorb 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. Since  $\epsilon$  and  $C$  were kept constant in this study,  $ABS$  or  $ABS/(\epsilon \times C)$  were linearly correlated to film thickness according to Beer-Lambert Law. And this allowed us to make direct in situ assessment of film thickness change during development.

## Results and Discussion

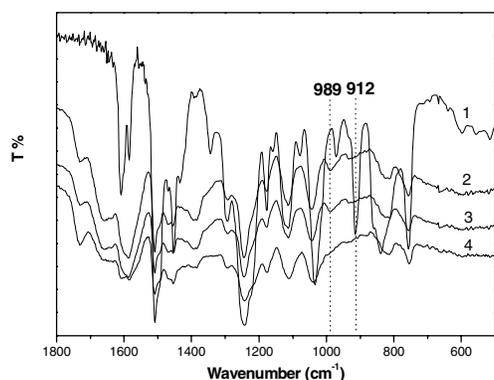
### Synthesis of the Modified Phenolic Resin

As shown in Scheme 1, phenolic resin with tertiary amino oxide functional side groups was prepared by the reaction of 3-(dimethylamino)propanoic acid oxide with epoxy phenolic resin.



**Scheme 1** Modification of the phenolic resin

The reaction was conducted at 70-75 °C and the temperature should not be higher than 80 °C to avoid unexpected side reactions, such as the thermal decomposition of tertiary amino oxide groups and the cross-linking of the epoxy groups. FTIR spectra were used to trace the reaction. Figure 1 compares the IR spectra of the epoxy phenolic resin before and after the modification (curve 1 and 2). The strong absorption band at 912  $\text{cm}^{-1}$  of the epoxy phenolic resin (curve 1) was the characteristic absorption for the terminal epoxy groups. However, this absorption band was not observed after the modification reaction with 3-(dimethylamino) propanoic acid oxide and the characteristic absorptions of the tertiary amino oxide groups of the modified phenolic resin (curve 2) appeared at 989  $\text{cm}^{-1}$ , indicating that most of the epoxy groups had been converted into the tertiary amino oxide groups.



**Figure 1** Comparison of the FTIR spectra of epoxy phenolic resin (1), modified epoxy phenolic resin (2) and modified epoxy phenolic resin treated at 120 °C (3) and 140 °C (4)

### Solubility of the Resins

Table 1 lists the solubility of the epoxy phenolic resin before and after the modification reaction in various organic solvents and water. It can be seen that the epoxy phenolic resin had good solubility in organic solvents, but was insoluble in water. However, the modified phenolic resin could be dissolved in water and strong polar solvents, including NMP and N,N-dimethylformamide (DMF), but showed poor solubility in common organic solvents such as acetone, chloroform and ethanol. This can be explained that the modified phenolic resin contained many polar tertiary amino oxide groups that made the polymer behave as an ionic polymer.

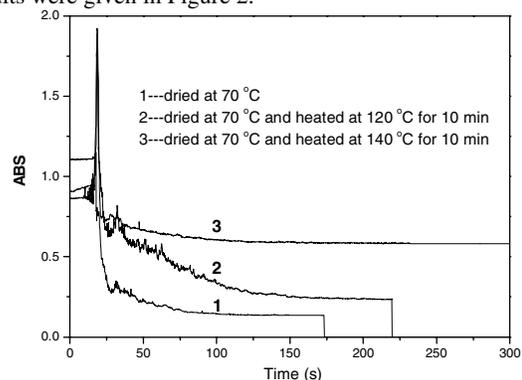
**Table 1** Solubility of the Resins

Solvent	Epoxy phenolic resin	Modified epoxy phenolic resin
Water	-	+
Acetone	+	-
NMP	+	+
DMF	+	+
Chloroform	+	-
Ethanol	-	-

Note: +: soluble; -: insoluble.

### Thermo-induced Solubility Change of the Modified Phenolic Resin Films

The resin films were prepared by the dissolution of the modified phenolic resin in water at room temperature with a solid content of 10 % (w/w). The solution was spin cast onto a quartz glass plate, followed by baking at 70 °C for the removal of water. Considering that the tertiary amino oxide group is not very stable and will decompose at elevated temperatures, say, higher than 100 °C, we may suppose that the modified phenolic resin film will undergo solubility change after heat treatment. To verify this assumption, we measured the dissolution behavior of the modified phenolic resin film before and after heat treatment. In this paper, a homemade apparatus for in situ monitoring film thickness change was used to measure the dissolving rate of the polymer matrix in a selected solvent, here water was chosen as the solvent and the results were given in Figure 2.



**Figure 2** Comparison of the dissolving rate of the resin films (film thickness: 20-25 nm)

It is clear that the solubility of the modified phenolic resin films treated at various temperatures was quite different. For the film dried at 70 °C (Figure 2(1)), the dissolving rate was fast as indicated by the steeper slope of the curve. Upon being heated at

120 °C for a short period of time (Figure 2(2)), the dissolving rate became slower, and the complete dissolution time was about 50 s longer than that of the original film, but the film could still be dissolved in water. However, once the film was heated at 140 °C (Figure 2(3)), it was no longer soluble in water. The changes of solubility in water were believed to be the results of the decomposition of the thermo-sensitive tertiary amino oxide groups, which were converted into other non-polar groups. This argument is supported by the FTIR spectra of the films. Let's go back to Figure 1, in which curve 3 and 4 were the IR spectra of the films treated at 120 °C and 140 °C, respectively. Compared with curve 2, the characteristic absorption of the tertiary amino oxide group still appeared in curve 3, but disappeared in curve 4, indicating that the tertiary amino oxide groups undergone no or only partial decomposition at 120 °C, but were completely broken down into other components at 140 °C. This result showed that the decomposition rate of the tertiary amino oxide groups was highly dependent upon the temperature.

## Conclusion

A new phenolic resin containing tertiary amino oxide groups was synthesized and the properties were measured. Results showed that the polymer was water-soluble and thermo-sensitive. At higher temperatures above 140 °C, the tertiary amino oxide groups undergo thermolysis. As a result of this change, the polymer matrix lost its aqueous solubility in water. This polymer matrix

may find application in the new thermal imaging material system requiring no chemical post treatment.

## References

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## Author Biography

Li Zhongxiao received his MS degree from Huazhong University of Science and Technology in 2000 and PhD (in Polymer Chemistry) from Institute of Chemistry, Chinese Academy of Sciences in 2003. Since 2003 he has been involved in the development of new functional polymers and their properties as information recording materials, including core-shell particles, thermo-sensitive polymers and photosensitive polymers.