# Photogenerated Base in Polymer Curing and Imaging: Cross-Linking of Base-Sensitive Polymers Containing Enolizable Pendant Groups

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The ability of photogenerated amine catalysts to effect the insolubilization of polymers containing acidic methylene units is explored. Cross-linking of films of poly(2-acetoacetoxyethyl methacrylate)-*co*-(methyl methacrylate) or poly(2-cyanoacetoxyethyl methacrylate)-*co*-(methyl methacrylate) containing [[(2,6-dinitrobenzyl)oxy]carbonyl] cyclohexylamine as photobase generator and a bifunctional aldehyde molecule can be achieved upon exposure to deep-UV irradiation and subsequent heating. Polymers containing the cyanoacetate functionality displayed high resist sensitivities (ca. 20 mJ/cm$^2$) in simple contact imaging experiments. Monitoring of the resist films using UV−vis spectroscopy suggested that cross-linking of the polymers in the presence of the aldehyde moiety proceeds via a Knoevenagel reaction. Photo-cross-linking and imaging can also be achieved in the absence of the added acceptor molecule and possible mechanisms for this insolubilization are discussed. Incorporation of the reactive cyanoacetate functionality into a phenolic polymer to provide aqueous base development is examined via the synthesis of poly[4-(2-cyanoacetoxymethyl)styrene]-*co*-[4-hydroxystyrene].

## Introduction

Radiation-cured polymer thin films have been used extensively in the coatings industry as well as in the development of imaging materials for microelectronic device manufacturing.[1] The development of photochemical precursors to strong acid catalysts[2] and their incorporation into chemically amplified[3] imaging systems provided an increase in resist sensitivity over the previously studied novolak-based[4] imaging materials. The catalytic nature of the acid-triggered modification process amplifies the effective quantum efficiency of the photochemical step, and this has led to the design of many novel resist systems based on cationic processes.[5] A number of radiation-cured imaging systems based on electrophilic aromatic substitution[6] have been developed that combine the high sensitivity of chemically amplified processes with the excellent resolution demonstrated by the aqueous base developable phenolic matrixes.[7] In these systems, generation of the acid catalyst within the coating leads to the formation of a carbocationic moiety from a latent electrophile attached to the phenolic polymer matrix or added as a third component in the resist formulation. Alkylation of the phenolic polymer by the generated electrophilic species causes insolubilization in the exposed areas of the matrix and formation of a negative tone image upon aqueous base development.

The development of photoactive compounds that can liberate amines and other bases[8] upon irradiation has opened a new avenue for the development of novel radiation-curable coatings, resists, and imaging materials involving base-catalyzed processes. For example, these precursors to amines have been used along with a thermally labile acid generator to effect image reversal in the previously described negative-tone resist system based on electrophilic aromatic substitution.[9] Subsequently, a number of imaging systems designed to function via a base-catalyzed decarboxylation,[10] imi-

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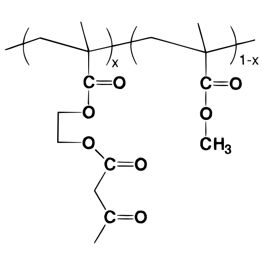
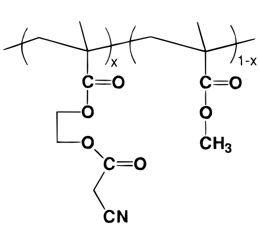
dization,[11] or $\beta$ elimination[12] have also been investigated. One of the earliest studies utilizing the photochemical generation of a basic moiety examined the cross-linking of a glycidyl methacrylate copolymer via reaction of the generated amine with the pendant epoxide groups.[13] This study demonstrated that the lithographic sensitivity of this system was dependent on the strength and/or volatility of the liberated base. A number of other studies have also examined similar processes involving a variety of photoactive precursors of amines,[14] as well as polymeric amines[15] in the cross-linking of epoxides.

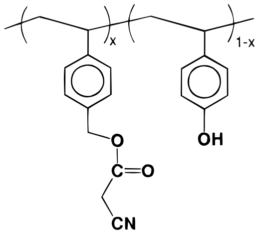
Base-sensitive coatings containing pendant acetoacetate functionalities have been examined previously for use as resins in thermoset coatings.[16] Because of their acidic methylene units, these materials can participate in a variety of addition reactions that lead to functionalization or cross-linking of the acetoacetylated polymer. The thermoset resins were initially obtained by copolymerization of the commercially available 2-acetoacetoxyethyl methacrylate (AAEM) monomer with an appropriate comonomer or via direct acetoacetylation of cellulose[17] using diketene. It was found that polymers obtained by copolymerization of AAEM with methyl methacrylate formed highly cross-linked gels at room temperature via a Michael reaction when formulated with polyacrylates and strong base catalysts. This finding suggested that functionalized copolymers containing AAEM units might be used in the design of novel radiation curable coatings operating via a Michael or Knoevenagel-type reaction. For this study, we chose to examine three families of copolymers (**1**−**3**) that contained either acetoacetate or cyanoacetate pendant groups. Copolymers **1** and **2**, which are similar in structure, allowed us to investigate the relative reactivity of the two different enolizable functionalities toward the photogenerated base catalyst. Copolymer **3** incorporates the highly reactive cyanoacetate functionality into a phenolic matrix to take advantage of both the alkaline development process and the superior lithographic properties afforded by this class of polymers. To enable our evaluation of the cross-linking process through spectroscopic analysis, we examined the ability of photogenerated base to catalyze a Knoevenagel condensation[18] between the reactive copolymers **1**−**3** and an added bifunctional aldehyde. We also examined the use of these materials in a 2-component cross-linking system in which the functionalized polymer is formulated with photobase generator without further additive.



**1**



**2**



**3**

## Results and Discussion

**Synthesis of the Functionalized Copolymers.** To obtain polymers containing the reactive acetoacetate functionality, the commercially available 2-acetoacetoxyethyl methacrylate (AAEM) was copolymerized with various amounts of methyl methacrylate under free radical conditions to provide copolymers **1a**−**c**. Since incorporation of the very reactive cyanoacetate functionality into an analogous polymer system offered attractive possibilities for use in condensation reactions, such as the Knoevenagel reaction, the appropriate monomer, 2-cyanoacetoxyethyl methacrylate (CAEM, **4**) was also prepared. This enolizable monomer was obtained by esterification of 2-hydroxyethyl methacrylate (HEMA) with cyanoacetic acid using dicyclohexylcarbodiimide (DCC) as the coupling agent (Scheme 1). Free radical copolymerization of CAEM with various amounts of methyl methacrylate led to copolymers **2a**−**c**. While both families of polymers were highly soluble in organic solvents such as acetone, THF, and chloroform, neither provided the alkaline solubility that would allow their development using standard lithographic developers. Therefore copolymer **3**, which couples the high reactivity of the cyanoacetate functionality to the desirable resist characteristics of a phenolic matrix, was also prepared. The desired cyanoacetate-functionalized styrene monomer was obtained by reaction of 4-vinylbenzyl chloride with the potassium salt of cyanoacetic acid or via the dicyclohexylcarbodiimide-assisted coupling of cyanoacetic acid with 4-vinylbenzyl alcohol (Scheme 2). Both reactions provided 4-(2-cyanoacetoxymethyl)styrene (**5**) in high yield as a white crystalline solid. Copolymerization of **5** and 4-[(trimethylsilyl)oxy]styrene (**6**), followed by acid cleavage of the TMS protecting groups provided the desired phenol-containing polymer **3** (Scheme 3). The TMS moiety was chosen as the phenolic protecting group during polymerization because it allowed deprotection under mild conditions without hydrolysis of the ester functionality. The ratio of benzylic methylene protons to aromatic protons in the

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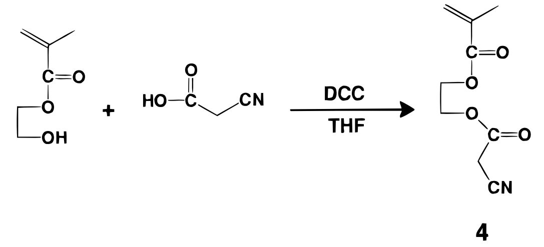
**Scheme 1**



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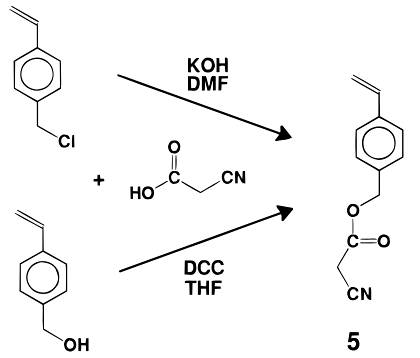
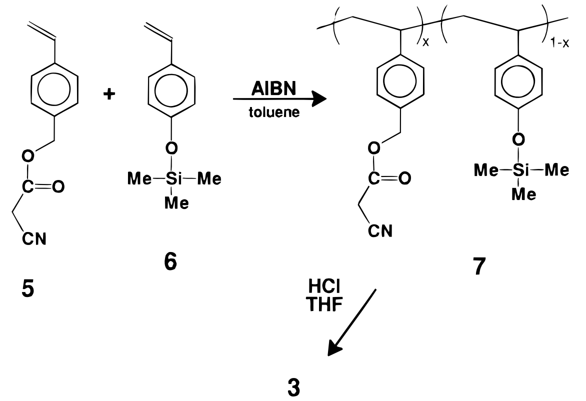


**Scheme 3**



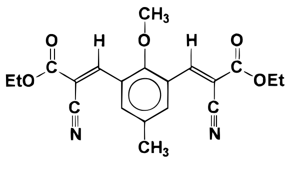
$^1$H NMR spectrum of the polymer suggested that 30 mol % of monomer **5** was incorporated into polymer **3**. This is in good agreement with both the composition expected from the monomer feed ratio and that observed prior to deprotection. The deprotection of **7** into **3** may be monitored by $^1$H NMR spectroscopy. Upon deprotection, the resonance at 0.20 ppm due to the TMS methyl groups disappears while a phenolic resonance appears at 8.0 ppm. The signals for the benzylic (5.2 ppm) and acidic methylene (3.9 ppm) hydrogens remain unchanged during the deprotection step. A very small signal at 4.6 ppm also appears in the spectrum of **3** that corresponds to an impurity due to a side reaction forming a few benzyl alcohol units within the polymer. From the integration of the various signals in the $^1$H NMR spectrum, this side reaction which accompanies the deprotection step is estimated to affect 2−3% of the total ester functionalities within the polymer. The deprotection reaction is also clearly confirmed by $^{13}$C NMR data as shown below in the experimental section. Molecular weights, compositions and glass transition values for the various polymers are given in Table 1. As expected, increasing the amount of active methylene-containing monomer in the methacrylate copolymers brings about a decrease in the measured glass transition temperatures ($T_g$) of these materials. The materials containing pendant cyanoacetate groups display slightly higher $T_g$ values at similar compositions than the acetoacetate functionalized polymers. One of the advantages derived from the presence of phenolic structures in polymer **3** is the relatively high $T_g$ values that result. Poly[(4-acetoxymethyl)styrene]-*co*-[4-hydroxystyrene], which was designed for use in resists based on acid-catalyzed electrophilic cross-linking reactions[6] and is similar in structure to polymer **3**, has a $T_g$ of 145 °C and shows a thermal decomposition near 200 °C. Thermal analysis of polymer **3** by differential scanning calorimetry (DSC) does not show any $T_g$ near 140 °C, but the polymer undergoes a thermal loss of the ester functionalities starting near 150 °C as confirmed by thermogravimetric analysis. This suggests that incorporation of the electron withdrawing nitrile group reduces the thermal stability of the pendant ester functionality. Nevertheless, the presence of acidic phenol units within the polymer enables the use of this material in resist films that are both aqueous base developable and designed to take advantage of the base susceptibility provided by the cyanoacetate functionalities.

**Table 1. Polymer Molecular Weight and Glass Transition Values**

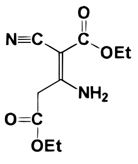
| polymer | mole fraction of active methylene containing monomer[a] | $M_n$[b] ($\times 10^3$) | $M_w$[b] ($\times 10^3$) | $T_g$ (°C) |
|---|---|---|---|---|
| **1a** | 0.10 AAEM | 27.9 | 77.8 | 97.7 |
| **1b** | 0.28 AAEM | 32.5 | 204 | 63.6 |
| **1c** | 0.53 AAEM | 22.0 | 68.6 | 33.8 |
| **2a** | 0.12 CAEM | 69.7 | 169 | 105.8 |
| **2b** | 0.32 CAEM | 37.3 | 507 | 72.8 |
| **2c** | 0.53 CAEM | 14.0 | 35.1 | 56.8 |
| **7** | 0.31 | 42.8 | 92.2 | 72.9 |
| **3** | 0.30 | 21.5 | 39.6 | >140[c] |

[a] Determined experimentally by $^1$H NMR. [b] Measured by GPC. [c] Polymer displays a weight loss at 150 °C by thermogravimetric analysis.

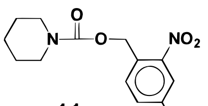
**Photochemical Cross-Linking Studies of the Methacrylate Polymers.** All of the polymers prepared were spin coated as ca. 1 $\mu$m thin films containing 11 wt % of the [[(2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine (**11**) photoamine generator and then exposed to ultraviolet (UV) light. As will be seen below, a cross-linking additive, 2-methoxy-5-methylisophthalaldehyde (**8**) was also used in combination with the polymer and the photobase generator in some experiments. Generation of the cyclohexylamine catalyst within the exposed areas of the films followed by baking at 110 °C results in the insolubilization of the exposed



**9**



**10**



**11**

**Table 2. Deep-UV Sensitivity Results for Functionalized Polymers.**

| polymer | wt % of **8** in resist | sensitivity[a] (mJ/cm$^2$) | wt% of **8** in resist | sensitivity[a] (mJ/cm$^2$) |
|---|---|---|---|---|
| **1c** | 20 | 75 | 0 | 85 |
| **1b** | 20 | 75 | 0 | 85 |
| **1a** | 20 | 85 | 0 | 110 |
| **2c** | 20 | 15 | 0 | 40 |
| **2b** | 20 | 20 | 0 | 70 |
| **2a** | 20 | 20 | 0 | 75 |
| **2a** | 10 | 25 | 5 | 25 |
| **2a** | 10 | 38[b] | | |
| **3** | 10 | 19[c] | 0 | 100[c] |
| **3** | 5 | 50[c] | | |

[a] Resist films containing 11 wt % [[(2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine were exposed to 254 nm irradiation, baked at 110 °C for 5 min and developed in acetone for 15 s. [b] Resist films contained 5 wt % [[(2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine. [c] Resist films containing 11 wt % [[(2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine were exposed to 254 nm irradiation, baked at 120 °C for 5 min, and developed in 2:1 MF312: $H_2O$ for 30 s.

areas while the unexposed areas can be removed with an appropriate developer. The deep-UV resist compositions and sensitivities of the various copolymers are summarized in Table 2. In all cases, two distinct modes of base-catalyzed cross-linking, self-cross-linking and reaction with an added bifunctional moiety, are possible. In the absence of added cross-linker, self-cross-linking is observed but at the cost of lower sensitivities. Control experiments carried out in the absence of the photobase generator confirm that the cross-linking process is not thermal but base catalyzed. Highest sensitivities are observed with three component resists containing an added dialdehyde. Generally, acetoacetate resists formulated with a dialdehyde have sensitivities at least 10−20 mJ/cm$^2$ higher than similar resists without added aldehyde. For resists containing the cyanoacetate functionality the sensitivity increase is significantly larger (ca. 25−60 mJ/cm$^2$). The higher reactivity of the cyanoacetate group toward the added aldehyde is expected as Knoevenagel condensations involving cyanoacetate have been shown to proceed approximately 3 times faster than those with the acetoacetate functionality.[19] Even in the absence of added aldehyde, the cyanoacetate-containing methacrylate copolymers have higher sensitivities than the corresponding acetoacetate copolymers. These finding are not unexpected in view of the electron withdrawing nature of the cyano group which affects the acidity of the adjacent methylene protons. Best results are obtained with films formulated with cross-linker **8** which exhibited very high sensitivities on the order of 20 mJ/cm$^2$. However, in the case of the cyanoacetate copolymer, the added aldehyde must be chosen carefully to avoid premature cross-linking. For example, attempts to use terephthalaldehyde as a cross-linker for films of polymer **2** were marred by the thermal cross-linking of the films while the resist solution itself became a gel within a few hours. The reduced sensitivity of polymer **1** enabled the use of terephthalaldehyde without the occurrence of a thermal reaction. Surprisingly, the sensitivity of the resulting resist was comparable to that observed with **8** as a cross-linker. All resist formulations containing polymer **2** and cross-linker **8**, which is less prone to nucleophilic attack due to deactivation by the ortho methoxy group, did not gel after 24 h and showed no signs of cross-linking during thermal treatment of the resist films.

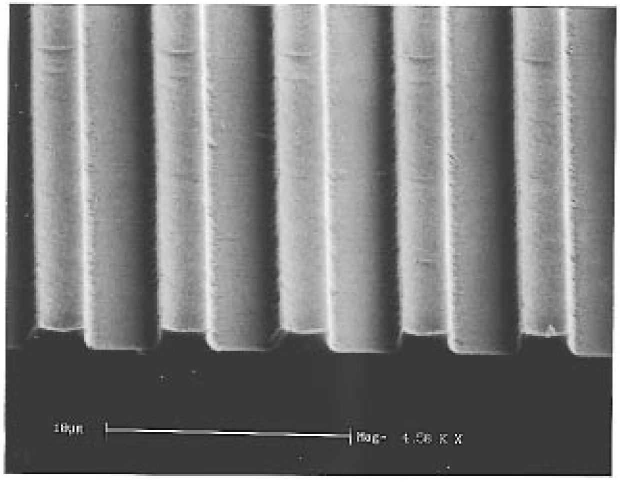


**Figure 1.** SEM of contact printed relief image obtained for resist of polymer **2a** containing 11 wt % of photobase generator **11** and 5 wt % cross-linker **8**. Film was exposed to ca. 25 mJ/cm$^2$ of 254 nm irradiation, baked at 100 °C for 3 min, and developed in 5:3 (v/v) 2-butanone/ethanol for 30 s.

The effect of varying the mole fraction of the enolizable monomer within the copolymers was also examined. In a limited set of experiments, little change in sensitivity was observed when the mole fraction of the enolizable monomer was increased from 30% to 50%. The only exception was seen for polymer **2c** in the absence of added aldehyde as sensitivity increased with an increase in the amount of enolizable units. This suggests that one possible mode of cross-linking in the two-component systems may involve the reaction of pendant active methylene units. Additional evidence supporting this hypothesis is presented below. The very high reactivity of the cyanoacetate functionality toward the added aldehyde was demonstrated in experiments where polymer **2a** (12 mol % CAEM) was formulated with 5 wt % of cross-linker leading to a sensitivity of 25 mJ/cm$^2$. In imaging experiments a small reduction in the film thickness retained after development (87%) of these films was observed compared to the resists containing the larger amount of the cross-linker (95%). Reducing the amount of photobase generator within the polymer films has a more profound effect on the sensitivity of the resist than is observed upon decreasing the amount of cross-linker in the system.

Figure 1 shows the contact relief image obtained for polymer **2a** containing 11 wt % photobase generator and 5 wt % cross-linker **8**. It was found that higher resolution images were obtained upon changing the developer for these systems to a mixture of 2-butanone and ethanol (5:3) to reduce the amount of swelling that is observed when pure acetone is used as the developer.

**Photochemical Cross-Linking Studies of the Phenolic Polymer.** The increased sensitivity displayed by the polymers bearing the cyanoacetate functionality led us to explore the possibility of extending this cross-linking chemistry to a more robust lithographic system, such as polymer **3**, to take advantage of the aqueous base solubility inherent to phenolic resins. In addition to solubility in aqueous base, this polymer also has an increased glass transition temperature, but this is at the cost of optical transparency.

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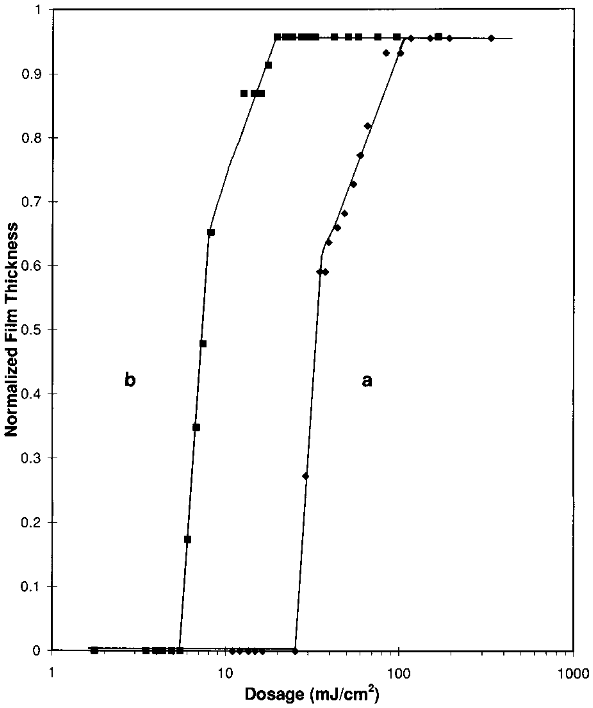
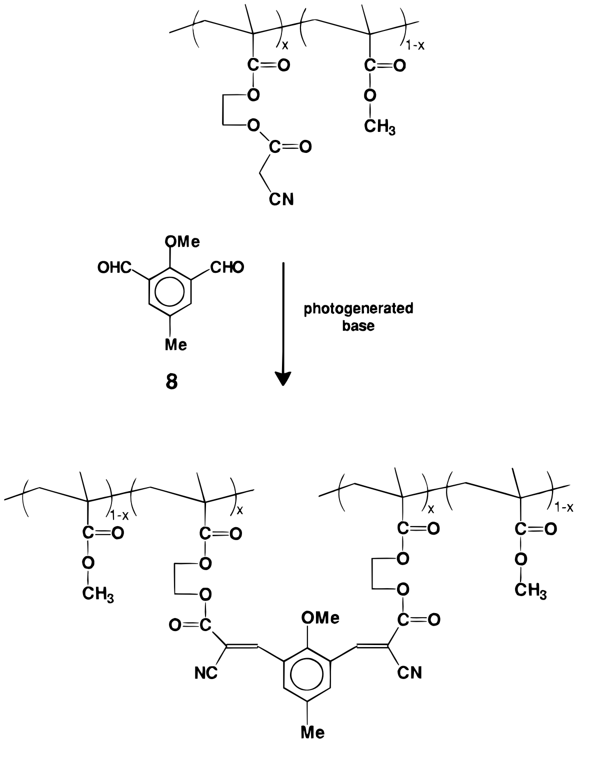


**Figure 2.** Sensitivity curve for two- (curve a) and three- (curve b) component resist of polymer **3** after exposure to 254 nm irradiation, baking at 120 °C for 5 min, and development in 2:1 (v/v) MF312/$H_2O$ for 30 s.

When compared to the methacrylate based polymers which displayed virtually no absorbance at 254 nm, polymer **3** has a much higher, but still manageable, optical density of 0.212 A/$\mu$m. Nevertheless, polymer **3** still demonstrates a fairly high resist sensitivity when formulated with cross-linker **8** and used with aqueous base developers. The postexposure bake temperature can be increased slightly, taking advantage of the higher glass transition temperature of this material. Interestingly, polymer **3** also functions as a two component resist when formulated with the photobase generator (**11**), but a small decrease in resist sensitivity is seen when compared to the methacrylate systems. Figure 2 displays the sensitivity curves obtained for polymer **3** in both the two component and three component resist systems. In the presence of photobase generator alone, polymer **3** displays a sensitivity of 100 mJ/cm$^2$ (curve a) upon development with dilute aqueous base. However, upon addition of 10 wt % of cross-linker **8** to the formulation, an increase in resist sensitivity to 19 mJ/cm$^2$ (curve b) is observed. While the measured sensitivities of the resist systems incorporating polymer **3** are comparable to those observed with the methacrylate-based polymers, this appears to be related to the change in developer. Imaging experiments with resists based on **3** and acetone as the developer show that less cross-linking takes place in the case of **3** as evidenced by the partial dissolution of the exposed film in acetone. Perhaps the decreased cross-linking is a direct result of the increased optical absorbance of the phenolic films which, in turn, decreases the amount of amine generated within the coating. It must be emphasized that this possible reduction in extent of cross-linking has no practical effect in the experiments involving aqueous base developers as 95% of the original film thickness is still retained in the exposed areas. Unfortunately, our preliminary experiments with these base-developable films did not afford the expected enhancement in resolution over the methacrylate-based system. However, it may be possible to increase the resolution of this system by varying the mole fraction of **5** within the copolymer to optimize the sensitivity and development characteristics of the reactive polymer.

**Scheme 4**



**Spectroscopic Studies of the Three-Component Resist.** The overall cross-linking process of polymer **2** with cross-linker **8** via a Knoevenagel reaction is shown in Scheme 4. Our lithographic studies have suggested that other reactions may also be contributing to the overall cross-linking of these materials and Scheme 4 provides a simplified view of only one of several possible cross-linking processes. One advantage of the base-catalyzed Knoevenagel reaction as the primary cross-linking pathway for our systems is that it is amenable to monitoring by UV spectroscopy. For example, because the Knoevenagel condensation proceeds with formation of a new carbon−carbon double bond, cross-linking should proceed with formation of a highly conjugated chromophore leading to increased UV absorption at longer wavelengths. A model of the chromophore formed during the cross-linking reaction was prepared by reaction of ethyl cyanoacetate with cross-linker **8** to afford the bis-Knoevenagel adduct **9**.

Figure 3 shows the results of monitoring the UV−vis spectrum of a film of polymer **2c** containing base generator **11** and cross-linker **8**. The UV−vis spectrum of the unexposed resist film that has been baked at 110 °C (curve a) displays very little absorption past 280 nm. The small peak at 310 nm can be attributed to the absorption band of **8**. However, upon exposure (ca. 160 mJ/cm$^2$ at 254 nm) and baking (110 °C, 5 min) a large increase in absorption above 280 nm is seen (curve b) with a clear shoulder at 300 nm. The UV−vis spectrum of model compound **9** incorporated into a poly(methyl

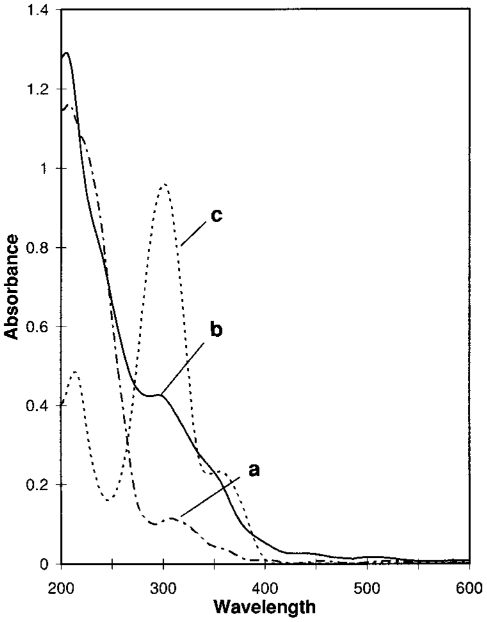


**Figure 3.** Ultraviolet spectra obtained from (a) three component resist film of polymer **2c** prior to irradiation and after baking at 110 °C, (b) three component resist film of polymer **2c** after exposure to ca. 160 mJ/cm$^2$ of 254 nm irradiation and baking at 110 °C for 5 min, and (c) film of poly(methyl methacrylate) containing 10 wt % of the bis-Knoevenagel adduct **9**.

methacrylate) film (curve c) suggests that the large shoulder seen at 300 nm in the spectrum of the cross-linked film is due to the formation of the expected conjugated chromophore analogous to **9** within the polymer film. We therefore believe that in the presence of the added bisaldehyde cross-linker, the photogenerated amine catalyzes the desired Knoevenagel reaction leading to cross-linking of the cyanoacetate-containing polymers. Similar results are also seen in the photochemically induced cross-linking of polymer **1** or **3** with added bisaldehyde. With AAEM copolymers the absorption band corresponding to the generated chromophore is much less pronounced than with the cyanoacetate copolymers, in agreement with the observed lower sensitivity of the AAEM-based resists.

It is also possible that the increased absorption seen in the films upon exposure is the result of the photodecomposition of the base generator leading to an aldehyde byproduct which reacts with the matrix polymer. However, such a reaction would have minimal effect on the solubility of the copolymer film, though such a process would increase the optical density of the methacrylate copolymers. Monitoring the photoinduced cross-linking of the methacrylate copolymers using FTIR spectroscopy failed to provide conclusive information on the cross-linking process due to the large carbonyl absorption bands associated with the polymer ester groups.

**Spectroscopic Studies of the Two-Component Resist.** While monitoring the exposed three-component resist films by UV−vis spectroscopy supported the anticipated cross-linking mechanism, similar experiments using the two-component systems did not provide insight into the mode of cross-linking under these circumstances. The strong absorption band of the photobase generator extends out to 280 nm and masks any change in the optical absorption of the polymer below this wavelength which may take place during the cross-linking of the two-component resist. We chose to examine more closely the base-catalyzed cross-linking of polymer **2** due to the apparent increased reactivity of the cyanoacetate-functionalized polymers during the lithographic study. It is possible that the pendant cyanoacetate groups might undergo the Thorpe reaction,[20] in which the α carbon of one nitrile molecule adds to the nitrile carbon of another to form an enamine species. Ethyl cyanoacetate undergoes such a reaction under basic conditions to form the dimerized product **10**, used previously[21] for the synthesis of substituted heterocycles. 3-Amino-2-cyano-2-pentenedioate (**10**) is readily formed via reaction of ethyl cyanoacetate with sodium ethoxide. However, weaker bases such as amines are much less efficient catalysts for this dimerization reaction. For example, the reaction of cyclohexylamine (10 mol %) with neat ethyl cyanoacetate at 110 °C led almost exclusively to *N*-(cyclohexyl)-2-cyanoacetamide via the nucleophilic attack of the amine on the ester functionality. Analysis of the reaction by gas chromatography only shows that formation of **10** is a minor reaction accounting for less than 1% of the products.

To better examine the cross-linking reaction of polymer **2** under base-catalyzed conditions, the photobase generator was removed from the resist solution and the corresponding amine was added to the dissolved polymer. Addition of cyclohexylamine to a concentrated solution of polymer **2c** leads to rapid gel formation. FTIR analysis of the resulting cross-linked polymer after baking (110 °C, 5 min) and drying (vacuum, 24 h) suggest that cross-linking might indeed occur via formation of an enamine. Figure 4 shows a comparison of the FTIR spectrum of the amine-cross-linked polymer **2c** (spectrum b) with that of the un-cross-linked polymer (spectrum a) and the dimer of ethyl cyanoacetate **10** (spectrum c). Prior to cross-linking, the spectrum of **2c** contains strong carbonyl absorptions (1729 and 1756 cm$^{-1}$) characteristic of the ester functionality along with the small nitrile absorption at 2266 cm$^{-1}$. Upon addition of base and cross-linking of the polymer, new broad absorption bands appear at 3400, 2200, and 1600 cm$^{-1}$. These are consistent with the formation of an enamine structure, as demonstrated by the FTIR spectrum of **10** which also contains absorptions at 3300−3500 cm$^{-1}$ ($NH_2$), 2212 cm$^{-1}$ (conjugated CN), and 1680 and 1632 cm$^{-1}$ (C=C).

The UV−vis spectrum of a polymer film cross-linked through the addition of cyclohexylamine is also consistent with the formation of the enamine structure as it shows increased absorption at 260−280 nm (Figure 5). Compound **10** cast in a film of poly(methyl methacrylate) also exhibits an absorption maximum within this same range at 280 nm. In the resist films containing the photobase generator, the increased absorption resulting from this cross-linking reaction would be masked by the absorption band of the photoactive component. Other evidence supporting the possibility of cross-linking of polymer **2** via a Thorpe reaction is that addition of 5 wt % of succinonitrile as cross-linker to

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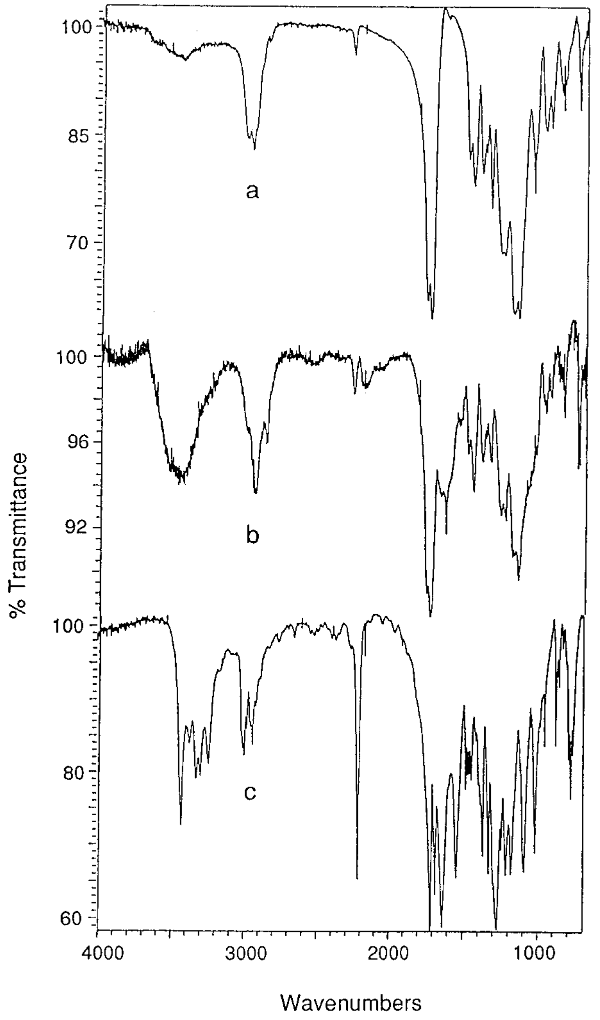

**Figure 4.** FTIR spectra obtained for (a) polymer **2c**, (b) cross-linked polymer **2c** after addition of cyclohexylamine, baking at 110 °C for 5 min and drying in vacuum, and (c) 3-amino-2-cyano-2-pentenedioate (**10**).

the resist film containing polymer **2a** and **11**, caused an increase in sensitivity from 100 to 40 mJ/cm$^2$. Therefore, addition of the bifunctional nitrile compound as a cross-linker has the same affect as increasing the amount of cyanoacetate groups in the copolymer. Similar experiments in which cyclohexylamine was added to polymer **3** also support the cross-linking of the cyanoacetate-containing polymer through the formation of a conjugated nitrile group. The FTIR spectrum of the cross-linked material once again displayed a new absorption at lower frequency (2200 cm$^{-1}$) suggesting a conjugated nitrile group. Unfortunately other areas of the spectrum were obscured by bands due to the phenolic matrix. While the spectroscopic and lithographic data point to a base-catalyzed cross-linking through a dimerization reaction between enolizable groups, we are unable to discount the possibility of other mechanisms playing a role in the insolubilization of these highly reactive polymers. In the case of the methacrylate-based polymers, it is possible that the enolizable units could react with the ester functionalities along the backbone of the polymer in a Claisen condensation. However, we have been unable to collect any direct evidence pointing to this alternate cross-linking mechanism, and it is possible that more than one mechanism may be responsible for the two-component cross-linking demonstrated by these active methylene-containing polymers.

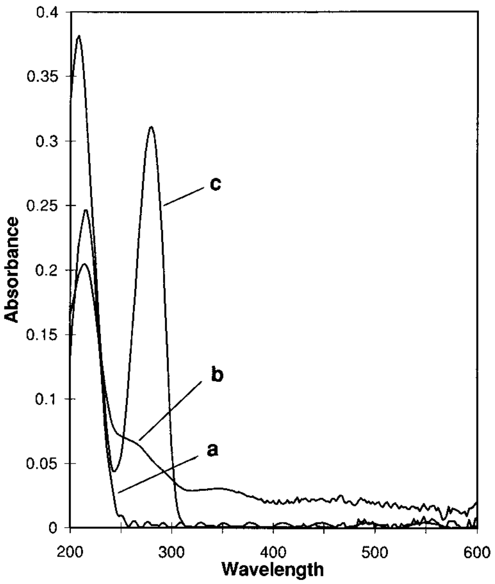

**Figure 5.** Ultraviolet spectra obtained from (a) film of polymer **2c**, (b) cross-linked film of polymer **2c** after addition of cyclohexylamine and baking at 110 °C for 5 min, and (c) film of poly(methyl methacrylate) containing 3 wt % of 3-amino-2-cyano-2-pentenedioate (**10**).

## Conclusions

We have demonstrated the use of polymers containing enolizable pendant groups in the design of radiation sensitive imaging materials. In the presence of photogenerated amine catalysts, these reactive polymers can participate in addition reactions, such as the Knoevenagel reaction, that lead to polymer insolubilization and subsequent patterning upon development. Matrices containing the cyanoacetate functionality were shown to be highly reactive in both three- and two-component resist formulations and provide relief images comparable to previously studied negative tone imaging systems utilizing photogenerated base. In the case of the two-component resist systems, spectroscopic and lithographic data suggest that a possible mode of cross-linking involves the dimerization of pendant enolizable units. While we examined the cross-linking of these materials via the addition of bifunctional aldehyde compounds, it is also expected that other highly reactive polyfunctional cross-linkers (e.g., ketones, nitriles, acrylates, and epoxides) could be used to cross-link these polymers.

## Experimental Section

**Instrumentation.** Melting points (Gallenkamp) are uncorrected. IR and UV spectra were recorded on a Nicolet IR/44 and HP 8452A diode array spectrophotometers. $^1$H and $^{13}$C NMR spectra were recorded ($CDCl_3$ or acetone-$d_6$ solvent and internal standard) on an IBM-Bruker AF300 (300 Mhz) spectrometer. Size exclusion chromatography was performed using a Waters 510 pump, a U6K injector (Waters), a Viscotek 110 differential viscometer and a differential refractometer–refractomonitor (Milton Roy) with the detectors connected in parallel. Four 5 $\mu$m PL gel columns connected in series in order of increasing pore size (100 Å, 500 Å, 1000 Å, and mixed bed C) were used with THF as the mobile phase at 40 °C. The molecular weight data are relative to 18 polystyrene standards. Thermal behavior of the polymers was monitored using a Seiko

Instruments SSC 5200 thermal analysis system (10 °C/min) with $T_g$ taken as the midpoint of the inflection tangent. Microanalysis were performed by M.H.W. Laboratories, Phoenix, AZ. Resist film thickness was measured with a Tencor Alpha-Step 200 surface profiler. Deep-UV exposures were performed by contact printing using an Oriel 87301 exposure system comprising a medium-pressure mercury lamp with a shutter system and an exposure timer. Photon flux was measured using an Optical Associates Inc. 354 exposure monitor. Hg lamp output wasfiltered through a 254 nm narrow-bandwidth interference filter (Oriel). Varying dosages of light for deep-UV sensitivity measurement were obtained with a Series 1 multidensity resolution target, Ditric Optics Inc. 2-Methoxy-5-methylisophthalaldehyde (**8**) was prepared in 58% yield by oxidation of 2,6-bis(hydroxymethyl)-4-methylanisole using the procedure of Konig et al.[22] The latter compound was obtained in 75% yield by methylation of 2,6-bis(hydroxymethyl)-4-methylphenol using dimethyl sulfate. The amine photogenerator [[(2,6-dinitrobenzyl)-oxy]carbonyl]-cyclohexylamine (**11**) was prepared according to the published procedure.[8] 3-Amino-2-cyano-2-pentenedioate (**10**) was obtained by dimerization of ethyl cyanoacetate.[21]

**Synthesis of 2-Cyanoacetoxyethyl Methacrylate (4).** To a stirred solution of previously purified[23] 2-hydroxyethyl methacrylate (13.0 g,100 mmol) and cyanoacetic acid (8.90 g, 105 mmol) dissolved in dry $CH_2Cl_2$ (60 mL) under $N_2$ and cooled with an ice bath was added dicyclohexylcarbodiimide (21.6 g, 105 mmol) dissolved in $CH_2Cl_2$ (60 mL). A white precipitate formed, and the mixture was allowed to warm to room temperature and stir for an additional 16 h. Filtration of the precipitate and purification of the crude product by flash chromotography on silica gel, eluting with $CH_2Cl_2$ provided 2-cyanoacetoxyethyl methacrylate (18.0 g, 91%) as a clear oil. Prior to use, the monomer was further purified by distillation, 90−92 °C at 0.3 mmHg. $^1$H NMR ($CDCl_3$) $\delta$ 1.92 (t, $CH_3$, 3H), 3.49 (s, $CH_2CN$, 2H), 4.36 (m, $CH_2O$, 2H), 4.43 (m, $CH_2O$, 2H), 5.59 (t, CH, 1H), 6.11 (s, CH, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 17.4, 23.9, 61.3, 63.6, 112.9, 125.5, 135.2, 162.9, 166.2; IR (NaCl) 2964, 2264 (CN), 1754 (C=O), 1719 (C=O), 1637, 1164 cm$^{-1}$. Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.85; H, 5.43; N, 6.92.

**General Procedure for the Copolymerization of 2-Cyanoacetoxyethyl Methacrylate and Methyl Methacrylate.** A solution of 2-cyanoacetoxyethyl methacrylate (**4**), methyl methacrylate, and azoisobutyronitrile (AIBN, 1 mol %) in dry toluene was heated under nitrogen at 65−70 °C for 20 h to provide a viscous solution. Solution was diluted with $CH_2Cl_2$ and precipitated twice into methanol to afford **2a**−**c** as a white powder (62−87%). $^1$H NMR ($d_6$-acetone) $\delta$ 0.8−1.7 ($CH_3$), 1.8−2.2 ($CH_2$), 3.6 ($CH_3O$), 3.9 ($CH_2$), 4.3 ($CH_2O$), 4.5 ($CH_2O$). $^{13}$C NMR ($d_6$-acetone) $\delta$ 17.4, 19.4, 24.9, 45.2−45.7, 52.0, 53.0−55.1, 63.3, 64.2, 114.7, 164.8, 177.8−178.4. IR (KBr) 2266 (CN), 1756 (C=O), 1729 (C=O), 1184, 1150 cm$^{-1}$.

**Synthesis of 4-(2-Cyanoacetoxymethyl)styrene (5).** To a solution of cyanoacetic acid (7.67 g, 90 mmol) dissolved in dimethylformamide (80 mL) was added potassium hydroxide pellets (5.05 g, 90 mmol), and the mixture was heated at 60 °C for 30 min during which time a white precipitate forms. 4-Vinylbenzyl chloride (Eastman Kodak, 12.50 g, 82 mmol) was added to the reaction mixture, and stirring was continued at 70 °C for 24 h. The mixture was poured onto ice water, extracted with ether, dried over $MgSO_4$, and concentrated at reduced pressure to leave a pale yellow solid. Flash chromotography on silica gel using $CH_2Cl_2$ as eluent and recrystallization from $CHCl_3$/hexane afforded **5** as white platelets (12.1 g, 73%), mp = 57−59 °C. $^1$H NMR ($CDCl_3$) $\delta$ 3.44 (s, 2H), 5.18 (s, 2H), 5.31 (dd, 1H), 5.80 (dd, 1H), 6.73 (dd, 1H), 7.33 and 7.42 (AA′BB′, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ 24.5, 67.9, 113.3, 114.6, 126.4, 128.7, 133.8, 136.0, 137.9, 163.0. IR (NaCl) 2264 (CN), 1747 (C=O), 1335, 1209, 1197, 992 cm$^{-1}$. Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.46; H, 5.74; N, 6.74. Alternatively, 4-(2-cyanoacetoxymethyl)styrene (**5**) was synthesized following the procedure for 2-cyanoacetoxyethyl methacrylate above, using 4-vinylbenzyl alcohol, cyanoacetic acid, and dicyclohexylcarbodiimide in 70% yield.

**Free Radical Copolymerization of 4-(2-Cyanoacetoxymethyl)styrene and 4-[(Trimethylsilyl)oxy]styrene.** A solution of 4-(2-cyanoacetoxymethyl)styrene (**5**, 3.62 g, 18 mmol), 4-[(trimethylsilyl)oxy]styrene[24] (**6**, 8.06 g, 42 mmol), and AIBN (1mol %) in dry toluene was heated under nitrogen at 70 °C for 40 h to provide a viscous solution. Solution was diluted with acetone and precipitated into methanol and then hexane to afford **7** as a white powder (8.3 g, 71%) upon drying. $^1$H NMR ($d_6$-acetone) $\delta$ 0.1−0.3 ($CH_3$−Si), 1.2−2.0 ($CH_2$, CH), 3.8−3.9 ($CH_2$−CN), 5.0−5.2 ($CH_2$−Ph), 6.2−7.4 (Ar−H). $^{13}$C NMR ($d_6$-acetone) $\delta$ 0.53, 25.0, 40.1−44.7, 68.4, 114.7, 120.2,-128.3−129.7, 133.5, 138.5−139.3, 146.0−147.0, 153.9, 164.7. IR (KBr) 2266 (CN), 1754 (C=O), 1509, 1250, 918 (Si−O), 845 cm$^{-1}$.

**Synthesis of Poly[4-(2-cyanoacetoxymethyl)styrene]-*co*-[4-hydroxystyrene] (3).** To a solution of poly[4-(2-cyanoacetoxymethyl)styrene]-*co*-[4-((trimethylsilyl)oxy)styrene] (**7**, 7.7 g) dissolved in dry THF (100 mL) and cooled with an ice bath was added concentrated hydrochloric acid (14 g). The ice bath was removed and the solution stirred at room temperature for 1 h. The deprotected polymer was purified by precipitation twice into distilled water to afford **3** as a white powder (5.7 g). $^1$H NMR ($d_6$-acetone) $\delta$ 1.2−2.4 ($CH_2$, CH), 3.8−4.0 ($CH_2$−CN), 5.1−5.3 ($CH_2$−Ph), 6.2−7.4 (Ar−H), 7.8−8.2 (O−H). $^{13}$C NMR ($d_6$-acetone) $\delta$ 24.7, 40.0−40.9, 42.0−48.0, 65.2, 114.6, 115.4, 128.2−129.7, 132.9−133.3, 136.7−137.6, 146.0−148.0, 164.6. IR (KBr) 3400 (OH), 2271 (CN), 1747 (C=O), 1613, 1513, 1222, 1172, 829 cm$^{-1}$.

**Synthesis of 2-Methoxy-5-methyl-1,3-bis(*β*-cyano-*β*-ethoxycarbonyl)benzylidene (9).** 2-Methoxy-5-methylisophthalaldehyde (8, 530 mg, 3 mmol) and ethyl cyanoacetate (740 mg, 6.5 mmol) dissolved in absolute ethanol (5 mL) were allowed to react in the presence of ammonium acetate (540 mg, 7 mmol). A white precipitate formed and the mixture was stirred at reflux for 2 h, cooled with an ice bath, and filtered. Precipitate was washed with cold ethanol and dried to afford **9** (820 mg, 75%) as a white fluffy solid, mp = 156−158 °C. $^1$H NMR ($CDCl_3$) $\delta$ 1.40 (t, 6H), 2.45 (s, 3H), 3.80 (s, 3H), 4.40 (q, 4H), 8.24 (s, 2H), 8.54 (s, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ 14.2, 21.1, 63.0, 65.5, 105.5, 115.0, 125.9, 134.0, 135.4, 148.3, 159.1, 162.0. IR (NaCl) 2222 (CN), 1724 (C=O), 1597, 1472, 1288, 1256, 756 cm$^{-1}$. Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 64.93; H, 5.22; N, 7.36.

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