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Parameters Affecting the Electron Beam Sensitivity of Poly(methyl methacrylate)

Abstract: Poly(methyl methacrylate), PMMA, is used as a model polymer to determine quantitatively the effect of molecular weight, molecular weight distribution, and tacticity on electron beam sensitivity. The heterotactic, syndiotactic, and isotactic stereoforms of PMMA were synthesized with molecular weights ranging from 10^4 to 10^7 and dispersivities from 1.2 to about 10. The G-values as determined by gamma radiation are about 1.3 and are independent of the three parameters. However, the solubility rate of PMMA is very dependent on the tacticity, and the relative solubility rates are in the order syndiotactic $<$ heterotactic $\ll$ isotactic. The weight-average molecular weight ratio was found to give a better correlation with solubility rate ratio than the number-average molecular weight ratio. The molecular size of the developer solvent was shown to have a much greater effect on the solubility rate than the molecular weight of the resist. An optimal developer solvent for PMMA can be systematically selected from a homologous series of *n*-alkyl acetates which enhance the resist sensitivity.

Introduction

Poly(methyl methacrylate), PMMA, has been used as the model polymer by many investigators to study the radiation properties of polymers that primarily degrade or undergo scission when irradiated [1-3]. Consequently, this class of polymers has been investigated as positive resists for electron beam lithography [4-6].

It has been qualitatively demonstrated that the electron beam sensitivity of PMMA and other positive resist systems does not have fixed values. The sensitivity is interpreted here as the minimum radiation dose required to obtain a predetermined solubility rate ratio, $S/S_0 = S_R$, where S and S_0 are the solubility rates of the irradiated and non-irradiated regions of the resist, respectively. The system and material parameters influencing sensitivity are beam acceleration voltage, resist thickness, developing conditions, glass transition temperature, chemical nature, G-value (number of chemical events produced per 100eV of absorbed radiation), molecular weight, and molecular weight distribution [7-12].

It has been reported [4] that the sensitivity of a positive resist, in contrast to that of a negative resist, is independent of the initial molecular weight and the molecular weight distribution of the polymer. This conclusion was based qualitatively on the difference in solubility (a thermodynamic property) of the exposed and unexposed resist. However, this conclusion may not be valid since the image in a positive resist is developed by differences in the solubility rates (a kinetic property) and not by differences in the solubility of the resist. An expression that relates the theoretical dependence of the degraded molecular weight to the initial molecular weight for any polymer undergoing random scission [1] has been used to demonstrate the importance of high molecular weight among the factors affecting sensitivity [12]. In addition, the contribution of molecular weight distribution to the sensitivity of a positive resist has been demonstrated theoretically and experimentally with PMMA [13]. However, there are still many unanswered questions regarding sensitivity. This investigation was carried out primarily to determine more quantitatively the dependence of the chain scission efficiency (G-value) and the solubility rate ratio (S_R) on molecular weight (weight and number averages), molecular weight distribution, and polymer stereochemistry. In addition, the effect of the molecular size of the solvent developer was investigated to determine its contribution to the resist sensitivity. Heterotactic, syndiotactic, and isotactic PMMAs with molecular weights from 10^4 to 10^7 and dispersivities from 1.2 to about 10 were synthesized for this study.

Experimental

- *Materials*

Methyl methacrylate monomer was passed through a column containing neutral grade alumina to remove the inhibitor (10 ppm methylethylhydroquinone) and was collected over calcium hydride. The fraction distilling at 40°C (313 K) and 100 mm Hg (13.3 kPa) pressure was collected and used for preparation of the polymers.

Polymerization procedures

Several synthetic techniques were used to obtain poly(methyl methacrylates) of very low, high, and very high molecular weight as follows:

Very low molecular weight PMMA was synthesized by the dropwise addition of methyl methacrylate monomer, 50 g (0.50 mole) containing 1.2 g (5×10^{-3} mole) benzoyl peroxide to 200 ml refluxing toluene solvent under nitrogen [14]. After 1.5 hours, the polymer was precipitated in cold acidified methyl alcohol. Repeated precipitation from acetone/methyl alcohol removed the oligomeric fractions. After vacuum drying at 338 K for 48 hours, 20 g (40 percent yield) white polymer were obtained with $M_w = 18100$, $M_n = 15400$ and $M_w/M_n = 1.18$.

High molecular weight PMMA was prepared in a sealed two-liter Parr stirring-type stainless steel pressure reactor. The reactor was charged with 250 g (2.5 mole) MMA monomer, 0.45 g (0.005 mole) *t*-butyl hydroperoxide, and 750 ml toluene, and then heated at 343 K for 48 hours. The amount of polymer obtained was 72.1 g (30 percent yield) with $M_w = 1.972 \times 10^6$, $M_n = 747 \times 10^3$, and $M_w/M_n = 2.64$.

Very high molecular weight PMMA was prepared by microwave initiation as follows: Ten-ml aliquots of MMA containing *t*-butyl peroxide as initiator were syringed into clean, dry vials and sealed under nitrogen. The vials were irradiated in a microwave oven at 2450 MHz at 0.5 mA for one minute or 0.3 mA for two minutes to activate the hydroperoxide. The samples were set aside for 100 hours at 25°C or 24 hours at 70°C. Both conditions gave essentially the same high M_w polymers: $M_w = 9.40 \times 10^6$, $M_n = 2.16 \times 10^6$, and $M_w/M_n = 4.35$ by gel permeation chromatography (GPC). The value of M_w was also determined by low angle laser light scattering as 9.10×10^6.

Isotactic PMMA was prepared in toluene at 0°C with phenylmagnesium bromide as the catalyst, to give, after 4 hours, an 82.3 percent yield of 100 percent isotactic product [15]; $M_w = 2.71 \times 10^6$, $M_n = 1.20 \times 10^6$ and $M_w/M_n = 2.26$.

High syndiotactic PMMAs were synthesized anionically using 2-(dimethylaminomethyl)-pyridine, DMAMP, as the cocatalyst in an inert atmosphere of dry nitrogen or argon. Fifty ml of THF (from $LiAH_4$) were distilled into a 125-ml serum bottle, to which 0.33 ml of 1.9 N *n*-butyllithium in *n*-hexane was added. This was followed by the addition of 0.22 ml of DMAMP and the deep red-orange reaction mixture was cooled to 183 K. Ten ml (9.4 g) of MMA were added and an instantaneous, quantitative polymerization took place. The product was dissolved in $CHCl_3$, precipitated in excess MeOH and vacuum dried with the result that $M_w = 32500$, $M_n = 19100$, and $M_w/M_n = 1.70$. The percentages of I, H, and S by proton nuclear magnetic resonance measurements were 0, 18, and 82, respectively.

A similar reaction was carried out by dissolving 0.1 g (0.0006 mole) recrystallized and dried fluorene in THF prior to the addition of *n*-butyllithium, thus forming fluorenyllithium as the catalyst. This product yielded $M_w = 350300$, $M_n = 239600$, and $M_w/M_n = 1.46$, with percentages of I, H, and S, also 0, 18, and 82, respectively.

• *Stereochemical assignments*

The stereochemical assignments for the methacrylate polymers were determined in *o*-dichlorobenzene at 148°C with a Varian HA-100 NMR spectrometer using hexamethyldisiloxane as an internal standard [16]. The peak areas resulting from the α-methyl protons in the isotactic, heterotactic, and syndiotactic triads at $\delta = 1.22$, 1.05, and 0.91 ppm, respectively, were measured with a planimeter and by a weighing technique.

• *Molecular weight characterization*

The chromatograph used in this study to determine the molecular weight of the polymer fractions before and after radiation was equipped with an automatic injection system and five fractionating columns with permeability limits of 500, 50, 10, 1, and 0.1 μm.

Samples were prepared by dissolving the polymers in $CHCl_3$ (distilled in glass with one percent ethanol as preservative) to make a solution with weight concentration between 0.15 and 0.20 percent. The samples were then injected into the automatic sample injector of the chromatograph by a syringe equipped with a 0.5 μm filter. All analytical determinations were at ambient temperature and at 1 ml/min ($1.67 \times 10^{-8} m^3/s$) flow rate. To prevent sample degradation, approximately 0.1 percent of Ionol (Shell Chemical Co. trademark) stabilizer was added to the sample solution.

The molecular weight distribution of the polymer samples was calculated from the GPC chromatograms using the universal calibration method proposed by Benoit [17]. The Mark-Houwink constants used in these calculations were obtained from light scattering/intrinsic viscosity measurements; details of this technique are described elsewhere [18]. The applicability of the universal calibration method for estimating the molecular weights from the GPC chromatogram was verified by comparing the values of M_w obtained by GPC with those obtained by a low angle light scattering technique [19].

- *γ-irradiation*

All polymer samples were carefully purified by dissolving them several times in appropriate solvents and reprecipitating them in cold methanol. The samples were dried in a vacuum oven at 60°C for 12 hours, measured into glass tubes, evacuated to less than 1 mm Hg pressure, and then sealed. The samples were irradiated at the facilities of International Nutronics Inc., Palo Alto, California, at gamma radiation dosages of 0.25, 0.50, 1, 3, 5, and 10 mrad.

- *Resist evaluation*

Resist films (1 μm thick) were spin-coated on SiO_2 surfaces from seven percent solutions in chlorobenzene with a Headway Research Model EC-101 spinner. The films were prebaked for one hour in air at 145°C, and the thickness of the resist and oxide films determined using a Rank Talystep instrument. The resist films were exposed to measured doses of 15kV electrons with a scanning raster-type electron beam and then developed in appropriate solvents.

Results and discussion

- *Radiation G-value*

Molecular weight stereochemistry effects

For polymers which undergo random chain scission and cross linking, the number-average molecular weight of the *exposed* polymer M_n^* can be expressed in terms of the initial M_n, the overall G-value (G), and the dosage (Q) as follows [1]:

$$\frac{1}{M_n^*} = \frac{1}{M_n} + \frac{GQ}{100N_A}, \qquad (1)$$

where $G = G_s - G_x$ and N_A is Avogadro's number; Q has the units of electron volts per gram; G has the units of the number of effective scissions produced per 100 eV of energy absorbed; and G_s and G_x are the scission and crosslinking G-values.

Equation (1) permits calculation of the G-value from the M_n as determined by GPC and the dosage Q because the slope of the plot of $1/M_n^*$ versus Q is $G/100N_A$. Equation (1) assumes G to be independent of molecular weight. However, the molecular weight limits and the tacticity effect on G have not been determined. The literature [20–23] reports values of G for PMMA from γ-radiation ranging between 1.1 and 1.69. However, the effect of the initial M_n has not yet been reported. Since the contribution of the end groups of the polymer to its physical and chemical properties becomes more pronounced as the molecular weight approaches that of oligomers [24], it is suspected that some anomalies in the G-value in the M_n^* versus Q relationship may take place in low molecular weight polymers.

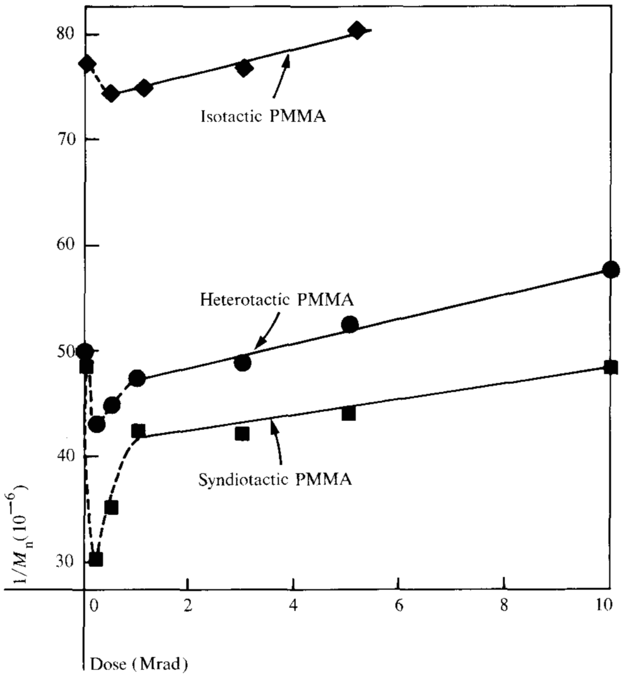


Figure 1 Determination of G-value from $1/M_n$ versus dosage of low molecular weight tactic PMMAs.

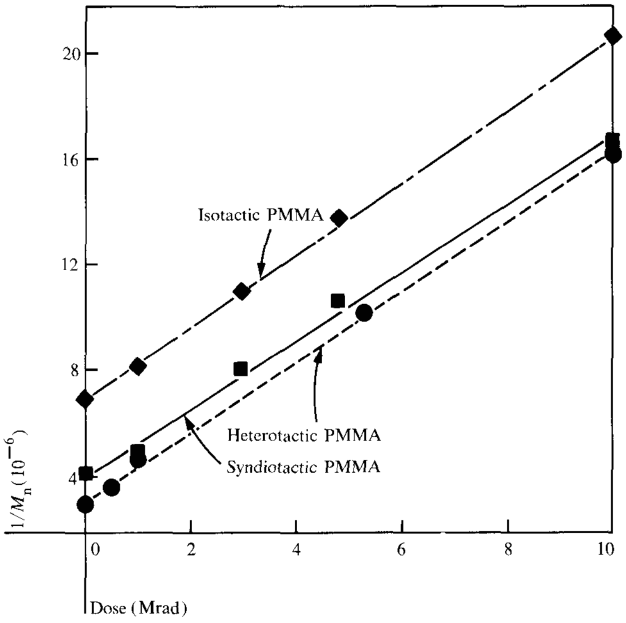


Figure 2 Determination of G-value from $1/M_n$ versus dosage of high molecular weight tactic PMMAs.

Plots of the inverse number-average molecular weight versus γ-radiation dosage (in megarad) for the three tactic PMMAs of low and high initial (before exposure) molecular weights are shown in Figs. 1 and 2, respec-

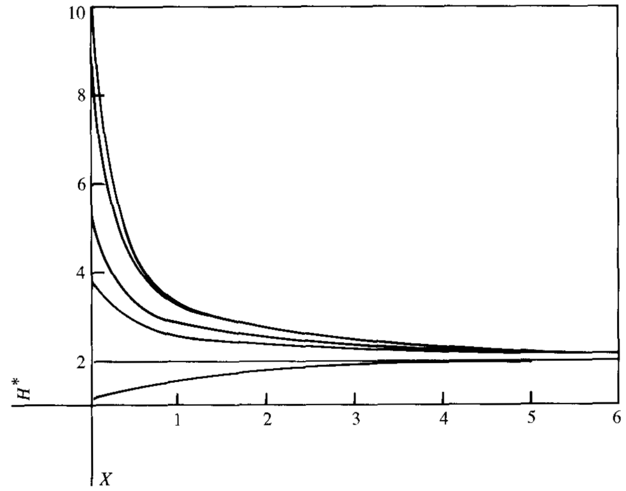


Figure 3 Change in heterogeneity index H^* versus average number of scissions per molecule (X) for various initial H indices.

tively. For PMMAs with initial M_n above 55000, the plots are reasonably well represented by parallel straight lines. The low molecular weight PMMA fractions, however, show a slightly lower slope and nonlinearity because of an apparent increase in molecular weight at low dosage (below one megarad). Currently, there is no clear explanation for the anomalous behavior of the low molecular weight PMMAs. However, one might speculatively attribute this behavior to an end-group effect.

End groups in PMMA are dependent upon the method of synthesis. The polymer resulting from a free radical reaction could have some unsaturated end groups because of termination by disproportionation [2]. These groups then could take part in crosslinking reactions. In anionic polymerizations using *n*-butyllithium as the initiator, one of the chain ends would be an aliphatic group five carbon atoms long. Such a molecular structure would also be sensitive to crosslinking [24, 25]. Thus, as the molecular weight decreases, the population density of these crosslinking sites increases, thereby increasing the G_x values. Since, by definition, the experimentally observed G-value is $G_s - G_x$, the apparent decrease in the G-value of low molecular weight PMMA could be expected. Also, the effects of the end groups and lower dosages could increase the value of G_x over that of G_s, which would result in an overall negative G-value. This argument could be used to explain the nonlinearity of the $1/M_n$ dosage plots for the low molecular weight PMMAs shown in Fig. 1. Although this preceding explanation is highly speculative, the results have been duplicated. By altering the end groups through the use of different anionic catalysts, one might gain further insight.

Table 1 G-values of tactic PMMAs from γ-ray exposure.

PMMA	$M_n(10^{-3})$	M_w/M_n	G
H[a]	18.5	1.80	1.04
S[b]	19.1	1.70	1.04
I[c]	52.2	1.78	1.05
H[a]	125.0	3.70	1.32
S[b]	206.9	1.46	1.27
I[c]	227.0	1.40	1.34

[a] H: heterotactic.
[b] S: syndiotactic.
[c] I: isotactic.

Table 1 lists the computed G-values from γ-radiation data of the PMMAs. The results indicate a G-value of 1.31 ± 0.04 for PMMAs with $M_n > 55000$ which is in agreement with the 1.2 reported by Todd [20]. The lower molecular weight PMMAs ($G = 1.04$), however, agree more closely with the 1.1 reported by Kircher et al. [21]. These results imply that the G-value is independent of the molecular weight ($M_n > 55000$) [26] and the tacticity of the polymer.

The dynamics of chain scissions in very thin polymer films on a substrate that scatters electrons are very complex in the most general case. To render this complex phenomenon tractable, some simplifying assumptions have to be made. By assuming random scission as the main mechanism for the decrease in molecular weight, Charlesby [1], Saito [27], Kotliar [28–30], and Inokuti [31] obtained the moments of the molecular weight distributions of irradiated polymers. The form of the expression for M_w^* and other higher moments of the molecular weight distribution after exposure depends on the initial molecular weight distribution of the resist. Inokuti [31] obtained a closed form expression for both M_n^* and M_w^* by assuming an initial generalized Poisson (Schulz-Zimm) distribution:

$$M_n^* = M_n/(1 + X), \tag{2}$$

and

$$M_w^* = \frac{2M_n}{X}\left\{1 - \frac{1}{X}\left[1 - \left(1 + \frac{X}{\gamma}\right)^{-\gamma}\right]\right\}, \tag{3}$$

where X is the number of scissions per initial number-average degree of polymerization, and γ is the broadness of the initial molecular weight distribution. In terms of the molecular weight heterogeneity index H, sometimes referred to as polydispersity index, $H = M_w/M_n$,

$$\gamma = 1/(H - 1), \tag{4}$$

the inverse variance of the molecular weight distribution multiplied by M_n^2 of the resist before exposure.

Table 2 Effect of molecular weight distribution on the G-value of PMMA.

Before γ radiation			*After 3 Mrad*			G *(calculated)*
$M_w(10^{-3})$	$M_n(10^{-3})$	M_w/M_n	$M_w(10^{-3})$	$M_n(10^{-3})$	M_w/M_n	
111	57.7	1.92	100.4	46.4	2.15	1.33
1927	819.1	2.36	320.8	139.3	2.29	1.87
2284	403.8	5.67	297.6	141.6	2.09	1.44
1484	257.4	5.78	251.3	102.1	2.45	1.86
693	74.5	9.29	153.4	57.4	2.66	1.26
1037	105.7	9.81	235.5	74.4	3.14	1.25

In addition to a decrease in molecular weight, random chain scission also changes the molecular weight distribution. For a truly random scission, H approaches a value of two at high exposure. The change in H as a function of the material and experimental parameters can be obtained from Eqs. (2) and (3). By definition, at any exposure

$$H^* = M^*_w / M^*_n. \tag{5}$$

Substituting Eqs. (2) and (3) in (5), we obtain

$$H^* = \frac{2(X^2-1)}{X^2}\left[1 + \frac{1}{(X-1)}\left(\frac{1}{1+\beta X}\right)^{1/\beta}\right], \tag{6}$$

where $\beta \equiv 1/\gamma$. It is evident from Eq. (6) that as X becomes large, H^* approaches a limiting value of two. Plots of H^* versus X for different values of the initial H in Fig. 3 show the rapid approach of H^* to its limiting value at a relatively low value of X. Experimentally, PMMAs with heterogeneities from 1.9 to 9.8 were exposed at 3 Mrad gamma radiation. The G-values shown in Table 2, although calculated from only two points, agree within experimental error with those obtained previously. The average G-value was found to be about 1.5 and the molecular weight distribution approached two after irradiation.

• *Solubility rates and development*

Effect of molecular weight/ molecular weight distribution

The formation of a resist image is dependent upon the difference in the rates of dissolution between the exposed and the unexposed areas. However, due to the complexity of the physics of the polymer dissolution process, the fundamental causes of this difference remain unknown. There are at least three different phenomena occurring during irradiation of a positive resist polymer that can be used to explain the difference in solubility: chain scission, chemical changes, and gas evolution. Recent experiments in this laboratory indicate that the porosity of the resist film after irradiation greatly affects the solubility rate. (Experimental details will be reported at a later date.) However, it cannot currently be said with certainty which, if any, of these physical and chemical changes controls the dissolution rate differences. Perhaps because it is the most obvious and the easiest quantity to measure, the change in the molecular weight is the popular explanation. Indeed, an empirical relationship between the solubility rate and molecular weight has been proposed [32–34]:

$$S = k\, M^{\alpha}, \tag{7}$$

where S is the dissolution rate, and k and α are polymer and developer material parameters. Care must be exercised in using Eq. (7) because of its empirical nature and because other physical and chemical changes also occur during irradiation which can affect the solubility rate. For example, the molecular weight may possibly be playing the role of an indicator to other changes that have a more profound effect on the solubility rate.

Using Eq. (7) we can show that the weight-average molecular weight M_w provides a better correlation with the solubility rate ratio S_R than does M_n. We can obtain S_R in terms of the ratio of the weight-average molecular weights of the exposed to the unexposed polymer:

$$S_R = \left(\frac{M_w}{M^*_w}\right)^{\alpha_s}, \tag{8}$$

or

$$S_R^{(1/\alpha_s)} = M_w / M^*_w, \tag{9}$$

where α_s is the developer solvent parameter. Combining Eqs. (3), (4), and (9) we obtain

$$\left(\frac{\beta+1}{2}\right)X^2 - S_R^{(1/\alpha_s)}\left[X + \left(\frac{1}{1+\beta X}\right)^{\frac{1}{\beta}} - 1\right] = 0. \tag{10}$$

To utilize Eq. (10) to describe the electron beam resist sensitivity, X must be defined in terms of material and processing variables, i.e., electron beam dosage, G-value, etc.

If E is the energy absorbed per incident electron in a unit volume of the resist and G_s is the number of bonds

Table 3 Effect of molecular weight distribution on S/S_0.

$M_w(10^{-3})$	$M_n(10^{-3})$	M_w/M_n	$S/S_0^{a,b,c}$
2295	394	5.9	5.0±0.5
1930	544	3.5	5.5±0.5
2315	937	2.5	5.5±0.5
2349	1080	2.2	5.0±0.5
2550	1184	2.2	5.5±0.5
2560	1263	2.0	5.0±0.5

[a]Exposure density 4×10^{-6} C/cm^2 at 25 kV.
[b]Developer: Isoamyl acetate at 40°C (313 K).
[c]Data from N. S. Viswanathan and W. Moreau, IBM System Products Division, E. Fishkill, New York, private communication, April 1974.

broken per 100 eV of absorbed energy, then the number of bonds broken per incident electron, unit volume, and unit dosage is

$$\Phi = \frac{E\,G_s}{100q}, \tag{11}$$

where q is the electronic charge. Thus, the chain scission probability π_s is expressed as

$$\pi_s = \frac{\Phi\,M_0 Q}{\rho t N_A}, \tag{12}$$

where ρ is the polymer density and t is the film thickness. It follows that the number of scissions per initial number-average degree of polymerization is

$$X = \frac{\pi_s M_n}{M_0}, \tag{13}$$

where M_0 in Eqs. (12) and (13) is the molecular weight of the segments between bonds in the polymer main chain sensitive to electron beam scission. By combining these equations we obtain

$$X = \Phi\,M_n Q. \tag{14}$$

Eqs. (10), (11), and (14) can now be used to investigate the factors that affect resist sensitivity. The values of X in Eq. (10) can be obtained numerically by using Newton's iterative method for different values of α_s, S_R, and β.

One must take into account the variation of the energy absorbed throughout the exposed volume of the resist. It has been shown that this spatial distribution is pear-shaped [35, 36]. Consequently, through Eqs. (10), (11), and (14), the value of S_R is expected to vary throughout the exposed volume of the resist. This is significant from the standpoint of understanding the factors that affect the geometry and resolution of the developed patterns of the resist. It is conceivable that the geometry of the cross-section of the developed pattern can be predicted and perhaps controlled if the spatial expression for Φ in the resist is known.

Figure 4 shows a plot of the solubility rate ratio S_R versus X for polymers with $H = 3$ at different values of α_s. The S_R versus X relationship shows the very large effect of the developer solvent parameter α_s on S_R. In fact, the second derivative of the curves representing the different values of α_s ranges from positive (concave) to negative (convex). This behavior could have an important role in controlling the contours of the cross-section of the developed pattern. For example, the uneven spatial distribution of the absorbed energy in the exposed volume of the resist could be compensated by multistage developing (developer solvent programming), i.e., with a system containing solutions with different dissolving rate powers. In this way it may be possible to control the shape of the cross-section of the developed pattern.

In comparing available experimental data with the model, Fig. 4 shows that PMMA ($M_n = 150 \times 10^3$) developed in methyl isobutyl ketone (MIBK) closely follows the curve when $\alpha_s = 1.3$. This agrees reasonably well with the experimental value of 1.4. Another PMMA ($M_n = 600 \times 10^3$) also follows the theoretical line with an $\alpha_s \approx 1.2$.

Figure 5 shows a plot of S_R versus X for $\alpha_s = 1.0$ at different values of H. This plot illustrates the large contribution of the initial width of the molecular weight distribution to the solubility rate ratio. This effect can be further exaggerated or attenuated depending on the value of α_s. Figure 5 also shows that the experimental points (Table 3) show good agreement with the theoretical lines suggesting that M_w has a better correlation with resist sensitivity than M_n. The six PMMAs in Table 3 have very different M_n values and yet have very similar S_R values. Note that the products of H and M_n, which is equal to M_w, are very similar for all six resist materials.

Solubility rates versus solvent molecular size

It had been demonstrated previously that the solubility of certain polymers in solvents of a homologous series depended upon the molecular size, i.e., molecular weight, of the solvent [37]. The solubility of the polymer decreased as the molecular size of the solvent increased. The data given in Table 4 confirm these results and also show that the dissolution rates for several molecular weight fractions of PMMA decreased with increasing size of the alkyl group in a series of *n*-alkyl acetate solvents. The logarithmic plot of the solubility rate versus the solvent molecular weight for these different molecular weight PMMAs gives a series of lines of increasing slope (Fig. 6). The relationship between these two quantities can be expressed in an Ueberreiter type equation [33, 34]:

$$S = k'\,M_s^{-B}. \tag{15}$$

This empirical equation represents the dependence of

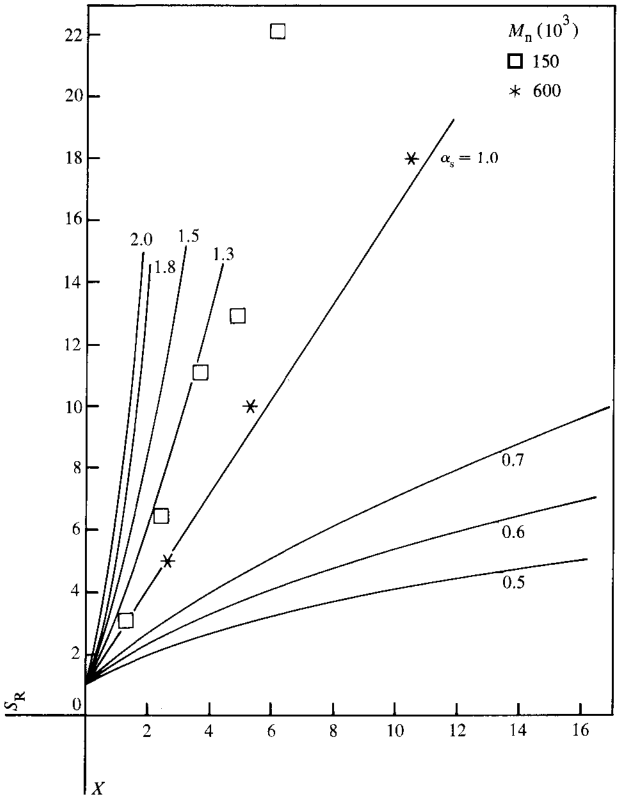


Figure 4 Solubility rate ratios (S_R) versus average number scissions per molecule (X) for various α_s values.

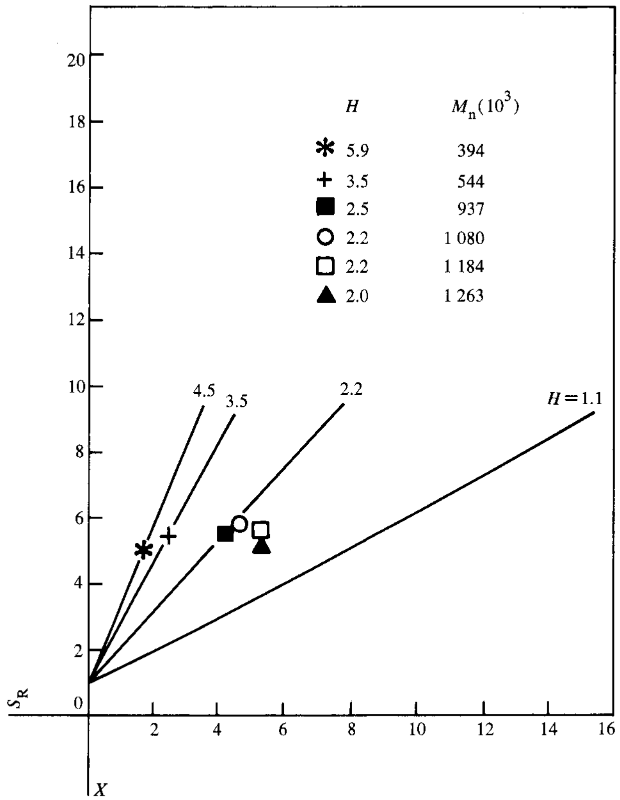


Figure 5 Solubility rate ratios (S_R) versus average number of scissions per molecule (X) for α_s = one at various H indices.

Table 4 Rates of dissolution in Å/min. (10^{-10} m/min.) of heterotactic PMMAs at 25°C (298 K) in n-alkyl acetate solvents in a homologous series.

$M_w(10^{-3})$	*Methyl*	*Ethyl*	*n-Propyl*	*n-Butyl*	*n-Amyl*	*n-Hexyl*
476	2240	1267	775	120	10	5.
95	4300	3250	1650	210	46	13.
39	4100	2400	1350	300	75	27.

the dissolution rate S on the molecular weight M_s of the solvent within the homologous series, where k' is a function of the molecular weight of the polymer and B is a constant.

The dependence of the dissolution rate on both the polymer molecular weight and the molecular size of the solvent is shown in Fig. 7. Two distinct solubility rate curves of different slope are obtained for each polymer fraction in solvents from methyl acetate through *n*-propyl acetate and in *n*-butyl acetate through *n*-hexyl acetate. Consequently, these solubility rate curves permit the dissolution rate of the resist to be controlled by a specific developer solvent which is selected from a homologous class of solvents.

Solubility rate versus polymer stereoregularity

The influence of the polymer stereoregularity on the dissolution rate (Table 5) is shown by the logarithmic plot of the solubility rate in *n*-amyl acetate of heterotactic, syndiotactic, and isotactic PMMAs versus their molecular weight (Fig. 8). The heterotactic and syndiotactic polymers have similar slopes, while the isotactic polymer has a much steeper slope. For comparable molecular weights of the three stereoforms, the solubility rates increase in the order syndiotactic $<$ heterotactic $\ll$ isotactic.

The large solubility rate difference between the isotactic-syndiotactic and isotactic-heterotactic polymers can be argued on the basis of a higher degree of freedom for

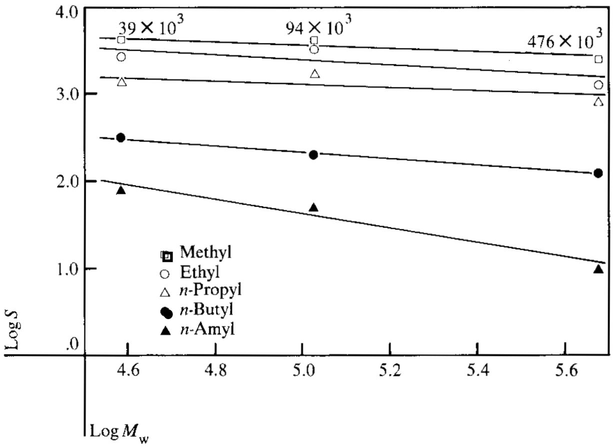
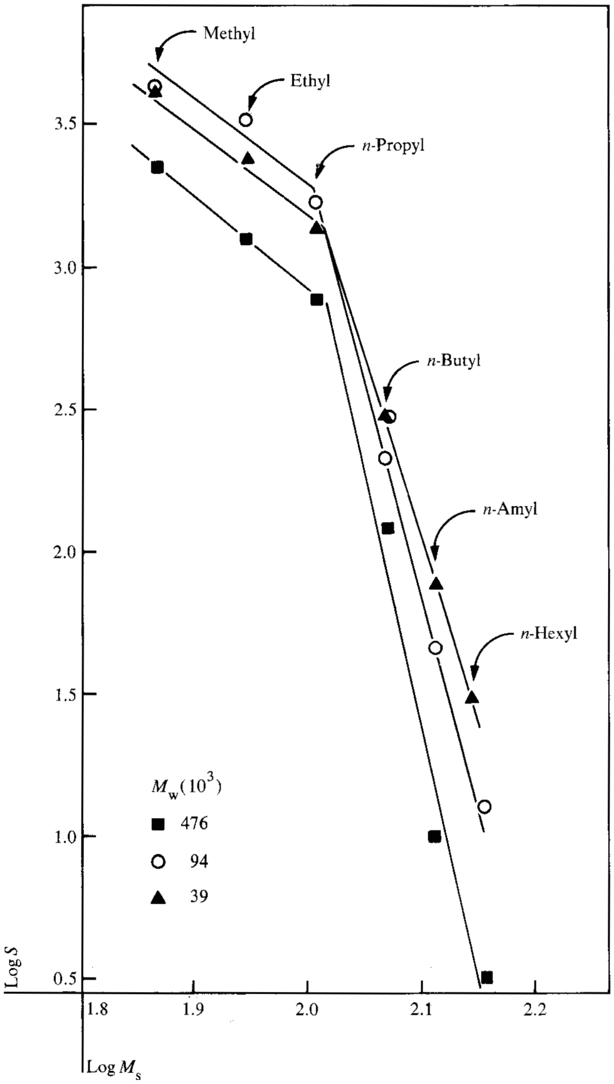


Figure 6 Solubility rates of PMMA fractions in acetate solvents at 25°C (298 K).

Figure 7 Dissolution rates of heterotactic PMMA fractions in a homologous series of *n*-alkyl acetates.



rotation about the main chain bonds in the isotactic polymer [38, 39]. The lower T_g (49°C) of the isotactic PMMA, despite a higher density [40, 41] than those of the syndiotactic ($T_g = 117$°C) and the heterotactic ($T_g = 105$°C) PMMAs, supports this contention. The solubility rate dependence on the glass transition temperature (T_g) for comparable molecular weight fractions of the stereoforms is shown in Fig. 9.

• *Sensitivity*

Effect of molecular weight

The sensitivity of any electron beam resist system is a function of the chain scission efficiency (G-value) and the solubility characteristics of the resist material. The dependence of the sensitivity on the molecular weight of the polymer at a fixed solubility rate ratio (Table 6) indicates that the sensitivity of PMMA can be increased by using the higher molecular weight fractions. In theory it would appear desirable to use very high molecular weight polymers to obtain higher sensitivities, but there are certain practical limitations. It is difficult to synthesize very high molecular weight polymers—high molecular weights give high solution viscosities and make it difficult to spin-coat uniform films. In addition, it has been observed that during solvent development, very high molecular weight polymers swell much more than lower molecular weight polymers. This results in distorted images.

Effect of molecular weight distribution

Figure 5 suggests that a higher heterogeneity index (H) resist will have a higher sensitivity for a given number-average molecular weight. For example, given two polymers with the same number-average molecular weight but different values of H, the resist having the higher H or higher M_w requires a lower value of X to achieve the same S_R. Consequently, this resist requires a lower dosage than the polymer of lower H.

Effect of stereoregularity

A dependence of sensitivity on molecular weight of the polymer is shown by each tactic PMMA (Table 7). For comparable molecular weights, the sensitivities of the three stereoforms are about the same. Although the solubility rate of the resist is strongly dependent on the stereoregularity of the polymer, the ratio of the solubility rates of the exposed and the unexposed resist appears to be insensitive to the tacticity of the polymer. This is not unexpected since irradiation at low doses does not produce a change in the tacticity of the resist.

Effect of developer solvent molecular weight

The G-value of PMMA is considered low, and improving the sensitivity through the development process is important. In selecting a developer solvent for positive

Table 5 Solubility rates of tactic PMMA fractions in *n*-amyl acetate at 25°C (298 K).

PMMA	$M_w(10^{-3})$	$M_n(10^{-3})$	S_0 *in Å/min* $(10^{-10}$ *m/min)*
H	476	170	10
	94	42	46
	39	19	75
S	350	240	6
	125	88	20
	51	30	25
I	1979	967	58
	567	369	500
	95	53	10100

electron beam resists such as PMMA, thermodynamic considerations are commonly applied in terms of a solubility parameter and an associated hydrogen bonding index [42, 43]. These principles were found to be unreliable when applied to the selection of optimized developer solvents. For example, the solubility of PMMA in solvents having identical Hildebrand δ values ranged from good to poor. Thus, for PMMA the solvent developer has been a combination of a poor solvent, isopropyl alcohol, and a borderline solvent, methyl isobutyl ketone (MIBK) [5].

The application of the homologous solvent process to the selection of an optimized developer solvent resulted in higher sensitivies for PMMA. The 476 × 10^3 fraction was soluble in *n*-alkyl acetates between methyl and *n*-butyl acetate, partially soluble in *n*-amyl acetate, and practically insoluble in *n*-hexyl acetate (Table 4). Thus, the developer choice was between *n*-butyl acetate and *n*-amyl acetate. The final selection between these solvents was made on the basis of the solubility rate of the polymer in these acetates. Development of the polymer (after exposure at 25 kV) in *n*-amyl acetate resulted in a sensitivity (in coulombs) of 3×10^{-6} C/cm^2 compared to 8×10^{-6} C/cm^2 in MIBK/H_2O ($S/S_0 = 4$).

Summary

This study has shown the relative contribution of the different material parameters of the polymer on the electron beam sensitivity of PMMA. The *G*-value is independent of the molecular weight, molecular weight distribution, and stereochemistry. Although the solubility rate of PMMA is strongly dependent on the stereoregularity—syndiotactic < heterotactic ≪ isotactic, the ratio of the solubility rates of the exposed and the unexposed resist appears to be insensitive to the tacticity. The solubility rate ratio is better correlated with the weight-average molecular weight ratio than with the number-average molecular weight ratio. The molecular size of the developer solvent has a much greater effect on the solubility rate than the molecular weight of the resist. A developer solvent selected from a homologous series of *n*-alkyl acetates greatly enhances the electron beam sensitivity of PMMA.

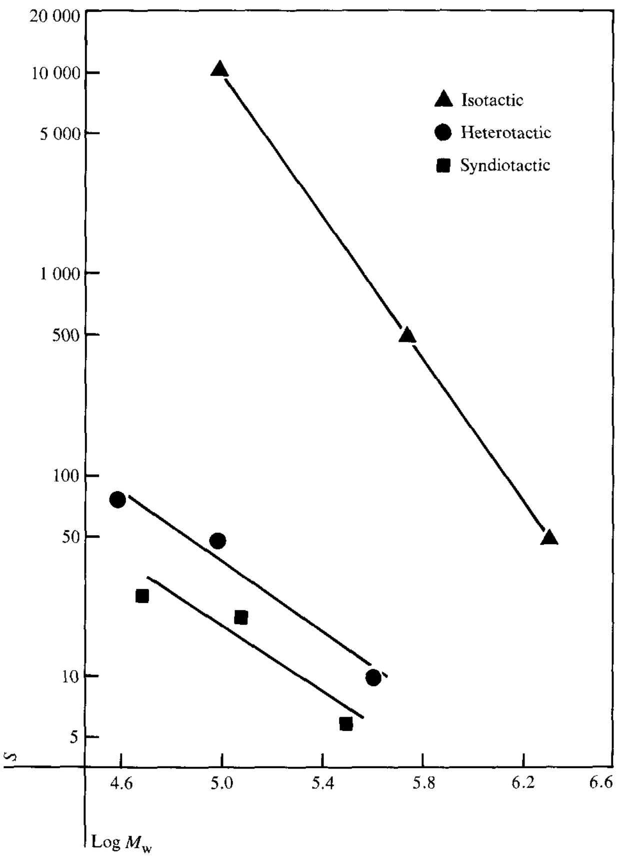


Figure 8 Solubility rates of tactic PMMAs in *n*-amyl acetate at 25°C (298 K).

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References

1. A. Charlesby, *Atomic Radiation and Polymers*, Pergamon Press, London, 1960.
2. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience Publishers, John Wiley and Sons, Inc., New York, 1962.
3. M. Dole, *The Radiation Chemistry of Macromolecules*, Vol. 2, Academic Press, Inc., New York, 1973, p. 97.
4. H. Ku and L. Scala, *J. Electrochem. Soc.* **116,** 980 (1969).
5. I. Haller, M. Hatzakis, and R. Srinivasan, *IBM J. Res. Develop.* **12,** 251 (1968).
6. M. Hatzakis, *J. Electrochem. Soc.* **116,** 1033 (1969).
7. M. Hatzakis, C. Ting, and N. Viswanathan, "Electron and Ion Beam Science and Technology," *Proceedings of the*

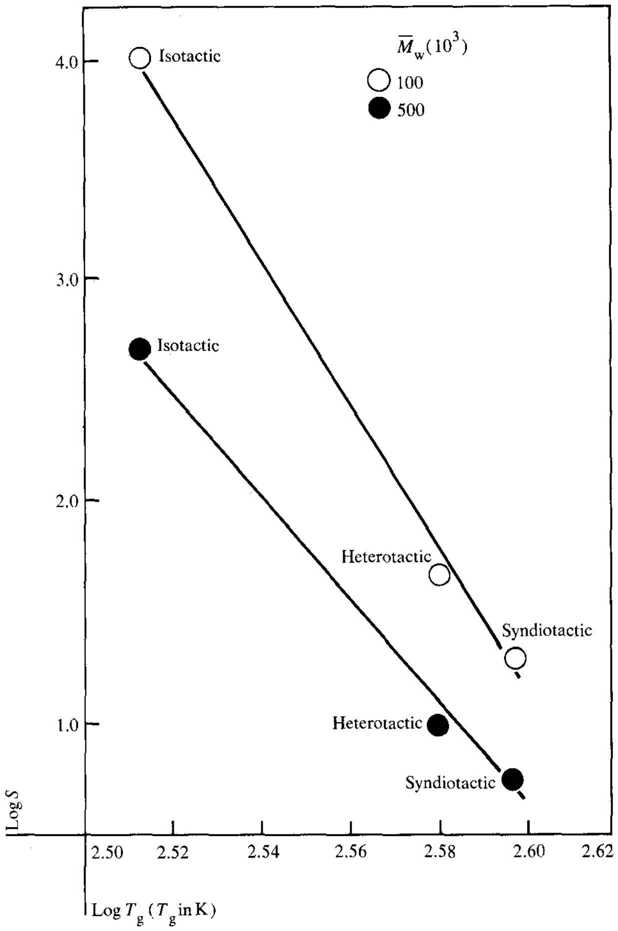

Figure 9 Solubility rates of tactic PMMAs versus T_g.

Sixth International Conference on Electron and Ion Beam Technology, San Francisco, California, May 1974, p. 542.

8. L. Thompson, *Solid State Technol.* **18,** 27 (July 1975).
9. L. Thompson, *Solid State Technol.* **18,** 41 (August 1975).
10. R. Harris, *J. Electrochem. Soc.* **120,** 270 (1973).
11. M. Hatzakis, "Applied Polymer Symposium," *J. Polymer Sci.* **23,** 73 (1974).
12. M. Bowden, "Symposium No. 49," *J. Polymer Sci.* 221 (1975).
13. A. Ouano, presented at First Chemical Congress of the North American Continent, Mexico City, Mexico, November 1975.
14. E. H. Riddle, *Monomeric Acrylic Esters*, Reinhold Publishing Corporation, New York, 1954, p. 42.
15. W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *J. Polymer Sci.* **46,** 317 (1960).
16. E. P. Chlanda and L. G. Donaruma, *J. Appl. Polymer Sci.* **15,** 1195 (1971).
17. H. Benoit, Z. Grubisic, P. Rempp, D. Decker, and J. Zilloix, presented at the Third International Seminar on Gel Permeation Chromatography (preprint), Geneva, Switzerland, May 1966.
18. A. Ouano, *J. Macromol. Sci. Rev.* **C9,** 123 (1973).
19. A. Ouano and W. Kaye, *J. Polymer Sci.* **12,** 1151 (1974).

Table 6 Electron beam sensitivity vs M_n for PMMA at 15 kV.

$M_n(10^{-3})$	$Dose^{a,b}(\mu C/cm^2)$
10	12
100	10
400	8
2000	5

[a] $S/S_0 = 4$, developed in 4:1::MIBK:H_2O at 21°C (294 K).
[b] Experimental data from W. Moreau, IBM System Product Division, East Fishkill, New York, private communication, April, 1974.

Table 7 Electron beam sensitivity of tactic PMMAs at 15 kV.

$M_n(10^{-3})$	Tacticity	$Dose^{a,b}(\mu C/cm^2)$
1271	H	3.5
48	H	10
20	H	11
1200	I	4
279	I	7.5
33	I	11
161	S	5.5
29	S	11

[a] $S/S_0 = 2$, developed in MIBK at 21°C (294 K).
[b] Experimental data from W. Moreau, IBM System Product Division, East Fishkill, New York, private communication, April, 1974.

20. A. Todd, *J. Polymer Sci.* **42,** 223 (1960).
21. J. Kircher, F. Sliemers, R. Markle, W. Gager, and R. Leininger, *J. Phys. Chem.* **69,** 189 (1965).
22. P. Alexander, A. Charlesby, and M. Ross, *Proc. Roy. Soc.* **A223,** 392 (1954).
23. A. Schultz, P. Roth, and G. B. Rathman, *J. Polymer Sci.* **22,** 495 (1956).
24. H. Jellinek, *The Stereochemistry of Macromolecules*, Vol. 3, edited by A. Ketley, Marcel Dekker, Inc., New York, 1968, p. 371.
25. A. Miller, E. Lawton, and J. Balwit, *J. Polymer Sci.* **14,** 503 (1954).
26. A. C. Ouano, D. E. Johnson, B. Dawson, and L. A. Pederson, *J. Polymer Sci.* **14,** 701 (1976).
27. O. Saito, *J. Phys. Soc. Jpn.* **13,** 198 (1958).
28. A. Kotliar and A. Anderson, *J. Polymer Sci.* **45,** 541 (1960).
29. A. Kotliar, *J. Polymer Sci.* **51,** 863 (1961).
30. A. Kotliar and S. Podgor, *J. Polymer Sci.* **55,** 423 (1961).
31. M. Inokuti, *J. Chem. Phys.* **38,** 1174 (1963).
32. K. Ueberreiter, *Diffusion in Polymers*, edited by J. Crank and G. Park, Academic Press, Inc., London, 1968, p. 219.
33. K. Ueberreiter, *ibid.*, Chapter 7.
34. K. Ueberreiter and F. Asmussen, *Makromol. Chem.* **46,** 327 (1961).
35. D. F. Kyser and K. Murata, *Proceedings of the Sixth International Conference on Electron and Ion Beam Science and Technology*, San Francisco, California, May 1974, p. 205.
36. D. F. Kyser and N. S. Viswanathan, *J. Vac. Sci. Technol.* **12,** 1305 (1975).
37. A. Doolittle, *Plasticizer Technology*, edited by P. Bruins, Reinhold Publishing Corporation, New York, 1965, Ch. 1.
38. D. Yoon and P. Flory, *Polymer* **16,** 645 (1975).

39. P. Flory, *Science* **188,** 1268 (1975).
40. E. Kiran, J. Gillham, and E. Gipstein, *J. Macromol. Sci. Phys.* **B9,** No. 2, 341 (1974).
41. J. Johnson and R. Porter, *The Stereochemistry of Macromolecules*, Vol. 1, edited by A. Kelty, Marcel Dekker, Inc., New York, 1968, p. 213.
42. J. Hildebrand and R. Scott, *The Solubility of Non-Electrolytes*, Reinhold Publishing Corporation, New York, 1949.
43. M. Bowden and L. Thompson, "Organic Coating Abstracts," presented at the 165th National ACS Meeting, Dallas, Texas, April 1973.

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