

# Electron Beam Chemistry of Polyvinylpyridinium Salts

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## SYNOPSIS

Various polyvinylpyridinium salts have been studied under electron beam. The relationship between electron beam sensitivities and chemical structural variables of polyvinylpyridinium salts has been studied by conventional scanning electron microscopy. Several possible mechanisms of radiation-induced solubility change in the polyvinylpyridine system have been discussed. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Currently, photo-optical lithography using ultraviolet light is the mainstay of the fabrication industry for circuit pattern image formation on semiconductor substrates.<sup>1</sup> However, due to conventional diffraction problems, photolithographic processing has inherent limitations in its resolution capability. Since microelectronics have entered the very large-scale integrated (VLSI) circuit era, and a whole new round of miniaturization is under way, there is increased interest in new means and techniques for fabrication other than UV light.<sup>2</sup> Since the electron beam system has resolution, power density, and deflection capabilities that are superior to those of the light optical system, electron beam lithography has become important for microcircuit fabrication. Naturally, the trend toward increasing use of electron beam lithography leads to the search for electron beam-sensitive materials.

When polymers are exposed to a sufficient dosage of electron beam radiation, many of their chemical and physical properties may change. But the electron beam-polymer interaction is nonspecific, since the energy of penetrating electrons is much larger than that associated with the chemical bond. Thus, one can characterize the interaction only by the overall chemical effects. Sensitivities of polymers to electron beams are dependent upon their chemical structure. In general, polymers have been classified into two groups, depending on their response to incident electron beam irradiation. Certain types of polymers can be degraded upon electron beam exposure in

order to produce polymers with lower average molecular weights than the original. Alternatively, electron beam irradiation can induce polymer cross-linking, in which adjacent chains crossconnect to form a complex three-dimensional network that has a higher average molecular weight than the original. Though many polymers have been evaluated for use as electron beam-sensitive resists, they tend to suffer from one of several undesirable properties, such as low sensitivities, poor resolution, unnecessary sensitivities to the ambient light, or poor dry etch resistance.<sup>3</sup> Furthermore, the increasingly sophisticated microelectronics technology has set stringent requirements for resist properties. For these reasons, it is necessary to search for new polymeric resist materials that combine optimum properties, such as high sensitivity, good resolution, and good dry etch resistance.

In this connection, we have studied various polyvinylpyridinium salts under electron beam and the possible use of these polymers as electron resist materials. In particular, this article discusses the relationship between electron beam sensitivities and various chemical structural variables in the polyvinylpyridine system. This model polymeric system can provide a basis for understanding the mechanism by which the electron beam interacts with the polymer.

## EXPERIMENTAL

### Synthesis and Characterization of Materials

Both 2- and 4-vinyl pyridines were purified by vacuum distillation. Methylene chloride was dried over

calcium hydride and was distilled prior to use. Nitromethane was distilled over phosphorous pentoxide. Tetrahydrofuran was refluxed over  $\text{LiAlH}_4$  for 4 h and was subsequently distilled and stored over molecular sieves (4Å). Ethyl magnesium bromide (2 M solution in tetrahydrofuran), benzoyl peroxide, *n*-butyl lithium (1.6 M solution in hexane), titanium tetrachloride, and triethyl aluminum were used as received.

NMR spectra were measured on a Varian EM390 spectrometer. IR spectra were obtained using a Perkin-Elmer Model 299B spectrophotometer. A Water Associates Model 404 gel permeation chromatograph (GPC) was used for the determination of molecular weight and molecular weight distribution. Four 7.8 mm  $\times$  12 cm Styragel columns of 500,  $10^3$ ,  $10^4$ , and  $10^5$  Å nominal pore ratings were employed for the analysis of poly(vinylpyridines) by using either THF or toluene as solvents at 24°C. A *u*-Bondagel column was employed for the analysis of the salts, using either water or methanol as solvents. The instrument was calibrated with polystyrene standards, and the "universal" calibration was employed in conjunction with Mark-Houwink constants for both poly(vinylpyridines) and polyvinylpyridinium salts in appropriate solvents to perform the various molecular weight parameter calculations.

Both 2- and 4-vinyl pyridines were polymerized with a variety of catalysts, such as benzoyl peroxide, *n*-butyl lithium,  $\text{TiCl}_4/\text{AlEt}_3$ , and ethyl magnesium bromide. Both poly(2-vinyl pyridines) and poly(4-vinyl pyridines) were characterized by IR, NMR, and GPC. The polymerization conditions in each case are described in Table I.

A typical polyvinylpyridinium salt preparation is as follows: five grams of poly(4-vinyl pyridine) were dissolved in 50 mL nitromethane. To this solution

was added, dropwise with stirring, a solution of 11.39 g (0.08 mol) methyl iodide, dissolved in 10 mL nitromethane. The resulting mixture was stirred overnight at ambient temperature. The supernatant was decanted from the rubbery poly(4-vinyl-*N*-methylpyridinium iodide), which was precipitated from solution. The resulting colloidal suspension was concentrated by removal of the solvent and methyl iodide under reduced pressure. Extensive washing of the residue with nitromethane and acetonitrile yielded, after drying, a water-soluble solid. The NMR spectrum ( $\text{D}_2\text{O}$ ) showed a peak at 6.2 ppm ( $\text{N}-\text{CH}_3$ ). The degree of quaternization was determined by NMR integration or elemental analyses. In some cases, methylene chloride was used as a solvent in the quaternization reaction in order to obtain a material having a low degree of *N*-quaternization.

### Evaluation

A typical procedure for evaluating polymers under electron beam is as follows: A film of poly(*N*-methyl-2-vinylpyridinium iodide), approximately 8000 Å units in thickness, was cast from a mixture of distilled water and methanol as a solvent system. Conventional spinning techniques were utilized, on a two-inch silicon wafer, by employing a Plat Engineering Spinner. The coated wafer was baked for one hour at 120°C before electron beam exposure. Each coated silicon wafer, mounted on the aluminum substrate with the aid of copper tapes, was exposed to a 20 kV electron beam using a Jeol U3 scanning electron microscope. Exposure-produced rectangles, each having a different dose by varying scan time, beam current, and magnification. The beam current was measured by means of a Faraday

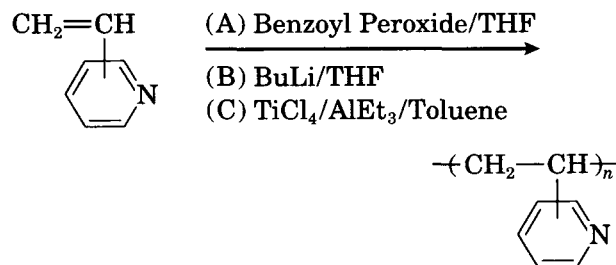
**Table I** Polymerization Conditions and Electron Beam Sensitivities of 2- and 4-Vinyl Pyridines

Monomer	Catalyst	Solvent	Polymerization Time (h)	Polymer Conversion		E Beam Sensitivity (coul/cm <sup>2</sup> )	
				(%)	$\bar{M}_n$		
2VP	$\text{TiCl}_4/\text{AlEt}_3$	Toluene	24	42	18,000	6.4	$1.0 \times 10^{-2}$
	EtMgBr	THF	20	22	80,000	2.8	$2.0 \times 10^{-3}$
	Benzoyl peroxide	Bulk	4	20	22,000	3.2	$3.2 \times 10^{-3}$
	<i>n</i> -BuLi	THF	1	8	100,000	1.6	$2.1 \times 10^{-4}$
4VP	$\text{TiCl}_4/\text{AlEt}_3$	Toluene	24	65	8,000	4.5	$7.0 \times 10^{-2}$
	EtMgBr	THF	20	36	20,000	2.8	$1.0 \times 10^{-2}$
	Benzoyl Peroxide	Bulk	4	32	70,000	1.9	$3.5 \times 10^{-3}$
	<i>n</i> -BuLi	THF	1	10	120,000	1.4	$1.1 \times 10^{-4}$

cup, located in the instrument, and a Keithley electrometer. The film was developed in a solvent mixture of distilled water and methanol (50/50 by volume) for 1–5 min. After drying the film in the oven for 30 min, the thickness was measured by a NANOSPEC/AFT film thickness monitor. Electron beam sensitivities of the film were calculated at the dose level at which 70% of the film remained after development. Resolution experiments were performed by a vector scan electron beam instrument, which was computer controlled.

## RESULTS

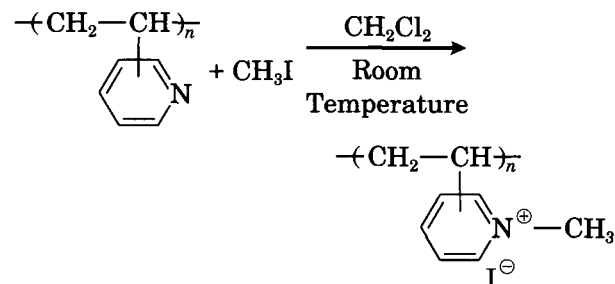
Both 2- and 4-vinyl pyridines were polymerized by utilizing various polymerization techniques, such as free radical (A), anionic (B), and Ziegler–Natta (C) processes.



The resulting polymers had a variety of molecular weights and molecular weight distributions. Some of the results are summarized in Table I. In general, one can obtain a polymer having a broad molecular weight distribution material with Ziegler–Natta polymerization, while a narrow molecular weight distribution material could be derived by employing the anionic polymerization technique. Electron beam sensitivities of the resulting polymers were estimated using conventional electron microscopy, as was described in the Experimental section. Although sensitivities of all polymers to electron beams were related to molecular weights, it was found that all poly(vinylpyridines) were extremely insensitive to the electron beam ( $10^{-4}$  coul/cm<sup>2</sup>) (Table I). In an attempt to improve electron beam sensitivities of the material, we have introduced various activating agents, such as iodine, *N*-methyl pyridinium iodide, and *N*-cetyl pyridinium chloride. Electron beam sensitivities of these blended materials were not improved. Rather, this approach resulted in the lowering of the film quality of the material.

Extensive chemical modification studies of poly(vinylpyridines) were carried out in order to investigate the relationship between electron beam

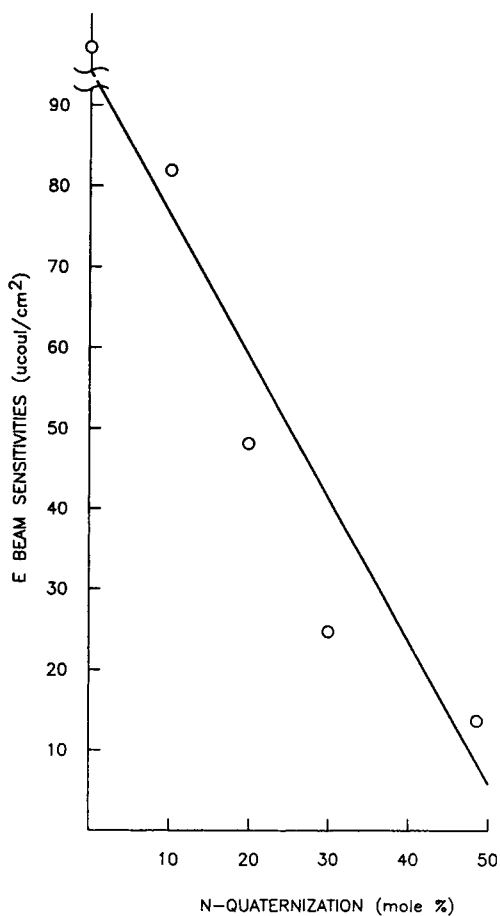
sensitivities and chemical structural variables. Each polymer, thus synthesized, has been quaternized with methyl iodide by employing the Menschutkin reaction technique.<sup>4</sup>



For example, the reaction carried out in methylene chloride for 10 h at room temperature afforded a 10 mol % quaternized material. Evaluation of the material under electron beam indicated that the electron beam sensitivity of the polyvinylpyridinium salt can be increased by many orders of magnitude upon quaternizing pyridine pendant groups of the polymer. To study systematically the effect of *N*-quaternization on the electron beam sensitivity of poly(2-vinyl pyridine) and poly(4-vinyl pyridine), we prepared a number of poly(2-vinyl-*N*-methylpyridinium iodides) and poly(4-vinyl-*N*-methylpyridinium iodides), having various degrees of *N*-quaternization, while keeping molecular weight and molecular weight distribution constant. In order to vary the quaternization levels in the reactions, either the ratio of reagents or solvents had to be adjusted accordingly. In general, it was found that higher *N*-quaternizations were achieved in the nitromethane solvent medium than in methylene chloride.

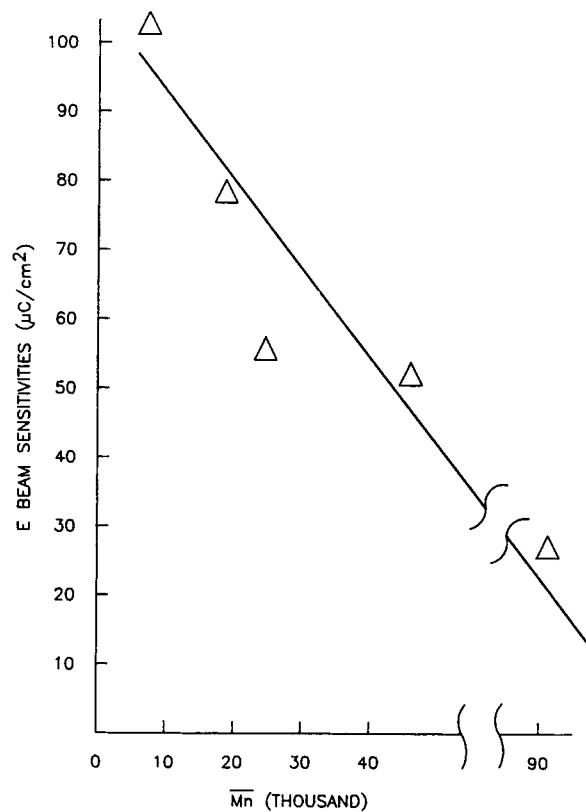
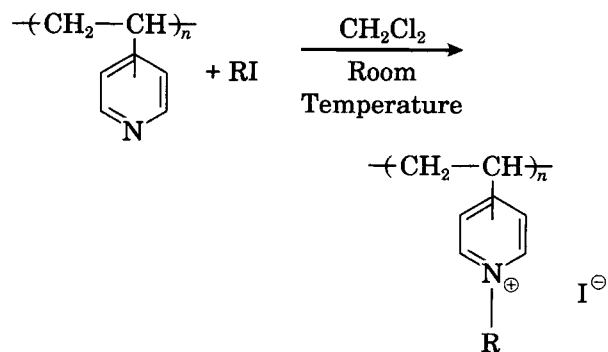
The relationship between the degree of *N*-quaternization and electron beam sensitivities of the resulting polymers is shown in Figure 1. It can be clearly seen that sensitivities were increased with an increased degree of *N*-quaternization. Since all polymers, thus tested, had identical molecular weights and molecular weight distributions, the degree of *N*-quaternization, that is, the relative abundance of positively charged nitrogen atoms, appears to be the influential factor in governing electron beam sensitivity.

It was also found that the molecular weight is another factor that influences electron beam sensitivity of the polymer. As shown in Figure 2, electron beam sensitivities of poly(2-vinyl-*N*-methylpyridinium iodide) were increased with an increase in its molecular weight. Figure 3 shows the relationship between electron beam sensitivities and molecular weight distribution. For example, it clearly indicates that poly(4-vinyl-*N*-methylpyridinium

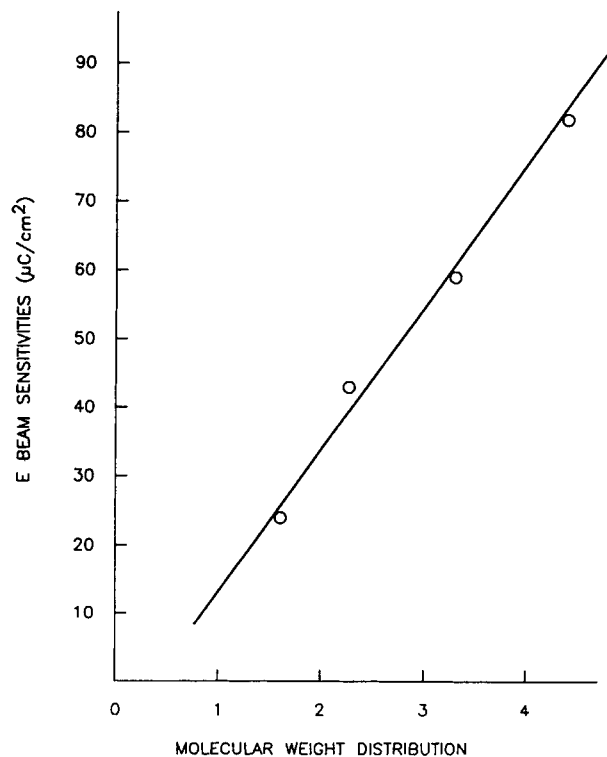


**Figure 1** Effect of *N*-quaternization on the electron beam sensitivities of poly(4-vinyl-*N*-methylpyridinium iodides).

iodide), having a molecular weight distribution of 4.3, was much less sensitive to the electron beam as compared to the polymer having a molecular weight distribution of 1.7, while keeping the number average molecular weight in the range of 20,000 to 30,000. In order to see the effect of *N*-alkyl chain length on electron beam sensitivities of various polyvinylpyridinium salts, a number of quaternization reactions were carried out using poly(4-vinyl pyridine) and different alkyl halides.



**Figure 2** Effect of  $M_n$  on electron beam sensitivities of poly(2-vinyl-*N*-methylpyridinium iodides).

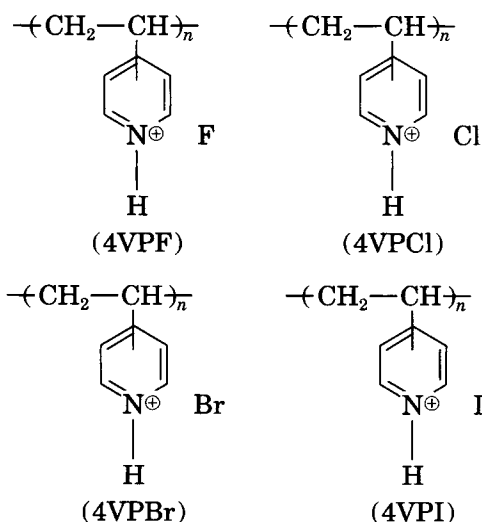


**Figure 3** Effect of molecular weight distribution on electron beam sensitivities of poly(4-vinyl-*N*-methylpyridinium iodides).

where R = H, methyl, *iso*-propyl, *n*-butyl, *n*-heptyl, and *n*-dodecyl.

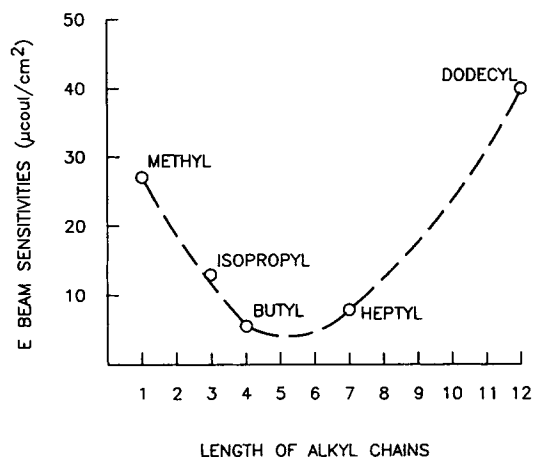
In all of the above cases, the degree of *N*-alkylation of the polymer was adjusted at 10 mol %. The degree of alkylation was determined by both elemental analysis and NMR integration methods. In general, electron beam sensitivities of poly(4-vinylpyridinium iodides) were improved by orders of magnitude upon quaternizing. Moreover, it is interesting to note that sensitivities were increased with an increased length of the alkyl groups, up to seven carbon atoms, after which they decreased significantly (Fig. 4).

The relationship between different counterions of the polymer and the electron beam sensitivities was also studied. Four different kinds of polyvinylpyridinium salts, such as poly(4-vinyl-*N*-pyridinium fluoride) (4VPF), poly(4-vinyl-*N*-pyridinium chloride) (4VPCl), poly(4-vinyl-*N*-pyridinium bromide) (4VPBr), and poly(4-vinyl-*N*-pyridinium iodide) (4VPI), were synthesized by reacting poly(4-vinyl pyridines) and respective hydrogen halides.



It can be clearly seen from Table II that the sensitivity of the iodide salt was higher than those of fluoride, chloride, and bromide.

Several experiments were performed in order to establish the ultimate resolution of various resist formulations. In one experiment, for instance, poly(2-vinyl-*N*-*iso*-propylpyridinium iodide) was exposed as a negative working resist and the resulting image contained lines of 0.3  $\mu\text{m}$  width (Fig. 5). This suggests that the material is potentially useful for submicron fabrication. The patterned substrate, using poly(4-vinyl-*N*-methylpyridinium iodide), was etched in a plasma etcher for 5 min at



**Figure 4** Effect of alkyl chain length on electron beam sensitivities of poly(4-vinyl-*N*-alkylpyridinium iodides) (10 mol % alkylated materials).

200 watts, with 6%  $\text{CCl}_4$  in He at 430 mTorr, 5 min at 150 watts, with 4%  $\text{CCl}_4$  in He at 420 mTorr, and 7 min at 50 watts, with 10%  $\text{O}_2$  in He at 480 mTorr. The material was eroded at an average rate of about 60  $\text{\AA}/\text{min}$ . Under the same conditions, the commercial shipley AZ 1470 resist was etched at an average rate of about 120  $\text{\AA}/\text{min}$ .

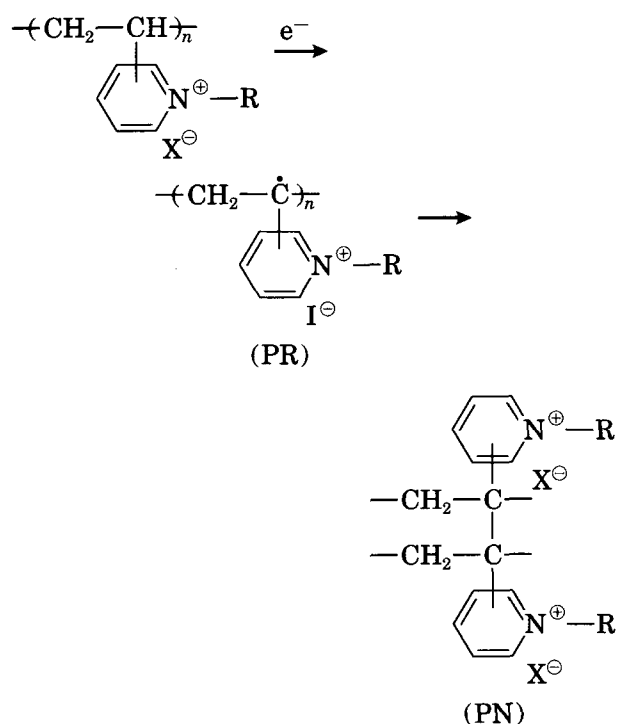
## DISCUSSION

It has been shown that electron beam sensitivities of polyvinylpyridinium salts were increased with increasing molecular weight of the polymer. This indicates a typical crosslinking behavior of the polymer upon electron beam exposure; as the polymer chains become longer, fewer crosslinking sites need to be generated. Furthermore, the relationship between electron beam sensitivities and molecular weight distributions of polyvinylpyridinium salts corroborates the crosslinking phenomena. It can be seen from Figure 3 that a polymer, having a narrow molecular weight distribution, was more sensitive to electron beams than a polymer having a broad molecular weight distribution. It is apparent that the homogeneous nature of the chain lengths in the polymer requires low levels of electron beam irradiation.

Based on the results obtained from the studies on the relationship between molecular weight, molecular weight distribution, and electron beam sensitivities of polyvinylpyridinium salts, a mechanism of the polymer transformation under electron beam can be postulated as follows:

**Table II** Effect of Counterions on Electron Beam Sensitivities of Polyvinylpyridinium Salts

Polymers	E Beam Sensitivities (coul/cm <sup>2</sup> )
Poly(4-vinyl- <i>N</i> -pyridinium fluoride) (4VPF)	1.8 × 10 <sup>-4</sup>
Poly(4-vinyl- <i>N</i> -pyridinium chloride) (4VPCl)	1.2 × 10 <sup>-4</sup>
Poly(4-vinyl- <i>N</i> -pyridinium bromide) (4VPBr)	1.0 × 10 <sup>-4</sup>
Poly(4-vinyl- <i>N</i> -pyridinium iodide) (4VPI)	6.0 × 10 <sup>-5</sup>

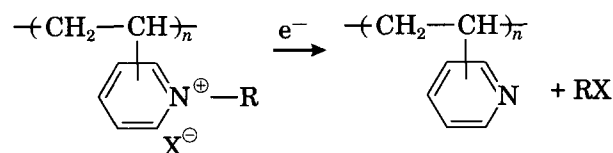


where R = alkyl groups and X = halides.

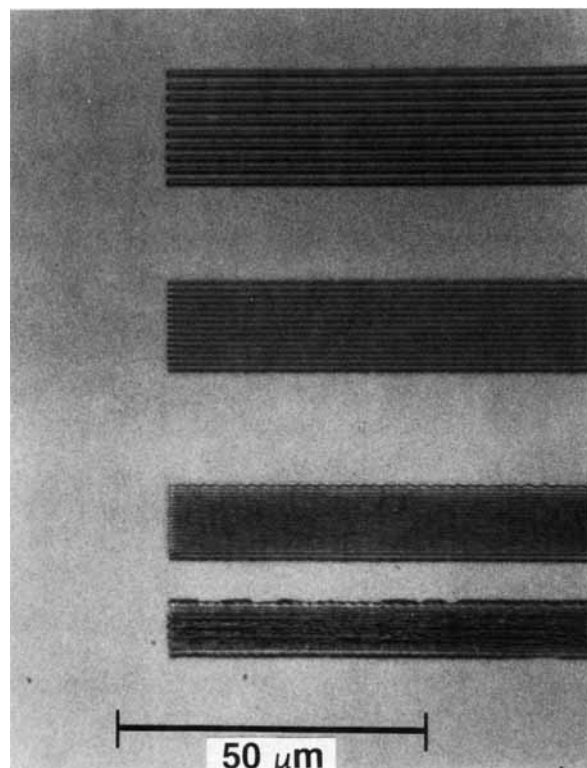
By quaternizing the pyridine pendant group of the polymer with alkyl halides, the resulting pyridinium moieties can exert a strong inductive force onto the polymer backbone carbon upon exposure to the electron beam. In turn, such an inductive effect can facilitate the removal of the hydrogen radical from the polymer backbone to readily generate the polymeric radical (PR). The polymeric radical can subsequently participate in the crosslinking reaction to produce an insoluble polymer network (PN). It may be argued that such insoluble polymeric networks may be difficult to form, due to the steric hindrance. However, the crosslinking, result-

ing from the coupling of the polymeric radical, is apparent from the relationship of the molecular weight with the electron beam sensitivity data of the polymer. Moreover, such a mode of crosslinking has been observed in the case of polystyrene under an electron beam environment.<sup>5</sup> It is also known that the coupling reaction of the polymer radical resulting in the formation of crosslinks, is favored below the glass transition temperature of the polymer, whereas, above the glass transition temperature, the chain scission reaction is favored. On the other hand, the radical generation of poly(vinylpyridines) requires an extremely high dose of electrons without quaternization (see Table I).

An alternative possibility of the crosslinking reactions of polyvinylpyridinium salts can be speculated as follows;

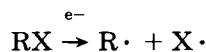


where R = alkyl groups and X = halides.

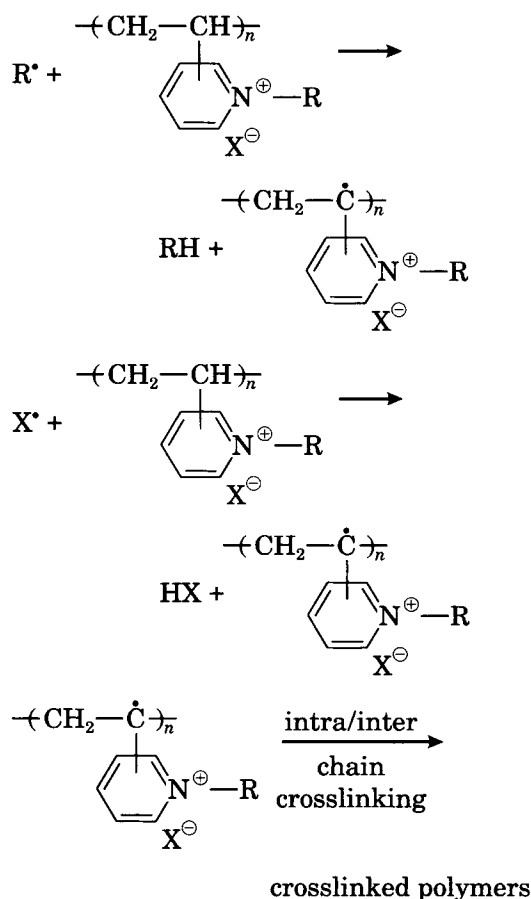


**Figure 5** Electron beam exposure patterns of poly(4-vinyl-*N*-iso-propylpyridinium iodides).

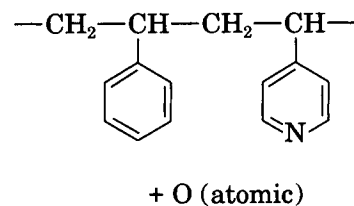
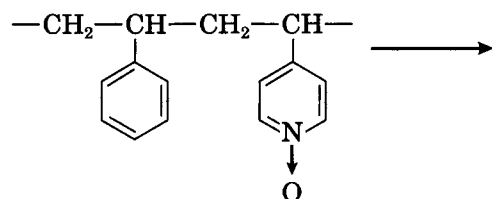
The N—C bond can be cleaved with electron beam to generate alkyl halides. Subsequently, the further cleavage of alkyl halides results in the generation of alkyl and halide radicals.



Either R<sup>•</sup> or X<sup>•</sup> can easily abstract tertiary hydrogens from the polymer backbone to produce polymeric radicals. They can subsequently participate in the crosslinking reaction.



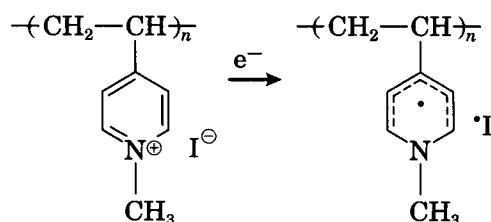
Recently, Decout et al.<sup>6</sup> reported that the cleavage of the N-oxide bond was responsible for photocrosslinking of the copolymer of styrene and 4-vinylpyridine-*N*-oxide.



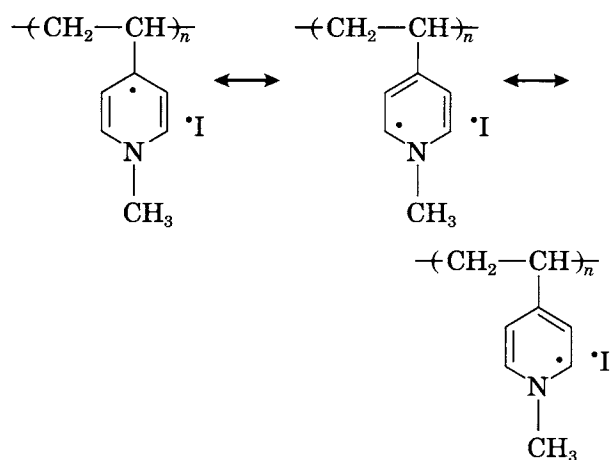
O + polymer → the crosslinked polymer (atomic)

To test whether this process actually occurs, we have carried out some model compound studies. For example, a monomeric pyridinium salt, such as *N*-cetylpyridinium iodide, was introduced into the poly(2-vinyl pyridine) matrix by a solution blending technique. A film of the blended material on silicon substrate was evaluated under electron beam. It was found that the electron beam sensitivity of poly(vinyl pyridines) was not improved by this approach. Thus, the N—C cleavage reaction does not appear to play an important role in the insolubilization of polyvinylpyridinium salt under electron beam.

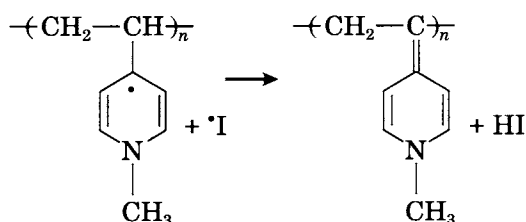
The above mentioned crosslinking mechanism, however, cannot fully account for the fact that the electron beam sensitivity of poly(vinyl pyridines) was improved by orders of magnitude upon quaternizing nitrogen sites of the polymer's pyridine pendant groups. The increasing electron beam sensitivity, in the order of I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup>, which was shown in the previous section, essentially coincided with the increasing electron releasing power of halides. This should lead to another important mechanism of the change in solubility of the polyvinylpyridinium salt under electron beam. In the case of poly(4-vinyl-*N*-methylpyridinium iodide), an electron-rich counterion, such as iodide, can donate electrons to the electron-poor pyridinium ring to form a charge-transfer complex.



When the electron transfer from the iodide ion to the antibonding orbital of the pyridinium ring occurs under electron beam, the polymeric salts can be viewed as having the following contributing resonance forms.



There is ample evidence in the literature of the existence of such a charge-transfer radical. For example, Kosower et al., and several other workers,<sup>8,9</sup> have reported that stable pyridinyl radicals can form upon exposure of 1-alkylpyridinium iodide salts to UV light in solution. Although the fate of such a neutral biradical is unknown, it is possible that the hydrogen radical can be abstracted by the iodine radical.



In support of this postulated mechanism, we have experimentally observed the formation of hydrogen iodide gas upon exposure of the polyvinylpyridinium iodide to electron beams. However, the possibility of a crosslinking reaction, initiated from the iodine radical, cannot be excluded.

If the aforementioned mechanism operates during electron beam exposure, the polymer can be totally converted by electron beam from ionic to nonionic in character. It has been reported that most negative working resists have swelling problems because the resist action is based upon simple molecular weight changes. Since polyvinylpyridinium salts undergo radiation-induced solubility changes, due to their polarity, in addition to crosslinking, these polymers can be useful resist materials with the potential for high resolution without much swelling.

As is shown in Figure 4, the studies on the effect of the alkyl chain length on the electron beam sensitivity of the polymer indicated that there appears

to be an optimum chain length of the alkyl group to possess good electron beam sensitivity. The film-forming properties of polyvinylpyridinium salts are improved with the increased *N*-alkyl chain length. The better sensitivity may be due to the formation of the better homogeneous film. The reason for the decreased sensitivity in the case of the polymer bearing the long *N*-dodecyl moieties could lie in the possible side chain crystallization in the polymer matrix. Thus, the crystalline region of the polymer film would scatter the electron beam, which results in decreased sensitivity.<sup>10</sup>

Figure 5 shows that the poly(2-vinyl-*N*-isopropylpyridinium iodide) was resolved clearly up to 0.3  $\mu\text{m}$ . As liquid processing of polymers is gradually being replaced by plasma treatment in the electronic fabrication process, the erosion of the organic resist during the plasma etching processes has been one of the limiting features.<sup>11</sup> Since it is evident that the polyvinylpyridinium salt is extremely resistant to plasma (e.g.,  $\text{CCl}_4\text{—O}_2$ ), the material can be developed without difficulties by dry-processing techniques.<sup>12</sup>

The crosslinking, along with the polarity change due to the charge transfer under electron beam, appears to proceed even in the inside of the polymer film. When several layers of the 8000 Å-thick film on the silicon wafer substrate were removed with the razor blade, the film is still insoluble. It is known that electrons in the 50–350 KV range could cure 25  $\mu$  to 380  $\mu$ -thick coatings. Thus, it is not surprising to crosslink all the way into the inside of such an 8000 Å-thick film, with a 10–100  $\mu\text{coul}/\text{cm}^2$  dose of electron beam, under a high vacuum environment.<sup>13</sup>

## REFERENCES

1. L. F. Thompson, in: *Introduction to Microlithography*, ACS Symposium Series, 219, L. F. Thompson, C. G. Willson, and M. J. Bowden, Eds., American Chemical Society, Washington, DC, 1983, pp. 1–13.
2. For review, see: *Electron-Beam Technology in Microelectronic Fabrication*, G. R. Brewer, Ed., Academic, New York, 1980.
3. M. J. Bowden and L. F. Thompson, *Solid State Technology*, May, 1979, p. 72.
4. (a) M. S. Gibson, in: *The Chemistry of the Amino Group*, S. Patai, Ed., Interscience, New York, 1968, pp. 440–483. (b) L. Spialter and J. A. Pappalardo, in: *The Acyclic Aliphatic Tertiary Amines*, MacMillan, New York, 1965, pp. 14–29. (c) A. T. Bottini, *Selective Organic Transformations*, 1, 89 (1970).



5. For review, see: *The Radiation Chemistry of Macromolecules*, M. Dole, Ed., Academic, New York, London, 1973, Vol. II, Chap. 5.
6. J.-L. Decout, A. Lablache-Combiere, and C. Loucheux, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2371 (1980).
7. E. M. Kosower, J. A. Skorcz, W. M. Schwarz, and J. W. Patten, *J. Amer. Chem. Soc.*, **82**, 2188 (1960).
8. J. W. Larsen, A. G. Edwards, and P. Dobi, *J. Amer. Chem. Soc.*, **102**, 6780 (1980).
9. T. J. van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, **94**, 8451 (1972).
10. R. D. Hedenreich, L. G. Thompson, E. D. Feit, and C. M. Melliar-Smith, *J. Appl. Phys.*, **44**, 4039 (1973).
11. L. M. Ephraath, *J. Electrochem. Soc. Reviews and News*, **129**, 62C (1982).
12. H. Hiraoka, *J. Electrochem. Soc., Solid State Science and Technology*, **128**, 1065 (1981).
13. For review, see: *Radiation Curing, An Introduction to Coatings, Varnishes, Adhesives, and Inks*, The Education Committee of the Radiation Curing Division AFP/SME, The Association for Finishing Processes of the Society of Manufacturing Engineers, Publications Development Department, Dearborn, Michigan, 1986.

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