# Affinity-Switching Polymer Matrixes and Their Properties

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## Abstract

*Several copolymers had been synthesized by the copolymerization of butyl methacrylate (BuMA), methacrylic acid (MAA) and styrene. Photoacid generators (PAGs) were incorporated with the copolymer and BVE to form photosensitive imaging materials. The imaging performances of the tercomponent system were systematically investigated, and results showed that the imaging performances of the tercomponent systems were strongly dependent on the specific composition of the copolymer, the photoacid generator, the baking temperature and the baking time. Meanwhile, the crosslinking degree could be increased by increasing the amount of BVE and the pre-baking temperature as well as prolonging the pre-baking time. Ideal results would be obtained when the three factors were adjusted properly. With 2-(3,4-dimethox) styrene triazine (DST) or triphenylamine sulfonium salt (TPSS) as PAGs and through sufficient high post-baking temperature, the tercomponent imaging system could exhibit high imaging sensitivity. The imaging sensitivity was not much dependent on post-baking temperature when DST was used in the systems. However, in the case that TPSS was used as PAG, the imaging sensitivity was found quite susceptible to post-baking temperature. In addition, the higher proportion of MMA unit in the copolymers, the better performance of the tercomponent system.*

*Keyword: Affinit-Switching Polymer, Imaging System, Imaging Performances*

## Introduction

Affinity-switching polymers are those which may undergo affinity change, say, from hydrophobic to hydrophilic or vice versa, when subjected to physical or chemical stimuli. They have found applications in DUV microlithography and computer to plate (CTP), and has become important functional polymer for imaging [1-4]. A linear copolymer, poly(butyl methacrylate – methacrylic acid-styrene) (p-(BMA-MMA-St)), contains carboxyl groups which could easily react with divinyl ether type cross-linker to form an acetal ester structure at suitable temperature (120℃) to form cross-linked structure in space. This structure makes the copolymer matrix more resistant to aqueous solution and the film become insoluble. Furthermore, this kind of cross-linking structure would readily decompose and generate carboxyl acid in the presence of strong acids and elevated temperatures, and became highly aqueous soluble. Therefore, an affinity-switching imaging system with high contrast can be built with the combination of the photoacid generator (PAG), divinyl ether and acid sensitive polymer. When the imaging material was subject to radiation, strong acids were generated through the decomposition of the PAG. The acetal ester structure is susceptible to strong acid and the scission reaction occurs at suitable temperature, leading to the regeneration of carboxyl groups. With the cross-linking and de-cross-linking processes of the polymer matrix, it should change from the hydrophobic state to the hydrophilic one [5-7]. This feature makes it possible to construct a high-contrast water-developable imaging material which may be used to develop new CTP (computer-to-plate) plates.

## Experimental

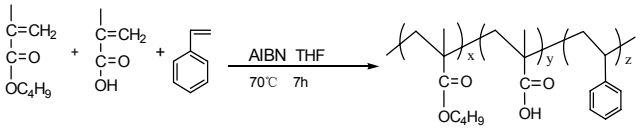
### *Reagents and instrumentals*

Methacrylic acid (MAA), n-butyl methacrylate (n-BuMA), styrene (St) and AIBN were commercial products. Other reagents were purchased and used as received. BPA-DEVE and PAG were synthesized in our Lab. All reagents were purified before used.

IR spectra were measured with a SHIMADZU FTIR-8400 spectrophotometer; 1H NMR was recorded on a ARIA EMAN FX-300 spectrometer; DSC spectra were recorded with a NETZSCH DSC 200PC; TG spectra were recorded with a NETZSCH TG209; 1H NMR spectra were recorded with an ARIA EMAN FX-300 spectrometer.

### *Copolymer preparation*

p-(BMA-MMA-St) was prepared according to the literatures [8]. Calculated amounts of MAA, BMA, St and AIBN were dissolved in THF. The solution was heated to 70°C and kept at that temperature for 6 hrs under the flow of nitrogen. Finally, the solution was poured into large quantity of petroleum ether, and the fibrous precipitation was filtered off, washed and dried in vacuum. Scheme 1 showed the copolymer molecule structure and reactive process. The actual composition the copolymer was measured by water free titration. Thermal behavious of the polymer was investigated by TG.




***Scheme 1. Synthesis of the copolymer.***

### *Preparation of Imaging System*

Under continuous agitation, the copolymer was completely dissolved in purified 1,4-dioxane and then divinyl ether type cross-linker and PAG were added, giving a transparent solution. The coating solution was applied to an aluminum substrate by using a modified spin-coater. The sample was dried in an open-air oven at 70 °C for 30 min.

### *Measurement of Imaging Performance*

The sample film was heated at the set temperature to allow for pre-crosslinking and the polymer matrix experienced changes from a linearly structure to a network structure. The effect of the fractions of carboxyl groups, the ratio of divinyl ether in imaging

system, the type of PAG and the baking on the imaging performance were investigated with the sample.

## Results and Discussion

### *Basic physical properties of copolymer*

The actual fraction of the carboxyl group of p-(BMA-MAA-St) was measured by using water free titration with a solution of sodium methanolate in methanol. The actual fraction of styrene in the copolymer was determined by $^1$H NMR, DSC was used to investigate glass transition temperature of the polymer, and the molecular weight and distribution were determined by GPC. Table1 lists the results of the copolymers with different feed ratio.

**Table1 Basic physical properties of the copolymer with different feed ratio**

| Polymer | TPB-1 | TPB-2 | TPB-3 |
|---|---|---|---|
| Feed ratio(mol) （BMA:MAA:St） | 1:2:0.5 | 1:3:0.5 | 1:4:1 |
| Actual Ratio of MAA (wt%) | 44.6 | 51.5 | 47.6 |
| Actual Ratio of St （wt%） | 18.7 | 14.8 | / |
| Tg（$^o$C） | 42.9 | 51.1 | / |
| $M_n$ | 14022 | 14237 | 14251 |
| $M_w$ | 23945 | 25320 | 24523 |
| $M_w/M_n$ | 1.71 | 1.78 | 1.72 |

As showed by Table 1, the actual ratios of MAA in the polymers and the glass transition temperature of the polymers increased with the feed ratio of MAA, however, the molecular weights and distributions of the polymers were independent on the feed ratio of MAA.

### *The influence of cross-linking conditions on the cross-linking degrees*

Fig. 2 and Fig. 3 showed the influence of pre-baking time and the amount of divinyl ether on the cross-linking degree at 140 $^o$C. The conversion ratio of divinyl ether reflected the cross-linking degree. It was found that the cross-linking degree of divinyl ether was strongly dependent on the pre-baking time. The initial reaction ratio of the carboxyl group with divinyl ether was very fast whereas decreased slowly with increasing pre-baking time, and the cross-linking degree was decreased with the increasing fed amount of divynyl ether under the same conditions. It is because that the concentration of vinyl group was higher at the beginning and then it gradually reduced with pre-baking time. With the progress of the cross-linking reaction, the mobility of the chain segment became lower and the reactive speed decreased. On the other hand, at the same pre-baking time and the concentration of divinyl ether was at the lower level, there was relatively higher concentration of carboxyl groups around every methoxyethene group, resulting in higher conversion of the divinyl ether.

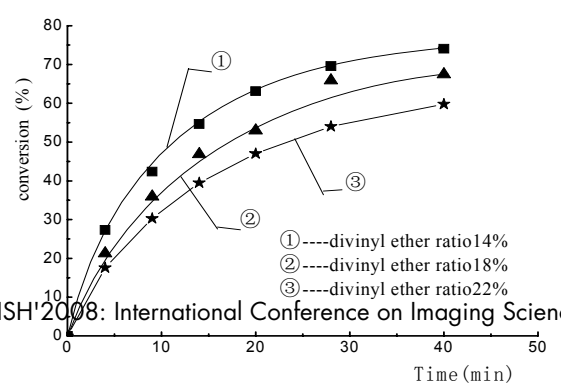
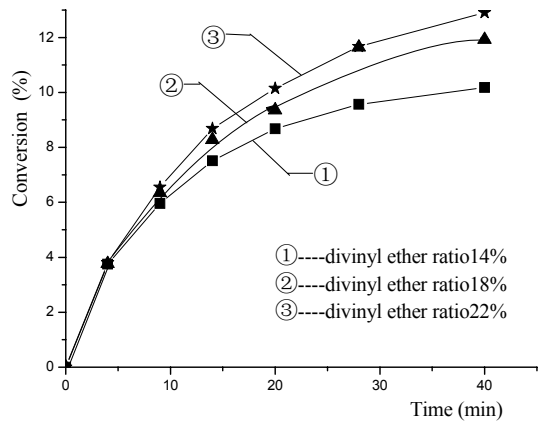



***Fig. 2 The relationship between baking time and the conversion ratio of divinyl ether***

***Fig. 3 The relationship between pre-baking time and the conversion ratio of MAA.***

### *The influence of pre-baking temperature*

The relationship between conversion of divinyl ether and baking temperature was shown in Fig.4. It is a linear curve and the conversion ratio increased with the increasing baking temperature.




After baking at 140$^o$C for 10 minutes and 100 $^o$C for 30 minutes, the conversion of divinyl ether was 47.64% and 54.15%, respectively. The results showed that the baking temperature and baking time have the similar effects. Higher cross-linking degree can be achieved by lowering the baking temperature or increasing the baking time.

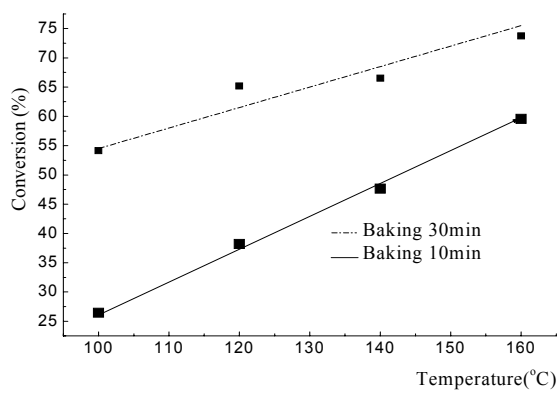



***Fig4. The relationship between conversion of divinyl ether and baking temperature***

The results showed that the degree of cross-linking can be achieved by increasing the amount of divinyl ether, the baking temperature and baking time. However, increasing the amount of divinyl would inevitably result in more unreacted compound which was unfavorable for the following de-crosslinking processs. The

cation polymerization of divinyl ether will not occur without the existence of acid and part of the acid will be consumed, meanwhile, the cross-linking structure produced by cation polymerization may lower the sensitivity of the imaging system. Thus, the usage of divinyl ether must be controlled for the imaging system in order to increase the imaging sensitivity. The degree of cross-linking can be achieved by increasing baking temperature and baking time, that is, the degree of the cross-linking can be achieved by two ways – increasing the baking temperature and extending the baking time.

### *The influences of PAGs*

The influences of post-baking temperature and different PAGs on the performances of the imaging system were summarized in Table 2. The results showed that the minimum exposing time decreased due to the increasing of sensitivity of the imaging system. Post-baking temperature has little effect on the sensitivity of imaging system when using DMOS-triazine as PAG, but when using TPASS as PAG, the manner was completely different. Due to high volatility of the generated HCl, it was especially typical in the TPB-2 system. Increasing post-baking temperature was favorable for de-crosslinking, but higher post-baking temperature will accelerate the evaporation of HCl that was unfavorable for de-crosslinking. The loss of HCl counteract the effect of baking temperature on the sensitivity of the imaging system. Trifluoromethanesulfonic acid produced by TPASS under UV light had relatively low volatility so that the baking temperature had great effect on this imaging system by using TPASS as PAG.

**Table 2 Imaging Performance of the Imaging system**

| Polymer | Post-baking Tempreture ($^{o}$C) | Least Exposure Time for DMOS-triazine (min) | Least Exposure Time for TPASS (min) |
|---|---|---|---|
| TPB-1 | Non-baking | 5 | 7 |
| | 120℃ | 2.5 | 2 |
| | 140℃ | 2 | 1.5 |
| TPB-2 | 120℃ | 3.5 | 5 |
| | 140℃ | 2.5 | 2 |

By comparing these two systems, it was found that the sensitivity of imaging system was decreased with the increasing amount of MAA moiety in the polymers and especially the decreesae of the post-baking temperature. The reason is that the higher contrast of the imaging system needs more divinyl ether in the system, and the degree of cross-linking was increased with the increasing amount of MAA in the polymers, hence the degree of de-crosslinking must be increased during the imaging process. The unreacted divinyl ether was in direct ratio to the amount originally added in the imaging system. The cation polymerization of divinyl ether occurs in the presence of acid and part of the acid will be consumed. The cross-linking structure created by cation polymerization will decrease the sensitivity of the imaging system. The results showed that the sensitivity of the TPB-2 system was lower than that of TPB-1 system.

## Conclusion

Three copolymers had been synthesized by the copolymerization of butyl methacrylate (BMA), methacrylic acid (MAA) and styrene. Photoacid generators (PAGs) were incorporated in the copolymers and BVE to form a photosensitive imaging material. The imaging performances of the tercomponent systems were strongly dependent on the specific composition of the copolymer, the photoacid generator, the baking temperature and the baking time. Meanwhile, the crosslinking degree could be deepened by increasing the amount of BVE and the pre-baking temperature as well as prolonging the pre-baking time. Ideal results would be obtained when the three factors were adjusted properly. With 2-(3,4-dimethox) styrene triazine (DST) or triphenylamine sulfonium salt (TPASS) as PAGs and through sufficient high post-baking temperature, the tercomponent imaging system could exhibit high imaging sensitivity. The imaging sensitivity was not much dependent on post-baking temperature when DST was used in the systems. However, in the case that TPSS was used as PAG, the imaging sensitivity was found quite susceptible to post-baking temperature. In addition, the higher proportion of MMA unit in the copolymers, the better performance of the tercomponent system.

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Weimin Zhang, male, professor, graduated in East China University of Science & Technology in 1986. He is working in Lab. Printing & Packaging Material and Technology (Beijing area major laboratory), in Beijing Institute of Graphic Communication. His work is focused on organic information recording materials, especially organic photoreceptor, functional materials.