

## An Investigation of the Effects of the Molecular Weight Distribution on the Sensitivity of Positive Electron Resists

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### Synopsis

The molecular weight distribution of two grades of poly(methyl methacrylate) was determined, and the solubility of that polymer in methyl ethyl ketone-2-propanol mixtures was studied. The effects of the molecular weight distribution of the polymer and the strength of the developing solvent on electron resist sensitivity were studied experimentally and compared with a computer model of the electron exposure process. The molecular weight and the molecular weight distribution were found to have a significant effect on the sensitivity of poly(methyl methacrylate) as an electron resist. Increased sensitivity is predicted for higher molecular weight and narrower molecular weight distribution.

### INTRODUCTION

Electron beam microfabrication requires polymeric materials which are sensitive to an electron beam. When a polymer is irradiated with an electron beam, some of the polymer molecules are excited or ionized, and the polymer undergoes both scission and crosslinking processes. A polymer which becomes predominantly crosslinked, and therefore becomes less soluble after irradiation, is termed a negative resist. Conversely, if the scission process predominates and the solubility of the polymer increases after irradiation, it is called a positive resist.<sup>1</sup> In electron beam microfabrication, a substrate is coated with a layer of polymer resist, and the resist is patterned by changing the solubility of the polymer with an electron beam. Subsequently, the unwanted area of polymer is dissolved (developed), and the pattern is used as a mask either for plating, chemical etching, ion etching, or ion implantation. A suitable electron resist needs to fulfill certain requirements. Mainly, the polymer should be sensitive to an electron beam and compatible to semiconductor fabrication. The details of these requirements have been discussed.<sup>2,3</sup>

The sensitivity of a positive resist has been defined by some as the electron dose (in coulombs/cm<sup>2</sup>) required for the desired degree of electron induced scission<sup>1</sup> and by others as "minimum electrical charge per unit area of resist film required for complete development of the area."<sup>2</sup> The degree of electron-induced scission depends on the absorbed energy density and the number of scission events taking place after the absorption of energy, i.e.,  $G(s)$  of the resist. The absorbed energy density depends on the beam voltage, the

substrate, and the thickness of the material, but is insensitive to the variation in chemical composition for most polymers. According to the first definition, the sensitivity is largely determined by the  $G(s)$  values of the resist. Although the second definition of sensitivity is very useful in actual practice, it is somewhat misleading. Complete development of a resist film depends not only on exposure but also on the development conditions such as the solvent strength, developing time, and developing temperature used. According to this definition, a less "sensitive" resist can be made more "sensitive" by simply applying a better solvent as long as the thickness loss in the unexposed area can be tolerated.<sup>1</sup> If one assumes that a suitable developer can always be found as long as the molecular weight of the exposed and unexposed polymer differ, a conceptually useful definition of sensitivity is to define it as the electron dose required for producing low molecular weight fragments such that the molecular weight distribution of the exposed polymer barely overlaps with the original, unexposed polymer. It is a useful concept because the defined sensitivity then does not depend explicitly on the developing conditions. It will be shown later that, based on such a concept, the effect of molecular weight and molecular weight distribution on the sensitivity of a positive resist can be clearly demonstrated.

In this paper, we report some results of a computer modeling of the random scission process of a positive resist, poly(methyl methacrylate). The effect of molecular weight and molecular weight distribution on the sensitivity has been investigated and found to be significant. Based on the model, the sensitivity of the poly(methyl methacrylate) was calculated and found to be in agreement with the experimental results.

## EXPERIMENTAL

### Materials

**PMMA.** Elvacite 2041, 2021, and 2008 were obtained from du Pont Co.

**Solvents.** Analytical grades of toluene, chloroform, methyl ethyl ketone, and 2-propanol were used without further purification.

### Polymer Characterization

The number-average molecular weight of PMMA,  $\bar{M}_n$ , was determined by an osmotic pressure method. In osmotic pressure measurements, a Wescan Model 231 recording membrane osmometer was used at 25°C with methyl ethyl ketone as the solvent. Number-average molecular weights of the polymers are shown in Table I. The molecular weight distributions of Elvacite

TABLE I  
Molecular Weight and Dispersity of PMMA

PMMA	Number-average molecular weight	Dispersity
Elvacite 2041	345,000	2.6
Elvacite 2021	171,000	2.4
Elvacite 2008	38,000	

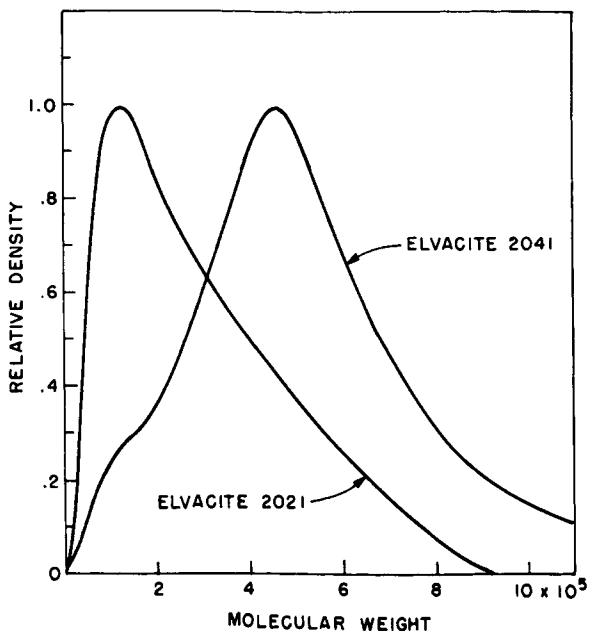


Fig. 1. Molecular weight distribution curves for Elvacite 2041 and 2021.

2041 and 2021 were determined by using a Water Associates Model 202 gel permeation chromatograph. Since the calibration of the chromatograph is based on polystyrene, not poly(methyl methacrylate), adjustments in the calibration curve were made so that the number-average molecular weights calculated from the distributions were consistent with the osmotic pressure measurements. The molecular weight distributions for Elvacite 2041 and 2021 are shown in Figure 1.

### Polymer Solubility Studies

To study the solubility of PMMA as a function of its molecular weight, a fractional precipitation method was employed. In this method, either Elvacite 2021 or Elvacite 2008 was dissolved in methyl ethyl ketone (1% solution), and 2-propanol was added gradually to the stirred solution at  $23^{\circ} \pm 0.1^{\circ}\text{C}$ . After addition of 2-propanol, the solution was aged for 2 hr. The solution was then warmed until it became transparent and then cooled gradually to the original temperature to let the precipitate settle. The precipitate was separated by decanting and was filtered and dried to constant weight under vacuum. Before determining the molecular weight of precipitated polymer, the polymer was redissolved in benzene and freeze dried. The number-average molecular weight of the precipitated polymer was determined by the osmotic pressure method. The results are shown in Figure 2.

### Electron Beam Exposure

Both 5% Elvacite 2041-MEK solution and 5% Elvacite 2021-toluene solution were spun at 2000 rpm on a 450-Å Al-Cu film on a glass substrate. The thickness of the PMMA films were approximately 5500 Å and 2500 Å, respec-

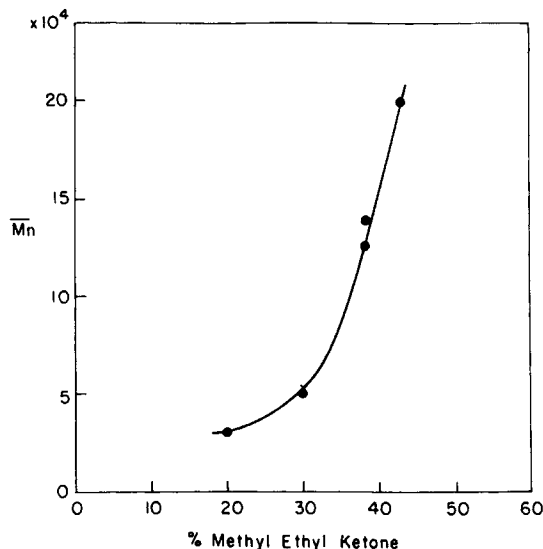


Fig. 2. Approximate solubility curve of poly(methyl methacrylate) in methyl ethyl ketone-2-propanol mixed solvent.

tively, for Elvacite 2041 and 2021. The polymer film was prebaked at 170°C for 30 min before irradiation. The resist was patterned by irradiating the PMMA film with a 15 keV electron beam at different exposures ranging from  $10^{-4}$  to  $10^{-7}$  coul/cm<sup>2</sup>. To generate the test patterns, a computer-controlled Electron Beam Micropattern Generator (Radiant Energy Systems, Inc.) was used. Development of the pattern was carried out by immersing the polymer film into a stirred developer at  $23^\circ \pm 0.1^\circ\text{C}$  for 30 min. Observation of the developed pattern was carried out under a phase-contrast microscope, and the thickness of the resist was measured by a Bendix Proficorder. The accuracy of the Proficorder is about 3%.

### The Computer Simulation

The degradation of positive electron resists occurs through the scission of the polymer bonds, so the exposed area has a lower molecular weight than the unexposed area and can be dissolved with an appropriate strength solvent. The progress in the degradation in molecular weight of the resist with exposure (scission events) can be modeled on a computer. In the model, the molecular weight distribution is broken into  $I$  intervals. Assuming the scission events occur in a random manner,<sup>6</sup> then the changes in the population of each molecular weight interval can be computed. If one defines  $D(i)$  = density of resist in  $i$ th interval,  $M_w(i)$  = molecular weight of molecules in the  $i$ th interval,  $M_m$  = monomer molecular weight (= 100 for methyl methacrylate),  $R(i)$  = number of polymer bonds per molecule in the  $i$ th interval,  $B(i)$  = number of polymer bonds per molecule in the  $i$ th interval,  $B_t = \sum_i B(i)$  the total number of polymer bonds,  $A$  = Avogadro's number,  $N$  = number of scission events over the entire distribution, the number of scission events occurring in the  $i$ th interval due to a small number of scission events  $dN$  is given by  $dN \cdot B(i)/B_t$ . Each event will create two molecules and eliminate one polymer

bond. It is assumed that these molecules will be evenly distributed among the lower  $(i - 1)$  intervals. The number of the molecules added to the  $j$ th interval ( $j < i$ ) due to scissions in the  $i$ th interval is

$$[2/(i - 1)] \cdot [dN \cdot B(i)/B_t]$$

where

$$B(i) = R(i) \cdot D(i) \cdot A/M_w(i)$$

and

$$R(i) = M_w(i)/M_m - 1.$$

The computer calculates the changes in the molecular weight distribution as the number of scission events is incremented. Assuming a developer is applied which can dissolve molecules up to a critical molecular weight  $M_c$ , then the fraction of the resist dissolved with that solvent can readily be calculated as a function of scission events (exposure).  $M_c$  could be taken from a solubility curve like the one shown in Figure 2.

## RESULTS AND DISCUSSION

We have obtained three different grades of PMMA and determined their number-average molecular weight  $\bar{M}_n$  by the osmotic pressure method and dispersity from the GPC data. The molecular weight and dispersity of PMMA determined are shown in Table I. The molecular weight distribution curves for both Elvacite 2041 and 2021 are shown in Figure 1. The molecular weight distribution of both polymers are seen to be fairly broad.

The solubility of PMMA in MEK-2-propanol was determined and is shown in Figure 2. In general, the solubility of a polymer in a solvent is characterized by their solubility parameters  $\delta$ . The closer the two values, the more likely that the two substances will be mutually soluble. The  $\delta$  value of PMMA is 9.5, while the  $\delta$  values of methyl ethyl ketone and 2-propanol are 9.3 and 11.5, respectively.<sup>4</sup> At room temperature, methyl ethyl ketone is a solvent for PMMA, while 2-propanol is a nonsolvent. By adding 2-propanol to a PMMA-methyl ethyl ketone solution, high molecular weight components will become increasingly insoluble and precipitate accordingly.

It is well known that the development of a resist is based on the principle of fractional solution. When a resist is immersed in a developer for a sufficiently long time and equilibrium is established between the precipitated phase and the solution phase, then, according to the theory of polymer fractionation,<sup>5</sup> the distribution of a polymer of degree of polymerization  $x$  between the two phases is

$$V'_x/V_x = e^{\sigma x}$$

where  $V'_x$  and  $V_x$  are, respectively, volume fractions of the polymer with degree of polymerization  $x$  in the precipitated phase and solution phase, and  $\sigma$  is given by the following expression:

$$\sigma = V_2(1 - 1/\bar{x}_n) - V'_2(1 - 1/\bar{x}'_n) + \chi_1[(1 - V_2)^2 - (1 - V'_2)^2]$$

where  $V'_2$  and  $V_2$  are volume fractions of polymer in precipitated and solution

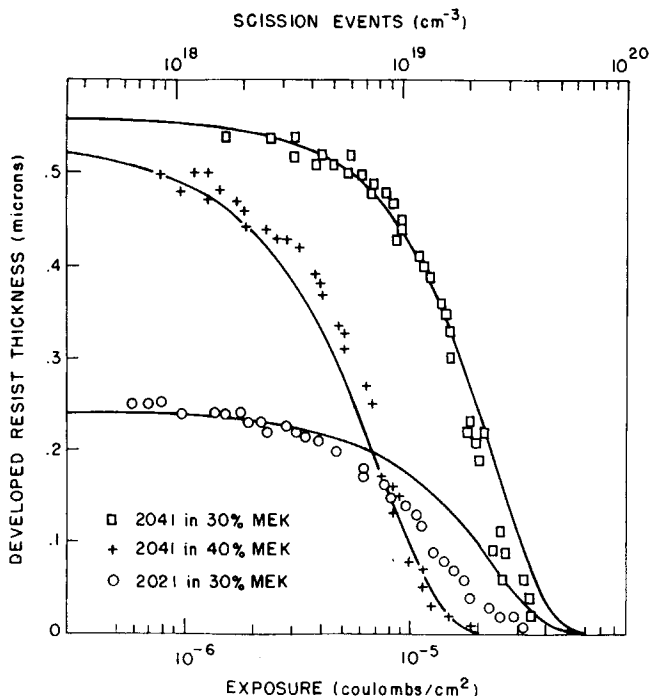


Fig. 3. Experimental (lower scale) and analytical (upper scale) development curves for PMMA in methyl ethyl ketone-2-propanol mixed solvent.

phase, respectively,  $\bar{x}'_n$  and  $\bar{x}_n$  are number-average degree of polymerization of the polymer in precipitated and solution phase, and  $\chi_1$  is the polymer solvent interaction parameter. Although accurate calculation of  $\sigma$  is generally difficult, it can be shown from the above equation that  $\sigma$  changes little with concentration in the dilute polymer concentration region. As the polymer concentration becomes extremely dilute, the fractionation becomes more efficient, and the distribution of a polymer between two phases depends largely on its molecular weight. The precipitated phase contains mostly molecules of higher molecular weight, while the solution phase retains mostly lower molecular weight species. In developing our resist pattern, approximately 0.10 mg PMMA is immersed in 100 ml developer until equilibrium is established. Since the concentration is extremely dilute, the development of the pattern can be considered solely dependent on the molecular weight of a polymer species. In our fractional precipitation studies, the initial polymer concentration was 1%. Although it is somewhat higher than the polymer concentration in the developer, it is clear that in such a dilute concentration region, this difference in concentration has an insignificant effect on the compositions of the precipitated and solution phases. To a first approximation, the results shown in Figure 2 should be valid for the development studies of PMMA resists.

It was mentioned in the experimental section that the development of the resist pattern was carried out by immersing the polymer film into a stirred developer at 23°C for at least 30 min. Our preliminary experiments indicate that additional 2 hr of immersion of the film in the developer did not produce

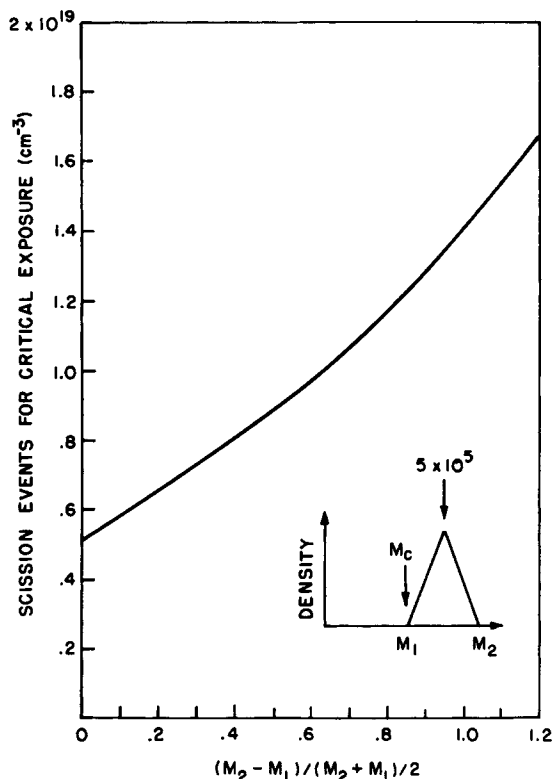


Fig. 4. The computed relationship between molecular weight distribution and sensitivity for poly(methyl methacrylate).

further loss in film thickness. The resist film was very thin ( $\approx 0.5 \mu$ ) and the amount of resist to be developed was very small ( $\approx 0.1 \text{ mg}$ ) compared with a large volume ( $\approx 100 \text{ ml}$ ) of stirred developer. Therefore, it was reasonable to assume that 30 min was sufficiently long for low molecular weight species to diffuse out of the film and to establish equilibrium between the precipitated (undissolved resist) and the solution phases.

The experimental data on PMMA resist development and exposure are shown in Figure 3. The developed resist thickness which depends on the composition of the developer used (see Fig. 2) is plotted as a function of exposure in this figure. Also included in this figure are the corresponding computer generated curves which relate the developed resist thickness as a function of scission events. In calculating these curves, the critical molecular weight was taken from the solubility curve in Figure 2, and the initial molecular weight distributions were an approximation of the curves in Figure 1.

The number of scission events,  $N$ , is related to the exposure  $Q$  by the following expression:

$$N = \frac{G(s)}{100} \cdot \frac{E}{l} \cdot \frac{Q}{q}$$

where  $q$  is electronic charge,  $l$  is the thickness of the resist film, and  $E$  is defined as the energy which an electron lost in passing through the PMMA film. Although the  $E$  value may be significantly affected by beam voltage, the sub-

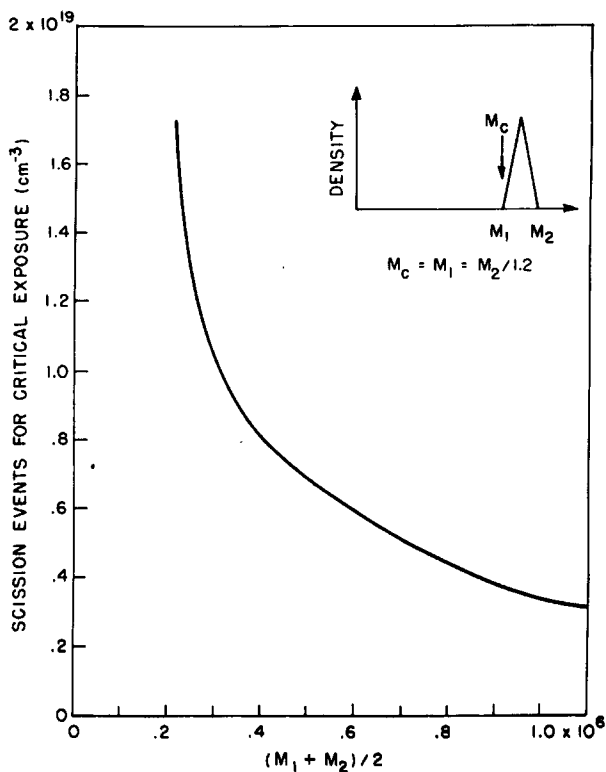


Fig. 5. The computed relationship between peak molecular weight and sensitivity for poly(methyl methacrylate).

strate, and the film thickness for a given system and exposure,  $E/l$  should be independent of  $Q$ . The number of scission events  $N$ , therefore, is directly proportional to the exposure  $Q$ . This proportionality can be determined by comparing the results of the computer simulation with experimental results. For the resist films investigated here, it is indicated by Figure 3 that an exposure of 1 coulomb/cm<sup>2</sup> results in  $1.2 \times 10^{24}$  scission events/cm<sup>2</sup>. The data also illustrate the fact that the minimum exposure required to obtain full development depends on the initial molecular weight and solvent strength.

The consistency of the experimental data and the theoretical curves suggests that the exposure model used and the assumption made regarding resist development are valid. The indication is that the changes in the molecular weight distribution can be computed from the model and that in developing the resist film an equilibrium (or near equilibrium) is established between the polymer in the precipitate and solution phases during the development process. It appears that 30 min is sufficient time for the low molecular weight polymer fragments to diffuse through the high molecular weight matrix and establish the equilibrium.

The relationship between molecular weight distribution and number of scission events for critical exposure is predicted by the model as shown in Figure 4. With a decreasing spread in the molecular weight distribution, the number of scission events required for critical exposure is seen to be decreased significantly. The sensitivity of a positive resist, therefore, can be in-



creased by decreasing the heterogeneity of the polymer through fractionation. The reason the sensitivity is so dependent on the width of the molecular weight distribution is that, with a narrow distribution, each scission event will likely produce fragments below the critical molecular weight of the solvent. With wide distributions, several scissions would have to occur in most molecules to achieve the required degradation.

It has been recognized<sup>7</sup> that high molecular weight positive resists are preferable to those of low molecular weight. The effect of molecular weight on the number of scission events for critical exposure derived from the present model for PMMA is shown in Figure 5. It is seen that an increase in molecular weight does significantly increase the sensitivity of the resist in the low molecular weight region. As the molecular weight becomes sufficiently high, further increase in molecular weight has a less significant effect on the sensitivity of the resist. The reason for the increased sensitivity of resists with higher molecular weight is that, for a given area and thickness of resist, there would be fewer molecules. Thus, fewer scission events would be needed to obtain sufficient degradation for complete development.

The improved sensitivity of a high molecular weight resist with a narrow molecular weight distribution can be predicted from this work. Our calculations show, for example, that if the high and low molecular weight tails of the Elvacite 2041 distribution were removed, the sensitivity could be increased by about a factor of 3. In addition, if the initial molecular weight distribution was narrow and centered twice as high (e.g., 1,000,000), then, with an appropriate developer, the sensitivity would be increased by an additional factor of 2.

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