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Sensitivity Enhancement of Polyorganophosphazenes to Radiation with 2,2,4,4,6,6-Hexakis(2-Hydroxyethyl Methacrylate)Cyclotriphosphazene Monomer and its Application for Negative Resists

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SENSITIVITY ENHANCEMENT OF POLYORGANOPHOSPHAZENES TO RADIATION WITH 2,2,4,4,6,6-HEXAKIS(2-HYDROXYETHYL METHACRYLATE)CYCLOTRIPHOSPHAZENE MONOMER AND ITS APPLICATION FOR NEGATIVE RESISTS

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ABSTRACT

This work focuses on the application of a multifunctional phosphazene monomer, 2,2,4,4,6,6-hexakis(2-hydroxyethyl methacrylate)-cyclotriphosphazene (6-Hema) for enhancement of the sensitivity of polyphosphazenes to both ^{60}Co and E-beam radiation. Specifically, elastomeric and glassy phosphazene polymer films treated with 6-Hema were irradiated under vacuum, and the gel content was determined. The Charlesby–Pinner approach was used to compare the radiation sensitivities of these films. This served as the basis for eventually preparing SiO_2 wafers with thin films of the glassy polyphosphazenes mixed with or overcoated by the 6-Hema monomer. The SiO_2 wafers prepared with the most sensitive polymer/monomer system were patterned with an ERC electron beam accelerator/scanning electron microscope computer-

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driven instrument. It was determined that these negative resist films were 1–2 orders of magnitude more sensitive to radiation than the polymers without the monomer.

INTRODUCTION

The radiation-induced crosslinking and graft copolymerization of certain phenoxy-substituted copolymer elastomeric [1] and glassy, amino-substituted [2] copolymer polyphosphazenes were reported recently. The purpose of the previous work was to determine the suitability of such polymers as negative resists for microlithographic applications. It was found that copolymers containing allyl groups gave excellent crosslinking yields with both elastomeric and glassy polyphosphazenes [1, 2]. A fully detailed presentation and analysis of both the previous and current work has been described in a recent Ph.D. thesis [3].

During the course of these investigations, a relatively new, commercially produced multifunctional monomer, 2,2,4,4,6,6-hexakis(2-hydroxyethyl methacrylate)-cyclotriphosphazene (6-Hema) was obtained [4]. The use of multifunctional monomers to increase the crosslinking efficiency of a number of polymers has been studied extensively starting with polyvinyl chloride by Pinner [5] and plasticized PVC by Miller [6] in early 1959. A phosphazene monomer containing six methacrylate groups was clearly an attractive possibility to further increase the radiation-induced crosslinking yields of the polyphosphazenes previously investigated.

Combinations of polymers and multifunctional monomers have been successfully used for the enhancement of electron beam crosslinking of polyvinyl chloride for wire coating [7], for photo and radiation curable solvent-free coatings, and, more recently, for negative resist materials, the so-called dry film resists. Early work through 1974 may be found in the monograph of DeForest [8] and in an excellent comprehensive account through 1986 by Moreau [9]. Polyphosphazenes have excellent thermal stability of value in high temperature resists, and they also have reactive ion etching (RIE) resistance properties [2, 10]. The availability of a multifunctional monomer to modify suitable polyphosphazenes is clearly of interest because it potentially represents a classical free-radical approach for the chemical amplification of negative resist materials. Recently, ionic approaches with extremely encouraging results have been developed [11].

The monomer itself is a clear, odorless liquid with a viscosity of approximately 10 poise, a specific gravity of 1.2–1.3, a refractive index (n_d) of 1.50 at 25°C, and a molecular weight of 813 g/mol. Presumably due to the six methacrylate groups, the monomer is extremely sensitive to many forms of radiation. Idemitsu claims that curing occurs in the presence of far-infrared, ultraviolet light, heat, or electron beams. The mechanism for curing is most probably free-radical generation and reaction with the methacrylate groups, leading to rather efficient crosslinking [12]. The possibility of some scission also exists; however, the radiation stability of the cyclic phosphorus-nitrogen structure and the relatively low molecular weight of the monomer most likely reduces the probability of this occurrence, except, perhaps, for the methacrylate moeties.

Once the 6-Hema monomer has been cured, its physical properties are improved in terms of hardness, adhesive qualities, shrinkage, and both thermal and

chemical stabilities. Postcuring optical and mechanical properties of the monomeric resin compare favorably with commercially available acrylic resins and polycarbonate [4].

The monomer is in the liquid state at room temperature, is compatible with the high molecular weight elastomeric and glassy organopolyphosphazenes used in this study, and has an extremely low vapor pressure as evidenced by thermal gravimetric analysis (TGA), with no weight loss until heated above 325°C [4]. It was therefore decided to determine what effect its physical incorporation into the polymers would have on their sensitivity to radiation. The chemical structure of the monomer is shown in Fig. 1.

The various experimental methods and results obtained by incorporating this unique monomer into both the elastomeric and glassy polyorganophosphazene films used for earlier studies are reported here. It is shown that radiation sensitivity levels can indeed be considerably increased with both the elastomeric and glassy films, and that a previously radiation-insensitive glassy film can be modified so that crosslinking can occur more readily. The monomer can be incorporated homogeneously or as a top, very thin layer approaching that of the concept of top surface imaging [7]. In both cases the proximity effects [13, 14] after E-beam exposure can be greatly reduced. Results of these studies are also included within this report.

EXPERIMENTAL

Materials and Methods

(A) The Monomer

The monomer, 2,2,4,4,6,6-hexakis(2-hydroxyethyl methacrylate)cyclotriphosphazene (referred to simply as "6-Hema" hereafter), was obtained from Idemitsu Petrochemical [4]. Its structure and some other properties as presented by the manufacturer [4] are given in the previous section.

(B) The Polymers and Subsequent Film Preparation

Polymers A and B were obtained from Ethyl Corporation, Baton Rouge, Louisiana. The film preparation for irradiation and subsequent gel dose analysis have been previously described [3], and their structures are depicted in Fig. 2. The

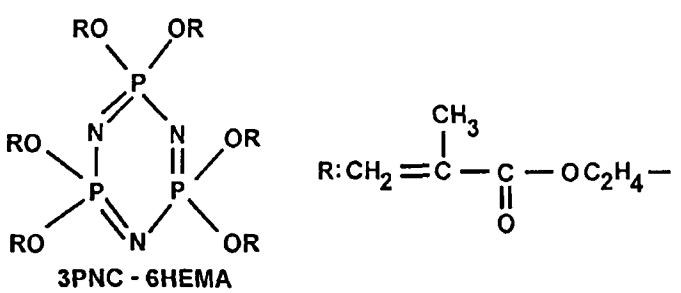

FIG. 1. The structure of the 6-Hema monomer [4].

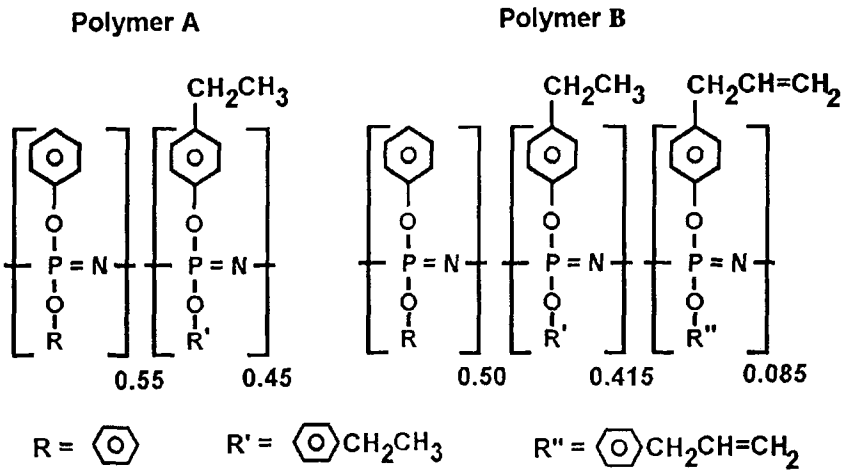

FIG. 2. Structures of elastomeric polyphosphazenes A and B from earlier model studies [1].

amino-substituted and allyl-amino-substituted polymers were synthesized by special techniques [2], the structures of which can be found in Fig. 3. Films were solution (20% w/v) cast to 0.0045″ on a 10″ × 12″ clean glass plate with a Pacific Scientific Knife. These glassy films were dried in a vacuum oven (no heat) to constant weight for a minimum of 48 hours to ensure removal of all traces of solvent.

Initially, films of elastomeric polyphosphazenes, Polymers A and B, the structures of which are detailed in Fig. 2, were available for modification. Having determined that Polymer B (with a 8.5 mol% allylic substituent) was more sensitive to crosslinking in the presence of radiation, several samples of these films (approxi-

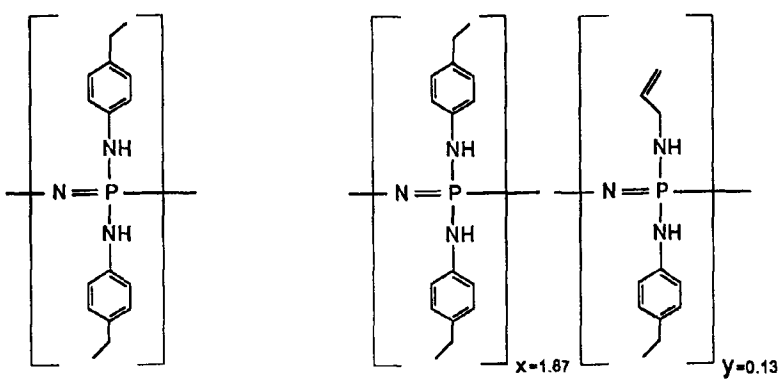

FIG. 3. Respective structures of amino-substituted polyphosphazenes used with 6-Hema monomer to enhance sensitivity to radiation.

mately 0.015–0.020″ thick and 0.100 g) were allowed to soak in small vials of the liquid 6-Hema monomer (approximately 5 mL each) for 7 days.

The elastomeric films were then removed from the liquid monomer and "blotted" dry with Kimwipes prior to insertion in the same glass vials used for vacuum work as discussed in the earlier studies [1, 2]. This physical absorption of the cyclophosphazene monomer into the phosphazene elastomer allowed for an average weight gain of 7%. Film samples of Elastomer B with absorbed 6-Hema were then placed in the glass vials and evacuated to 1×10^{-6} torr at room temperature and sealed for exposure to the ^{60}Co source. The vials were then exposed for short times corresponding to 10–50 kGy doses based on the previously determined radiation sensitivity of Polymer B [1].

Because the initial method of allowing the 6-Hema monomer to simply sorb into the polymeric film matrix was not too reproducible, it was decided to add precise amounts of the monomer to the polymer during film preparation. For example, Polymer A was dissolved in THF to which 0.95, 3.03, and 7.20 wt% equivalents of the 6-Hema monomer were added. For Polymer B (with the allylic substituent), 1.27, 4.18, and 7.03 wt% equivalents of the 6-Hema monomer were added. The respective solutions were allowed to mix thoroughly by magnetic stirrer agitation for several hours, followed by film casting in aluminum pans. Drying was accomplished in vacuum ovens for a minimum of 24 hours. These films were then placed in glass vials and sealed under vacuum (1×10^{-6} torr) prior to irradiation.

(C) Methods

Sealed vials were placed in a ^{60}Co source, and the required dose time was based on Fricke dosimetry and a source calibration curve determined from the "half-life" dependency of the radioisotope. Film samples (within glass vials) were removed from the Gammacell 60 ^{60}cobalt radiation source after the required dose. The glass vials were then "fire-cracked" at the top portion so that the film could be removed. After crosslinking, extraction with THF was performed by placing the polymer films in an extraction vial and refluxing for 18 hours. After extraction was complete, the glass extraction vials were placed in a vacuum oven (1×10^{-3} torr) for a minimum of 3 hours. The gel content was then determined by weight difference.

Spin coating of the bilevel and two-component monomer/polymer systems is described in detail later. Subsequent E-beam patterning was performed with an ERC electron beam accelerator/scanning (JEOL 6400F FESEM) electron microscope instrument which was computer driven with an EPS 80386 computer complete with an ELPHY electron beam controller. Patterning of the wafer was accomplished using a 15-keV powered electron beam.

RESULTS AND DISCUSSION

Radiation Sensitivity Enhancement of Elastomeric and Glassy Polyorganophosphazene Films with 6-Hema Monomer

It was expected that simple physical absorption of the 6-Hema monomer into the Polymer B elastomer would enhance radiation crosslinking. The results, shown in Table 1, indicate the effects were indeed quite significant. In particular, the

TABLE 1. Comparison of Gelation for Polymer B Films Without and With Approximately 7 wt% 6-Hema Monomer Absorption after Radiation Exposure with ^{60}Co

Dose, kGy	Percent gel, Polymer B	Percent gel, Polymer B + 6-HEMA
1.0	44.2	63.6
2.0	65.4	83.8
8.0	78.5	96.9
10.0	90.5	

percent increase in gelation was considerably in excess of the percent of 6-Hema added. This clearly indicates the participation of Polymer B itself in the crosslinking reaction and not simply 6-Hema molecules individually crosslinking to microgels.

In addition to the obvious increase in crosslinking due to the addition of 6-Hema monomer, the physical texture of the elastomeric films after irradiation and subsequent extraction with THF was quite different from films without the 6-Hema addition. The elastomeric films with absorbed 6-Hema wre slightly cloudy in appearance, did not swell appreciably in the presence of hot THF, and retained their shape during the entire extraction period (18 hours). This indicated that perhaps a more efficient compact network was achieved which reduced the solvent penetration into the polymer. In addition, some mutual grafting of the 6-Hema monomer to the polymers could have occurred. The slight cloudiness could be due to incompatible microgels.

To determine if grafting had also occurred, a preirradiation grafting experiment was performed. First, the Polymer B elastomer was sealed in a glass vial under vacuum at 10^{-6} torr, followed by irradiation at a total dose of 10 kGy in a ^{60}Co source well below the glass transition temperature in order to insure longevity of the free radicals formed. Finally, the 6-Hema monomer was added to the side of the glass vial on the other side of the break-seal, freeze-thawed three times to deoxygenate, and then allowed to contact the preirradiated elastomeric film. The results of this experiment yielded an approximate 5% weight gain of the Polymer B film after extraction by THF. Therefore, it appears that some grafting of the polyorganophosphazene with a "polyhema" structure does occur. The bulkiness of the monomer structure and therefore limited diffusion to the trapped radicals could lead to the small amount of grafting. The role of 6-Hema as a polymerizable monomer was confirmed with the completion of another experiment whereby the 6-Hema monomer alone was simply sealed in a glass vial, after degassing, and then irradiated again in the ^{60}Co source to 10 kGy. The result was a hardened, clear material with the appearance of polymethyl methacrylate which did not dissolve in THF, and no residual 6-Hema monomer was detected by extraction.

Results for the experiments which provided an exact amount of 6-Hema monomer incorporation into the elastomeric Polymers A and B films by solution blending are provided in Tables 2 and 3 and Figures 4 and 5. Here the trend based on

TABLE 2. Crosslinking of Polymer A with Varying wt% of 6-HEMA with Increasing Doses

Dose, kGy	0% 6-HEMA	0.95% 6-HEMA	3.03% 6-HEMA	7.20% 6-HEMA
4.0	2.38% gel	75.76% gel	76.90% gel	80.55% gel
8.0	50.72%	84.50%	86.00%	89.50%
10.0	65.41%	89.26%	90.60%	93.54%
20.0	90.28%	98.06%	98.95%	99.17%

TABLE 3. Crosslinking of Polymer B with Varying wt% of 6-HEMA with Increasing Doses

Dose, kGy	0% 6-HEMA	1.27% 6-HEMA	4.18% 6-HEMA	7.03% 6-HEMA
0.60	24.13% gel	40.09% gel	47.51% gel	48.74% gel
1.0	42.14%	54.36%	56.31%	59.12%
2.0	65.36%	75.48%	76.41%	78.11%
10.0	90.00%	100.0%	100.0%	100.0%

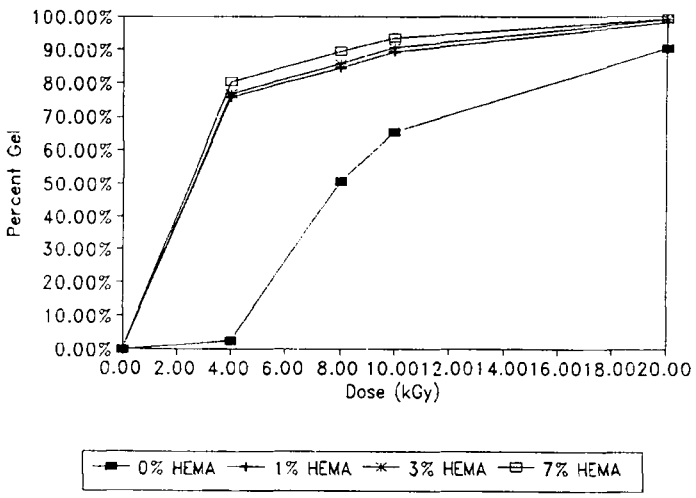

FIG. 4. Percent gelation of solution-blended Polymer A and 6-Hema monomer film vs dose after extraction in THF (18 hours).

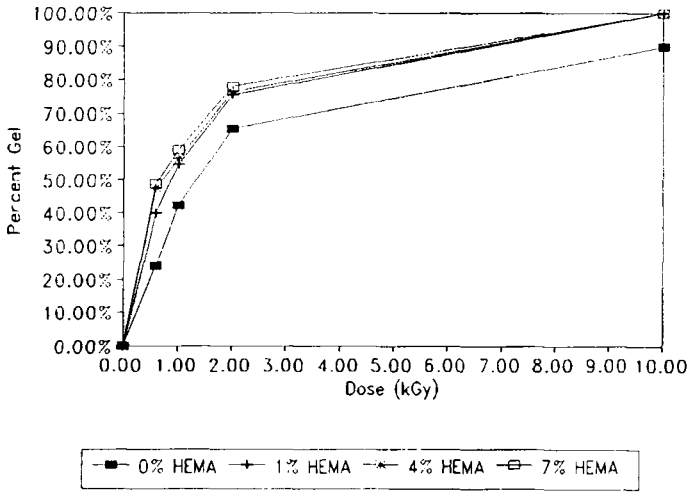

FIG. 5. Percent gelation of solution-blended Polymer B and 6-Hema monomer film vs dose after extraction in THF (18 hours).

the wt% 6-Hema is easily seen and confirmed our belief, based on simple sorption experiments, that even a small amount of the hexa-substituted monomer can result in substantial crosslinking with identical gamma radiation doses.

As would be expected, Polymer B (see Table 3), which contains 8.5% reactive allyl groups, gives substantial amounts of crosslinking even with 1.27% 6-Hema and only a 0.6-kGy dose. Increasing the percent of 6-Hema gave comparatively modest increases in the gel content, which also increased progressively with increasing dose.

Polymer A (Table 2 and Fig. 4), without the reactive allyl groups, gave substantial increases in the percent gel with only 0.95% of added 6-Hema. As with Polymer B, increasing the percent of 6-Hema only gave modest increases with increasing dose. Presumably, 6-Hema also crosslinks with itself, giving microgel and grafting, and reducing its initial effectiveness. The bulkiness of such microgels would diminish their effectiveness as crosslinking promoters, even when double bonds undoubtedly remain. The slight cloudiness of the gelled films and other physical properties may well be due to the presence of microgels, possibly with their partial attachment in the polymer main chains. Polymer B reaches 100% gelation with 6-Hema present at 10 kGy whereas Polymer A never completely crosslinks even at 20 kGy. This again illustrates the value of the allyl group in promoting crosslinking.

With the encouraging results obtained with the two elastomers, the effect of adding 6-Hema to two glassy polyphosphazenes (the structures shown in Figs. 2 and 3) was examined.

Glassy films of Polymers C and D were also allowed to physically absorb the 6-Hema monomer in an identical manner. This allowed for an average weight gain of 10%, presumably due to the fact that these films were different and much thinner (0.0045″ vs 0.0200″) than their elastomeric counterparts, allowing for more complete diffusion. Again, the films were sealed as before and exposed for corre-

TABLE 4. Required Dose and Subsequent Gelation of Polymer C After 10 wt% Absorption of 6-Hema Monomer

Dose, kGy	Percent gel
3.0	10.9
71.2	22.1
150.0	43.4

sponding doses based on previous results [1, 2] without the 6-Hema monomer. The consistency and reproducibility of the results were excellent, and solution blending was not necessary with these glassy polymers. Somewhat different observations were recorded for the glassy films of Polymers C and D. Polymer D is the allyl-amino-substituted polymer which exhibited the greatest sensitivity to radiation. As discussed in previous work [2], Polymer C was found to be noncrosslinked even with a 300-kGy dose when glassy and also when irradiated at 97°C (10° above the T_g). Postirradiated films of these polymers did not exhibit the slight cloudiness in appearance found for the A and B elastomers, perhaps due to the lower amounts of gel, after extraction with THF. Table 4 indicates that gelation could be induced in Polymer C with as much as 43% gel at 150 kGy.

Table 5 illustrates that gelation is enhanced by an order of magnitude with 10 wt% absorption of 6-Hema monomer into Polymer D which contained the allyl groups.

The mechanism by which the increased crosslinking occurs has been discussed by Odian and Bernstein [12], with considerable additional experimental details by

TABLE 5. Comparison of Gelation for Polymer D Films With 10 wt% and Without 6-Hema Absorption after Radiation Exposure with ^{60}Co

Dose, kGY	Polymer D,[a] %	Polymer D with HEMA monomer,[a] %
1.0	0.00	0.00
3.0	0.00	20.21
5.0	0.00	26.47
8.0	0.32	53.09
10.0	6.10	86.47
20.0	24.65	91.81
30.0	43.40	92.7
35.0	54.89	93.90

[a]Percent gel after gamma irradiation and subsequent extraction with THF.

Salmon and Loan [7]. It is clear that grafting and some microgel formation takes place. The few polymeric radicals produced by radiation react readily with the highly reactive multifunctional methacrylate groups. The radicals formed would be accompanied by grafted, attached, and also isolated insoluble gels. In the case of polyvinyl chloride and multifunctional methacrylates, the proportions of each were determined by Salmon and Loan [7]. As the radiation dose increases, the percent of actual polymer crosslinks increases but the multifunctional methacrylates become crosslinked at very low doses.

Presumably these on irradiation, can then extract (e.g., hydrogen atoms) from the base polymer, leading to more and more polymer crosslinks.

It was determined that the $G(X)$ value of Polymer D was 1.10 [2, 3]. However, it increased to 3.95 by estimation for Polymer D plus 10 wt% of the 6-Hema monomer by using an estimated molecular weight and the gel–dose values; a greater than threefold increase. Therefore we expected that the polymeric resist with 6-Hema monomer added would increase sensitivity significantly.

Increased Radiation Sensitivity for Bilevel and Two-Component Microlithographic Resists

The foregoing work with 6-Hema monomer indicated that the use of such an additive could increase the radiation sensitivities of the allyl-amino-substituted

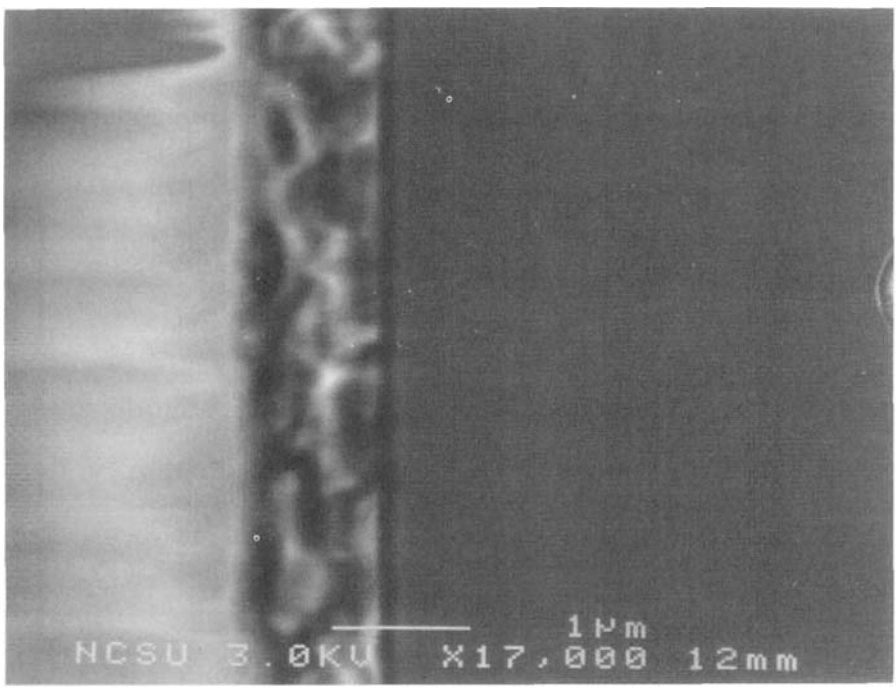

FIG. 6. SEM microphotograph (17,000×) of two-component resist system of 5 wt% Polymer D mixed with 0.835 wt% 6-Hema monomer indicating 10,000 Å film thickness.

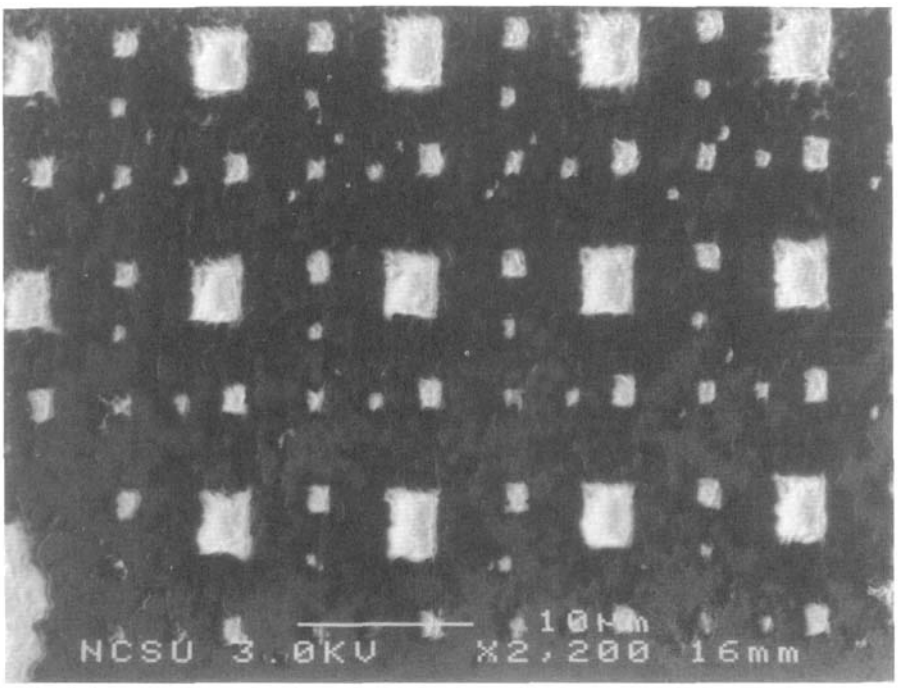

FIG. 7. SEM microphotograph (2000×) of portion of 8 × 8 grid of pattern (0.02–1 $\mu C/cm^2$) for which the bottom left corner was exposed at 0.1 $\mu C/cm^2$ and the top right corner was exposed to 10 $\mu C/cm^2$, indicating poor resolution (thick film) but improved sensitivity.

polyorganophosphazenes beyond what had already been demonstrated (4–6 $\mu C/cm^2$) [2]. In order to demonstrate that our studies to determine that the increased radiation sensitivity can carry over to actual resist applications, types of SiO_2 wafers with resists were prepared.

The first resist prepared, known as a two-component resist system, was prepared by spin coating a 5 wt% mixture of Polymer D in methyl isobutyl ketone (MIBK) with 0.835% of the 6-Hema (16.7 wt% of the polymer) onto 4″ SiO_2 wafers at 2000 rpm after initial precoating with hexamethyldisilazane (HMDS). Although this value was high, the monomer–polymer solution was still miscible. Because of the increased viscosity of this solution, the resist thickness was an order of magnitude greater than that of previous films spin-coated from MIBK and the polymer alone. Figure 6 indicates that the film was fairly homogeneously mixed and approximately 10,000 Å thick. Figure 7 indicates that sensitivity was increased but resolution and scumming, due to inadequate development in THF, was poor.

For the second resist prepared, often referred to as a bilevel resist, the top layer was not sufficiently thin for true top surface imaging, and included the base layer as Polymer D with the second layer as pure 6-Hema monomer. Figure 8 depicts the bilayer resist to be approximately 2000 Å thick, subdivided into 1000 Å film thickness of both the polymer and the multifunctional monomer. Figure 9

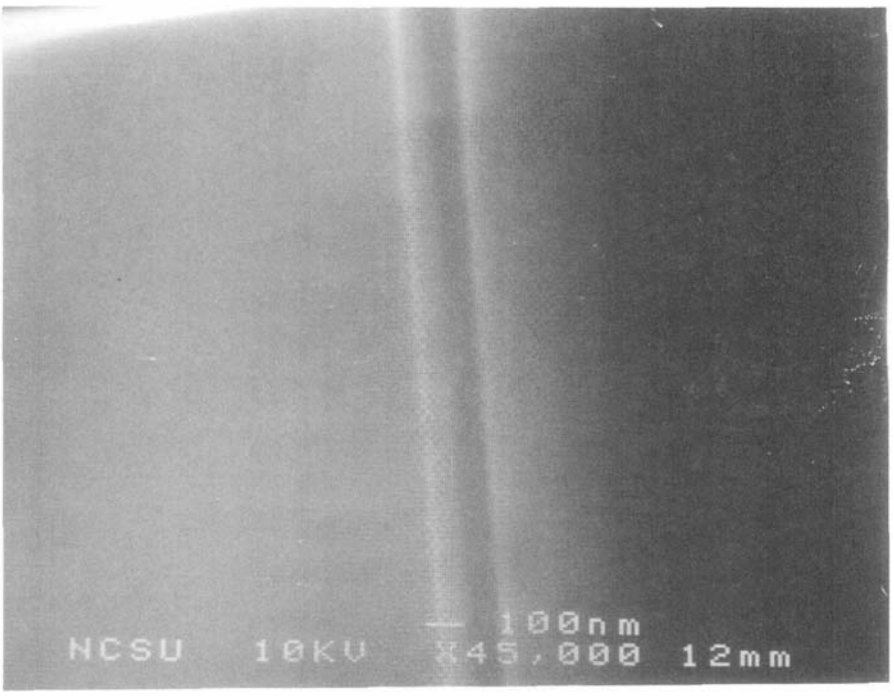

FIG. 8. SEM microphotograph (45,000×) of bilevel resist film consisting of Polymer D as the bottom layer and 6-Hema monomer as the top layer; both layers ~ 1000 Å thick.

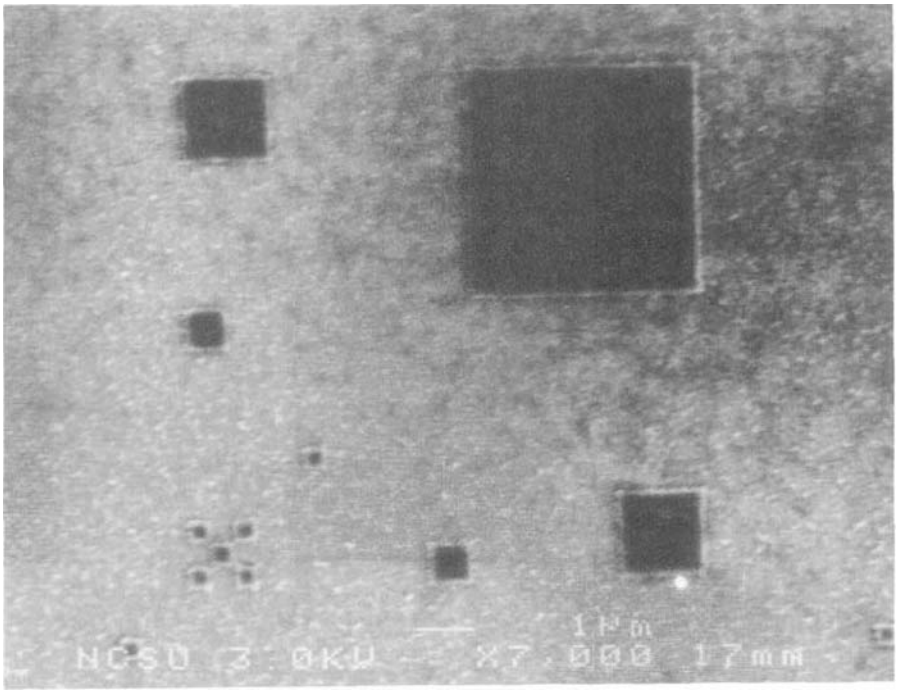

FIG. 9. Microphotograph (7000×) of 6th row and 3rd column of same 8 × 8 grid used for Fig. 8 illustrating a sensitivity of 0.21 $\mu C/cm^2$ and a resolution of <0.5 μm.

indicates that sensitivity down to 0.21 $\mu C/cm^2$ was achieved with resolution of <0.5 μm. This sensitivity level is more than an order of magnitude better than that achieved for a resist of only Polymer D spin-coated on the same wafer, with comparable resolution.

CONCLUSIONS

Initial studies [1] with model elastomeric polyorganophosphazenes indicated that the radiation sensitivities of these polymers could be greatly enhanced by the addition of allylic substituents in the side-group moeties. Later [2], this concept was applied with the synthesis of allyl-amino-substituted polymers, which exhibited not only better radiation sensitivity but also were sufficiently glassy and RIE-resistant to merit further investigation in the area of negative microlithographic resist applications.

This study extends the efforts of the previous work by determining the usefulness of incorporating a radiation-sensitive phosphazene multifunctional monomer with both the model polyorganophosphazene elastomers and the amino-substituted glassy polymers. It has been demonstrated that low (1–10 wt%) amounts of this monomer added, either by solution blending or by simple absorption, to the elastomers can greatly increase crosslinking efficiency. Similar results were found for both the amino-substituted heretofore very highly radiation-resistant Polymer C, and the already radiation-sensitive allyl-amino-substituted Polymer D.

Using basic film/irradiation studies as foundation, experiments with both a two-component and bilevel resist were performed which indicated the addition of 6-Hema monomer to base polyorganophosphazene films may increase the sensitivity of resists considerably. In addition, it was demonstrated that the possibility exists in crosslinking amino-based and potentially other polyphosphazenes which have previously been shown to be radiation stable. This could lead, in principle, to the development of a new family of multilevel negative resist systems with excellent thermal, radiation-sensitive, and RIE-resistance properties. Further work to determine if the 6-Hema monomer could enhance grafting capabilities to help change initial solubility parameters of polyphosphazene films is also warranted.

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