A new water-soluble photoresist used a polymeric azide compound as a photosensitizer

Hajime Morishita, Masato Ito, Nobuaki Hayashi, and Saburo Nonogaki
Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan
Yoshiyuki Odaka, and Masahiro Nishizawa
Mobara works, Hitachi, Ltd., Mobara, Chiba Prefecture 297, Japan

A new water-soluble photoresist consisting of a polymeric azide sensitizer and Poly(acrylamide-diacetone acrylamide) (PAD) was developed for this potential application to a black matrix process in a color picture tube fabrication. The polymeric azide sensitizer was prepared by the condensation reaction of Poly(4-vinylacetophenone-malefic acid) with 4-azidobenzaldehyde-2-sodium salt. This newly developed resist shows higher sensitivity than that of our current resist that is composed of 4,4'-diazidostilbene-2,2'-disulfonate and PAD. The resist exhibits the reciprocity-law failing characteristic that is desirable for high contrast patterning. One of the mechanisms of increase in sensitivity is presumed to be due to the tangle of polymers between a polymeric azide sensitizer and PAD.

Introduction

The water-soluble photoresists have been widely used, for example, in the production of a phosphor screen and a black matrix (BM) of a color cathode-ray tube or photoengraving processes. Many of these photoresists comprise the water-soluble polymers such as Poly(vinyl alcohol) or Poly(N-vinylpyrrolidone) and sensitizers such as dichromates or azide compounds. The photoresists have been required the high sensitivity for a productivity increase in the each field. The sensitivity of the negative working photoresists composing of bisazide compounds depend on the quantum efficiency of the photodecomposition of the azides and the crosslinking efficiency to other polymer molecules of nitrene liberated by photodecomposition of the azides.

We have previously reported on the water-soluble photoresists for a BM of a color cathode-ray tube, comprising Poly(acrylamide-diacetone acrylamide) as the base polymer and bisazide compounds or azide polymers as the sensitizers.[1,2,3] The fabrication of BM is formed as follows. First, a coating of a water-soluble photoresist is formed on the inner surface of a color cathode-ray tube faceplate, the phosphor dot-forming positions are exposed through a shadow mask, and the coating is developed to form dots of the photoresist. The liquid dispersed carbon powder is coated thereon, and the dots are removed by a remover liquid together with carbon coated thereon. Holes of BM are so formed. PAD-azide compound system photoresists exhibit the reciprocity-law failing characteristic that the sensitivity of them decreases considerably in low illumination intensity. For this reason, the resultant BM holes are clear and excellent in contrast. In manufacturing
the large-sized color cathode-ray tubes, its problem is that since the surface to be exposed is apart from a light source, the illumination intensity on an exposed surface decreases and the exposure therefore required a long period of time. Therefore, the photoresist having the high sensitivity have been required in the manufacturing in color cathode-ray tubes. We had an idea for increase in crosslinking efficiency as a method for obtaining the highly sensitive photoresist for responding to this requirement, and have tried the development of the water-soluble sensitizer having lots of azide groups (photo-crosslinkable radical) on a molecule as one of the methods for the increase in crosslinking efficiency.

In present paper, we report on the synthesis of a polymeric azide sensitizer that incorporated the aromatic azide groups into side chain of Poly (4-vinylacetophenone-maleic acid), the characteristics of the water-soluble photoresist used it.

Experimental
Synthesis of an azide copolymer

An azide copolymer was synthesized by means of the synthetic process described in the scheme 1. Sixteen grams of poly(styrene-maleic anhydride)(75 mol% styrene, molecular weight; 1,900, made by Polyscience Inc.) was dissolved in a 100 ml of chloroform. The resultant solution was added dropwise, with stirring at room temperature, to a solution of 25 g of acetyl chloride and 43 g of anhydrous aluminum chloride in a solvent of 200 ml of chloroform. Then, the mixture was heated and refluxed for 2 hours with stirring. The mixture was cooled and then filtered, and an insolubilized substance was dried. The dried substance was powdered, and then the powder was treated with a large amount of water, well washed with water, and then dried to give a polymer, which is a maleic acid-4-vinylacetophenone copolymer. In the polymer, about 10 mol% of the styrene unit, i.e., 7.5 mol% based on the total copolymer, remained unreacted. 1 g of the copolymer, 2 g of sodium 4-azidobenzaldehyde-2-sulfonate and 0.3 g of sodium hydroxide were dissolved in a mixed solvent of 40 ml of ethyl alcohol and 40 ml of water. The mixture was left to stand at room temperature for a period of two days, then the reaction solution was acidified with acetic acid, and a precipitate was filtered, well washed with water. The azide copolymer was stored as an aqueous solution of alkali of pH 10. The degree of condensation, the amount of 4-vinyl-4-azidochalcone-2-sulfonic sodium salt monomer units that are included on the azide copolymer was determined from the light absorption in an aqueous solution utilizing 4-methyl-4-azidochalcone-2-sulfonic sodium salt (molecular absorbance; \( \varepsilon = 2.3 \times 10^4 \) l/mol cm at 340 nm) as the model compound.
preparation of water-soluble photoresists

Poly(acrylamide-diacetone acrylamide) was used as a base polymer. Either an azide copolymer or a bisazide compound were used as photosensitizers. The compositional proportions of photoresists was showed in table 1.

![Chemical structures](image)
PAD  \hspace{2cm} \text{bisazide compound}

**Table 1 Composition of Photoresists**

<table>
<thead>
<tr>
<th>Compositional proportions:(wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(acrylamide-diacetone acrylamide)</td>
<td>2.0%</td>
</tr>
<tr>
<td>Azide group-containing copolymer</td>
<td>0.2% *</td>
</tr>
<tr>
<td>(in the case of bisazide compound)</td>
<td>(0.2%)</td>
</tr>
<tr>
<td>Silane coupling agent</td>
<td>0.002%</td>
</tr>
<tr>
<td>Water</td>
<td>residual portion</td>
</tr>
</tbody>
</table>

*: 2 x 10^{-4} mols of azide group-containing monomer units.

Optical characterization

A water-soluble photoresist is spread on a glass plate by spinning, and dried by an infrared lamp to form a film. The ultraviolet to visible light absorption spectra of the films were measured using a Hitachi 340 Recording Spectrometer. Infrared absorption spectrum of an azide copolymer was taken using a Hitachi 260-10 Infrared Spectrophotometer in transmittance mode.

Measurement of sensitivity in photoresists

The photoresists for measurement of sensitivity were prepared by the following processes. The aqueous solutions containing photosensitizers and PAD were spread on a glass plate by spinning, and dried by an infrared lamp. The thicknesses of the films were measured by an Alpha-Step 200 (TENCOR Instruments) profilometer. The film was exposed using a 500W ultra-high pressure mercury lamp through 365nm-band pass filter in conjunction with pure water filter. The intensity of the light used to irradiate a photoresist film was measured by a calibrated thermocouple. After the film was developed in water and dried, the remaining film thicknesses in the exposed areas were measured. The gel dose (sensitivity) was found by extrapolating the gel curve to zero film thickness. The quantum yield of insolubilization in a photoresist was calculated from the gel dose \( E_g \) (einstein/cm²) by the expression

\[
\Phi_g = \frac{Vd}{I_0A_M W}
\]

where \( V \) is the volume of a film (cm³), \( d \) is the density of a film, \( I_0 \) is the exposure dose (einstein/cm²), \( A \) is the fraction of incident photons absorbed by the azide.
groups of a film, \( M_w \) is the weight-average molecular weight of PAD. The progress of the photodecomposition of azide groups in a film during irradiation was monitored by spectrometry with a UV-visible spectrometer. The overall quantum yield of photodecomposition of azide groups was derived from the dependence of the rate of chemical conversion \( (dx/dt) \) on exposure dose, via the equation

\[
\Phi_A = \frac{n}{IA} \frac{dx}{dt}
\]

where \( n \) is the number of moles of azide groups in \( 1 \text{cm}^2 \) of the film, \( I \) is the irradiation flux (einstein/cm\(^2\) sec.), and \( A \) is the fraction of incident photons absorbed by the azide groups.\([4]\)

**Results and discussion**

The relationship between reaction time and the degree of condensation was showed in figure 1. The degree of condensation was saturated in a reaction time of a period of 48 hours. The amount of substituted azide groups on an azide copolymer was calculated to be 18 mole\% as azide group monomer units. The ultraviolet to visible light and infrared absorption spectra of a synthesized azide copolymer are showed in figure 2 and 3, respectively. In the figure of IR spectrum, it is clearly found that azide groups are introduced into 4-vinylacetophenone maleic acid copolymer by means of the condensation. It is found from figure 2 that the azide copolymer well absorbs light having a wavelength, particularly, of 340nm or 365nm among the lights excited from an ultra-high pressure mercury lamp.

The sensitivity on PAD-bisazide compound and PAD-azide copolymer was showed in figure 4. The photoresist from an azide copolymer showed higher sensitivity than that from a bisazide compound. Figure 5 showed the exposure characteristics of PAD-azide copolymer photoresist, together with that of PAD-bisazide compound photoresist. In these photoresists, reciprocity-law failing characteristics were observed and the sensitivity decreased rapidly with decreasing light intensity. The reason for exhibiting the reciprocity-law failing characteristic has been thought as follows.

The photodecomposition of an azide produces an unstable intermediate called nitrene. This intermediate is highly reactive and changes into more stable compounds through various reactions. The nitrene reacts with polymer molecules to form a water-insoluble three dimensional network. If, however, oxygen is present, this crosslinking reaction is inhibited by a preferential reaction between nitrene and oxygen. By this oxygen effect, the photoresists composing of azide compounds reveal significant reciprocity-law failing characteristics.

![fig. 1 Relationship between degree of condensation and reaction time](image-url)
fig. 2 Absorption spectrum of an azide copolymer.

fig. 3 IR absorption spectrum of an azide copolymer.

fig. 4 Curves of insolubilization for PAD-bisazide compound and PAD-azide copolymer.

fig. 5 Exposure characteristics for PAD-bisazide compound and PAD-azide copolymer.
Table 2 Viscosity and pH of aqueous solutions of polymeric azide sensitizers

<table>
<thead>
<tr>
<th>Alkali salts used in neutralization</th>
<th>Viscosity(mPa-s/25 °C)</th>
<th>pH(25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>TMAOH</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>TEAOH</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>TPAOH</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>TBAOH</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

solid content(2wt%)  

Table 3 Characteristics of photoresists used polymeric azide sensitizers

<table>
<thead>
<tr>
<th>Photoresists</th>
<th>Viscosity(mPa-s/25 °C)</th>
<th>pH(25 °C)</th>
<th>Φg</th>
<th>ΦA</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP</td>
<td>124</td>
<td>9</td>
<td>0.15</td>
<td>0.6</td>
</tr>
<tr>
<td>APNH₄</td>
<td>89</td>
<td>10</td>
<td>0.12</td>
<td>0.6</td>
</tr>
<tr>
<td>APTMA</td>
<td>72</td>
<td>8</td>
<td>0.10</td>
<td>0.6</td>
</tr>
<tr>
<td>APTEA</td>
<td>61</td>
<td>8</td>
<td>0.06</td>
<td>0.6</td>
</tr>
<tr>
<td>APTPA</td>
<td>57</td>
<td>8</td>
<td>0.03</td>
<td>0.6</td>
</tr>
<tr>
<td>APTBA</td>
<td>55</td>
<td>8</td>
<td>0.02</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The photoresists showed reciprocity-law properties in the range of light intensity used in the measurement of quantum yield(Φg).

fig. 6 Relationship between sensitivity and ion sizes.  
fig. 7 Relationship between viscosity and ion sizes.
The azide copolymer sensitizer has a higher molecular weight than a bisazide compound, and the number of azide groups which the sensitizer had per molecule is also higher. For this reason, it is thought that the photoresist composing of an azide copolymer has high probability of crosslinking reaction of nitrene liberated by photodecomposition of the azide groups with other polymer molecules. Therefore, the photoresist shows higher sensitivity. As another reason for the higher sensitivity, the following was found, since the azide copolymer is an electronic polymer and since the other base polymer (PAD) to be mixed therewith is also electrolytic, these two polymer, when mixed, attract each other electrically and form a tangle of polymers. As a result, when the azide group as photosensitive group is optically decomposed, the crosslinking efficiency of each of the polymers to the other is increased. That is because the distance between the azide group and the other polymer molecule, which is to undergo a crosslinkage reaction with the azide group, is shortened due to the tangle of polymers. Therefore, the photoresist shows higher sensitivity. As another reason for the higher sensitivity, it is thought that the photoresist composing of an azide copolymer has high probability of crosslinking reaction of nitrene liberated by photodecomposition of the azide groups with other polymer molecules. Therefore, the photoresist shows higher sensitivity. As another reason for the higher sensitivity, the following was found, since the azide copolymer is an electronic polymer and since the other base polymer (PAD) to be mixed therewith is also electrolytic, these two polymer, when mixed, attract each other electrically and form a tangle of polymers. As a result, when the azide group as photosensitive group is optically decomposed, the crosslinking efficiency of each of the polymers to the other is increased. That is because the distance between the azide group and the other polymer molecule, which is to undergo a crosslinkage reaction with the azide group, is shortened due to the tangle of polymers. Therefore, the photoresist shows higher sensitivity. As another reason for the higher sensitivity, it is thought that the photoresist composing of an azide copolymer has high probability of crosslinking reaction of nitrene liberated by photodecomposition of the azide groups with other polymer molecules.

Figure 6 shows that the use of the counter ion having the smallest size (use of ammonia water) exhibits the highest sensitivity. This result is caused by the fact that the distance between the azide group and the other polymer in the tangle of polymers is affected by the counter ion size. For this reason, it is seen that even if the molecular weight of the azide copolymer is small, and even if the proportion thereof in the mixture with the other polymer is small, the high sensitivity is well exhibited.

**Conclusion**

The polymeric azide sensitizer was prepared by the condensation reaction of poly(4-vinylacetophenone-maleic acid) with 4-azide benzaldehyde-2-sulfonic sodium salt. The new water-soluble photoresist that consists of PAD and the polymeric azide sensitizer showed higher sensitivity than that of a current photoresist used 4,4'-diazidostilbene-2,2'-disulfonate as a sensitizer. Furthermore, the photoresist exhibited the reciprocity-law-failing characteristic as a current photoresist. It was found that the increase in sensitivity did not depend only on to have a higher molecular weight and larger number of azide groups in the sensitizer. As another reason for the higher sensitivity is presumed to be due to the distance between the azide groups and other polymer molecule, which is to undergo a crosslinkage reaction with the azide group, is shortened due to the tangle of polymers that form by attracting each other, because both polymers are electrolytic polymers.
References