

Analysis of Radiation Chemical Yields of Chlorinated Polystyrene Derivatives

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Synopsis

A technique for determining radiation chemical yields from lithographic exposure curves for crosslinking type negative electron beam resists has been extended to include polymers with a general Poisson distribution. The technique is applied to several different chlorine-containing styrene-based resists. The radiation yields show good agreement with the differences in lithographic sensitivity and are explained by recent mechanistic studies. Optimal synthetic approaches for preparing this type of resist are described.

INTRODUCTION

The response of an organic polymer to various forms of radiation is an important aspect of its potential use as a resist for lithographic imaging. Two of the many possible avenues for structural modifications upon irradiation are crosslinking and scissioning. The effectiveness of radiation in modifying a polymer structure is expressed as a G value. The number of crosslinks and main chain scissions per 100 eV of absorbed radiation are defined as $G(x)$ and $G(s)$, respectively. The susceptibility of a polymer to undergo a structural change is directly related to its lithographic sensitivity and contrast;¹ thus the determination of the radiation yields for a resist candidate provides a useful screening criterion.

Polymers with $G(s)/G(x)$ ratios of greater than 4 show decreased molecular weights upon exposure to radiation,² which leads to increased solubility and/or solubility rate which denotes positive resist behavior. Polymers with $G(s)/G(x)$ ratios of less than 4 exhibit increasing molecular weights and ultimately gelation upon exposure to radiation, which is characteristic of negative resists.

For a polymer with a random molecular weight distribution, (i.e., a polydispersity of 2), the Charlesby–Pinner relation³ expresses the change in molecular weight distribution as a function of absorbed radiation when simultaneous crosslinking and scissioning occur. For polymers which form gels, the relationship between the ungelled, and hence, soluble fraction and the absorbed dose is represented by

$$S + S^{1/2} = \frac{G(s)}{2G(x)} + \frac{9.65 \times 10^5}{M_w G(x) r} \quad (1)$$

where S is the soluble fraction, r is the absorbed dose (Mrad), and M_w is the initial weight average molecular weight.

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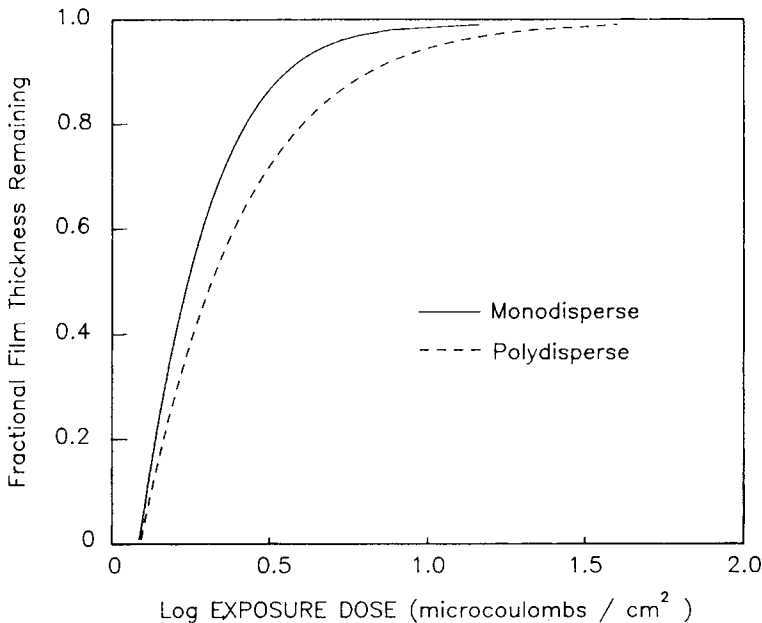


Fig. 1. Theoretical exposure curves for two resists, each with $M_w = 100,000$, $G(x) = 2.00$, and $G(s) = 0.20$. Polydisperse curve(---) is for a polydispersity of 2.00; monodisperse curve (—) is for a polydispersity of 1.05. Resist density is 1.05 g/cm^3 , initial thickness is $0.5 \text{ }\mu\text{m}$, and electron beam accelerating voltage is 20 kV.

By plotting the left hand side of eq. (1) as a function of the reciprocal of absorbed dose, the Charlesby–Pinner relationship can be used to determine $G(x)$ from the slope and $G(s)$ from the intercept once $G(x)$ is known. Typically, radiation yields of crosslinking polymers are measured by exposing them to gamma radiation from a Cobalt-60 source followed by determining the soluble fraction by Soxhlet extraction in a suitable solvent.⁴

A recent study by Novembre and Bowmer⁵ described an alternative method for determining the extent of crosslinking. In this technique, data from an electron beam exposure response curve are used to calculate the radiation yields. A typical exposure curve is shown in Figure 1, where the fractional thickness remaining in a resist film is plotted as a function of log incident exposure dose. By assuming that the gelation is uniform throughout the film and that the resist development process efficiently removes all soluble material, the soluble fraction is simply the percentage of film removed. The incident dose from the electron beam is converted to an absorbed dose by integrating the appropriate depth-dose functionality over the initial resist film thickness. Novembre and Bowmer⁵ compared this technique to the standard gamma irradiation and extraction method and found that the $G(s)$ and $G(x)$ values determined by the two techniques agreed to within 10% for polystyrene, poly(3-chlorostyrene), and GMC resist, a copolymer of 3-chlorostyrene, and glycidyl methacrylate.

Recent studies with negative resists have shown that contrast can be significantly improved by using nearly monodisperse resists,^{6–8} for which the Charlesby–Pinner relationship is not valid. The utility of the approach used

by Novembre and Bowmer⁵ demonstrates that an extension of this technique to cover nonrandom molecular weight distributions, particularly for monodisperse resists, would be useful.

A more general theory developed by Inokuti,⁹ considers the simultaneous crosslinking and scissioning of a polymer with a generalized Poisson distribution. This introduces another parameter which merely characterizes the breadth of this distribution, and is related to the polydispersity. The resulting equation (significantly more complicated than that of Charlesby and Pinner) is

$$1 - g = (1/A^3) \left\{ \lambda^2 A + (4\lambda g/y) \left[1 - (1 + Ay/\beta)^{-\beta} \right] + 4g^2 A (1 + Ay/\beta)^{-\beta-1} \right\} \quad (2)$$

where g is the gel fraction, λ is $G(s)/G(x)$, β is $1/(M_w/M_n - 1)$, A is $\lambda + 2g$, and y is $1.04 \times 10^{-6} G(x)M_n r$, with r in Mrad, M_n the initial number average molecular weight, and M_w the initial weight average molecular weight. For the case where M_w/M_n is 2, β becomes 1, and the equation reduces to the Charlesby–Pinner relationship [eq.(1)].

Graphical analysis is no longer sufficient in this case, and an analytic solution for $G(s)$ and $G(x)$ is not possible. The molecular weight and polydispersity of a resist are generally known, and the gel fraction can be determined as a function of incident dose from an exposure curve. The procedure employed here is to iterate on values of $G(s)$ and $G(x)$, while comparing the resulting value of gel fraction to experimental data for the same dose. The sum of the squared deviations between experimental and predicted gel fraction is calculated for each dose, and iteration proceeds until this sum is minimized.

The importance of correcting for a non-random molecular weight distribution can be seen in Figures 1 and 2. Figure 1 shows an exposure curve calculated for two polymers with identical $G(s)$ and $G(x)$ values, weight average molecular weights, film thicknesses, and densities. The only difference is that one has a random distribution and a polydispersity of 2 ($\beta = 1$) and the other has a polydispersity of 1.05 ($\beta = 20$). The difference in the lithographic exposure response is apparent, as is the higher contrast available from the nearly monodisperse material (3.30 compared with 2.15 for the polydisperse resist). Note that the two materials have the same initial gel dose, due to their same weight average molecular weight, but the more monodisperse sample would have a higher sensitivity when defined as the dose required to cause 50% gelation. Figure 2 is a Charlesby–Pinner plot of the data from Figure 1, and demonstrates the error resulting from trying to apply eq. (1) to the data for a monodisperse resist. The curve for the narrow distribution resist is nonlinear at high gel fractions, the slope of the linear portion is steeper [which would indicate an erroneously low $G(x)$ value], and the intercept of the linearly extrapolated portion would have a physically meaningless negative value.

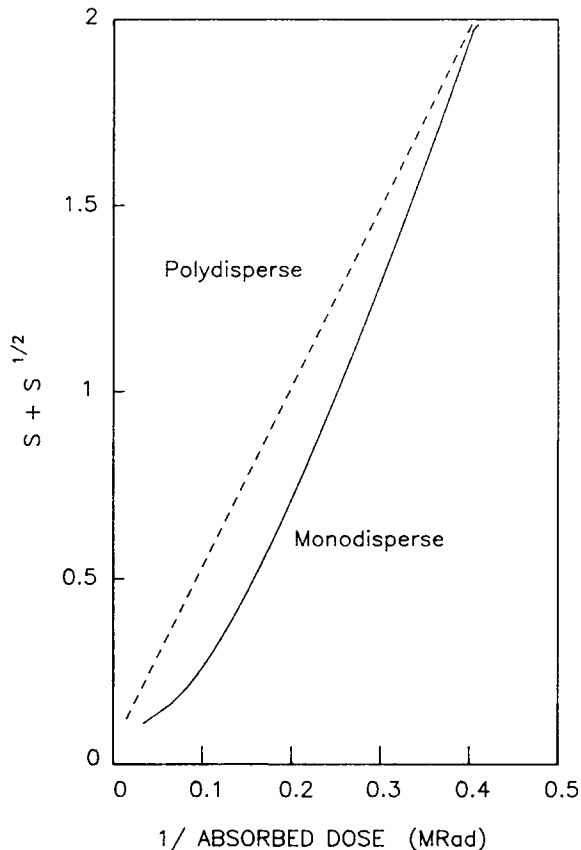


Fig. 2. Charlesby-Pinner plot for resists shown in Figure 1.

RESISTS STUDIED

The motivation for extending the technique of determining radiation yields was primarily due to the differences in lithographic sensitivity found between several chlorine containing styrene based resists. Several materials have been developed in recent years which are quite similar, but show distinct variations in sensitivity.^{6-8,10-18} The materials studied in this analysis, shown in Table I, have all been reported previously in the references listed.

All the resists are based on chlorinating or chloromethylating a styrene polymer. Polystyrene¹¹ has several desirable resist properties such as good film forming capability and dry etch resistance, but suffers primarily from low sensitivity, particularly to electron beam irradiation. Polychlorostyrenes¹¹ show nearly a tenfold increase in sensitivity, due to the lower bond strength of the aromatic carbon to chlorine bond,¹⁹ which is more easily cleaved during irradiation. Polychloromethylstyrene⁶ gives another factor of two increase in sensitivity due to the still lower carbon—chlorine bond strength as well as the stability and greater lifetime of the benzyl radical formed.

A two-step approach to preparing a similar resist material is to chloromethylate polystyrene,¹² poly(α -methylstyrene),¹⁵ or to chlorinate polymethylstyrene.^{16,17} These approaches allow a series of materials with different

TABLE I

Resist	Structure ^a	Reference
Polychlorostyrene	$\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{Cl}}{\text{CH}} \right)_n$	11
Polychloromethylstyrene (PCMS)	$\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{CH}_2\text{Cl}}{\text{CH}} \right)_n$	6
Chloromethylated poly(α -methylstyrene) (CMP α MS)	$\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{CH}_2\text{Cl}}{\overset{\text{CH}_3}{\text{C}}} \right)_n$	14
Poly(<i>p</i> -methylstyrene-co-chloromethylstyrene) (PMSCMS)	$\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{CH}_3}{\text{CH}} \right)_x \left(\text{CH}_2 - \underset{\text{C}_6\text{H}_4\text{CH}_2\text{Cl}}{\text{CH}} \right)_y$	18
Chlorinated polymethylstyrene (CPMS)	$\left(\overset{\cdot}{\text{C}}\text{H}_2 - \overset{\cdot}{\text{C}}\text{H} - \underset{\text{C}_6\text{H}_4\text{CH}_2\text{Cl}}{\text{C}} \right)_n$	16
Chlorinated poly(<i>p</i> -methylstyrene) (CPpMS)	$\left(\overset{\cdot}{\text{C}}\text{H}_2 - \overset{\cdot}{\text{C}}\text{H} - \underset{\text{C}_6\text{H}_4\text{CH}_2\text{Cl}}{\text{C}} \right)_n$	16

^a**Means additional chlorination may occur at these sites.

chlorine contents to be prepared, and also enable preparation of narrow molecular weight distribution resists through anionic polymerization and careful control of the chlorination or chloromethylation reaction. Another variation is to prepare a copolymer of chloromethylstyrene and methylstyrene,¹⁸ although the polymers produced are not nearly as monodisperse. Generally, it is found that a very small amount of chlorine is quite effective at increasing the sensitivity to electron beam as well as deep UV irradiation, and

a saturation effect takes place as the chlorine content approaches one chlorine per monomer unit.¹²⁻¹⁸ In the case of chlorinated methylstyrenes,¹⁶ however, the chlorine content can be increased beyond that point, and a decrease in sensitivity is actually observed at higher chlorine contents. This was attributed¹⁶ to the increased likelihood of chain scissioning at high chlorine contents, where quaternary carbons are formed in the polymer backbone.

ANALYSIS

Exposure curves are reported in the references shown for each resist in Table I. The polynomial approximation of Everhart and Hoff²⁰ was used to convert the incident electron dose to absorbed dose. The resist density and beam accelerating voltage are required to calculate the electron Grun range in the resist. Exposure voltages were reported in each reference, and densities were calculated using a group contribution method with a reported average accuracy of 1.2%.²¹ In addition, the initial resist thickness is required, since the depth dose function is integrated over this range. Typically resist literature reports nominal film thicknesses, although, in one case, the actual thicknesses were known.¹⁶ The calculated conversion factor shows at most a 5% error even with as much as a 20% error in initial film thickness or density. The developer solvents used are not always reported either, so an implicit assumption is made that the solvents used are effective in removing all of the uncrosslinked material. The molecular weight and molecular weight distributions for each of the resists were reported in the literature, and these parameters are required for evaluating $G(s)$ and $G(x)$. For some of the materials listed in Table I, the actual data points for the exposure curve were not given, and only a curve was provided. Data points for the regression analysis were taken at 5% intervals, from 10–80% fractional film thickness remaining. Even when actual data points were given in the references, points with film thicknesses less than 10% were not included due to the uncertainty in thickness and because the assumption of uniform gelation in the resist film is not valid.

RESULTS

An example of the fit obtained using Inokuti's equation is shown in Figure 3 for a chloromethylated poly(α -methylstyrene) resist.¹⁵ For comparison, a linear fit from the standard Charlesby–Pinner analysis (which is not appropriate here) is also shown. Table II lists the $G(x)$ and $G(s)$ values for each resist corresponding to the best fit of eq. (2) to the experimental data. The average number of chlorine atoms per monomer unit is also shown for the copolymers and resists prepared by post-polymerization chlorinating reactions.

The radiation yields in Table II agree well with the sensitivity trends described earlier. Poly(4-chlorostyrene) shows a slightly higher $G(x)$ and a slightly lower $G(s)$ than poly(3-chlorostyrene). Since the reactions involved in the radiation chemistry are the same for these two isomers, the difference could be explained by an induction effect or a steric effect which makes crosslinking more likely for the para-substituted isomer once the radical has been formed. The sensitivity for 50% gelation was shown to be somewhat

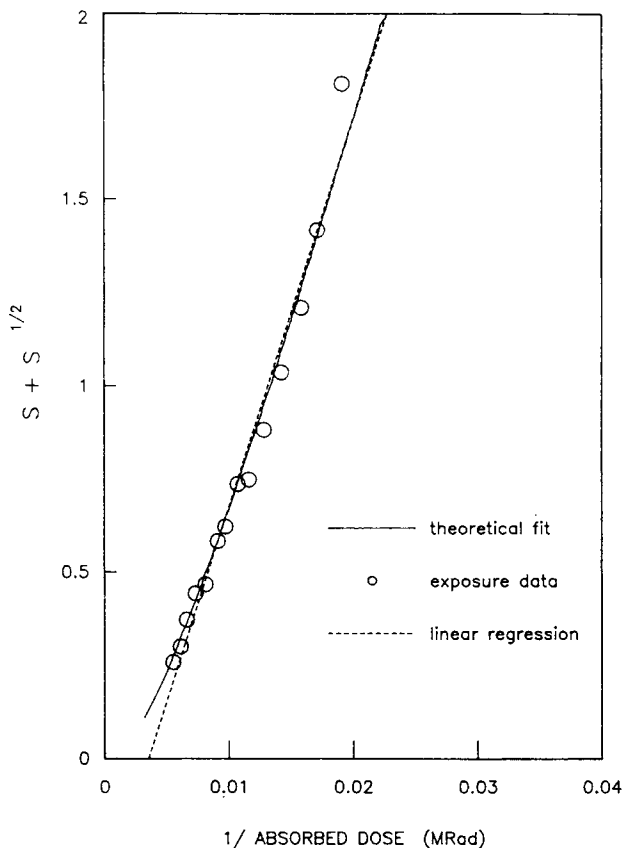


Fig. 3. Theoretical fit of eq. (2) (—) to exposure data for a chloromethylated poly(α -methylstyrene) resist. Linear regression from Charlesby-Pinner plot is also shown (---). Exposure data (O) is from Ref. 15.

higher for the para isomer,¹¹ even though M_w was lower, which agrees with these results. The value of $G(x)$ determined for the poly(3-chlorostyrene) is in rough agreement with that of Novembre and Bowmer (0.61 vs. 0.71 found here), although the $G(s)$ values differ appreciably (0.16 vs. 0.34).

Polychloromethylstyrene shows a significantly higher yield of crosslink formation and a much higher degree of scissioning as well. This material, a mixture of 60% meta and 40% para isomers, is two to three times more sensitive than the chlorinated styrenes. In comparing the chlorinated polymethylstyrenes, a distinction should be made between the two starting polymers which were chlorinated. One series was also a mixture of 60% meta and 40% para isomers, which was polymerized free radically, while the other materials were polymerized anionically from the pure para isomer (denoted as P-pMS). In addition, the chlorination reactions used were not selective to the pendant methyl group, and about half of the chlorine was added to the backbone carbons of these polymers. The mixed isomer material with about one chlorine atom per monomer unit shows $G(x)$ and $G(s)$ values somewhat lower than polychloromethylstyrene, as might be expected, since not all of the chlorine added forms the easily cleaved benzyl-chloride bond. The chlo-

TABLE II

Resist	Chlorine atoms Per monomer unit	$G(x)$	$G(s)$
Poly(3-chlorostyrene)	1.00	0.71	0.34
Poly(4-chlorostyrene)	1.00	0.88	0.32
Polychloromethylstyrene (PCMS)	1.00	2.60	1.44
Chloromethylated poly(α -methylstyrene) (CMP α MS)	0.95	0.61	0.00
Poly(<i>p</i> -methylstyrene-co-chloromethylstyrene) (PMSCMS)	0.00	0.09	0.00
	0.04	1.40	0.01
	0.13	1.71	0.00
	0.20	1.90	0.38
	0.33	2.08	0.82
	0.52	3.00	1.07
Chlorinated polymethylstyrene (CPMS)	0.00	0.10	0.05
	0.04	1.10	0.26
	0.56	1.95	0.92
	1.20	1.93	1.26
	1.88	1.43	1.07
	2.42	0.80	0.51
Chlorinated poly(<i>para</i> -methylstyrene) (CPpMS)	0.00	0.09	0.01
	0.58	2.11	0.15
	0.92	2.91	0.54
	1.79	1.52	0.14
	2.28	1.32	0.08

minated P-pMS polymer, however, shows a much higher $G(x)$ value, with a large reduction in $G(s)$ as well. Part of this may be attributed to the steric effect observed in the polychlorostyrenes, but the difference is significantly greater for the polymethylstyrenes shown here.

The chloromethylated poly(α -methylstyrene) resists show a much lower crosslinking yield than the other chloromethyl containing resists, although this agrees with the lower sensitivity observed.¹⁵ In addition, no main chain scission is observed, which is surprising, since poly(α -methylstyrene) acts as a positive resist without chloromethylation. Other studies have found decreased $G(s)$ values for *para*-substituted halogenated derivatives, although an increase in $G(s)$ was found for the chloromethyl derivative.²²

Figures 4 and 5 show $G(x)$ and $G(s)$, respectively, as functions of chlorine content for the copolymers of methylstyrene and chloromethylstyrene, as well as for the chlorinated polymethylstyrene resists. The increase in sensitivity observed for even slight degrees of chlorination is evident here, with an order of magnitude increase in $G(x)$ with less than 10% of the monomer units chlorinated. Comparing the two chlorinated polymethylstyrene resists, P-pMS has a higher $G(x)$ and lower $G(s)$ than the mixed isomer resist for all degrees of chlorination. Both materials show a maximum for radiation events of either type at about one chlorine per monomer unit, which is where their maximum sensitivity was observed.¹⁶ Increasing chlorination beyond this point actually reduces the number of crosslinks and scissions that occur, which differs from

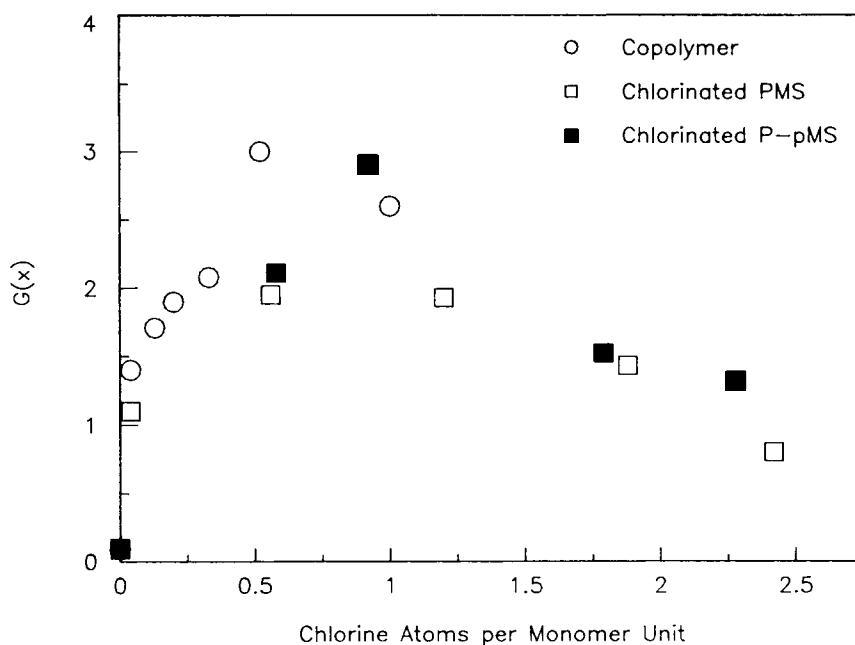


Fig. 4. $G(x)$ values as a function of chlorine content for PMSCMS copolymer resist (○), CPMS resist (□), and CP-pMS resist (■).

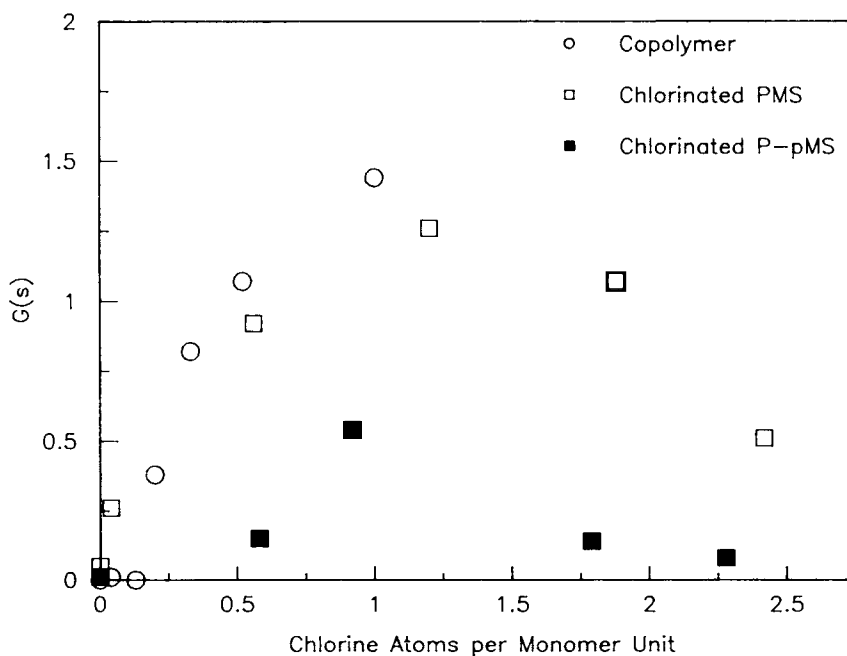


Fig. 5. $G(s)$ values as a function of chlorine content for PMSCMS copolymer resist (○), CPMS resist (□), and CP-pMS resist (■).

the explanation proposed by those authors. The copolymer resists also show a maximum value for $G(x)$, which occurs at a composition of about 50% chloromethylstyrene. An additional feature of these resists is the apparent suppression of chain scissioning for low chlorine content copolymers.

DISCUSSION

In general, the results are in good agreement with the sensitivity trends previously noted, although further insight is provided by consideration of mechanistic studies on this class of resists. Recent analysis by Tanigaki and co-workers²³ on the radiolysis of model compounds clearly shows that further hydrogen abstraction may occur due to the radicals generated by the initial radiation event. ESR studies showed that alpha radicals are formed initially from styrene and methylstyrene, while chloromethylstyrene produces primarily benzyl radicals with a factor of 10 improvement in efficiency. Subsequent alpha hydrogen abstraction by the active chlorine produced may occur, as well as hydrogen abstraction of ring substituent groups. The susceptibility to further hydrogen abstraction is increased by the electron donating ability of any ring substituents; thus a pendant methyl group will be a more likely target for abstraction than an unsubstituted ring, and a chloromethylated ring will be less likely.

These observations explain the decrease in $G(x)$ as chlorine content is increased. The greatest efficiency in forming radicals which lead to crosslinking will occur when there are a large number of methylstyrene groups available for the active chlorine to abstract hydrogen. When all the monomer units contain chloromethyl groups, the likelihood for further hydrogen abstraction is decreased, and $G(x)$ will fall. Thus, the maximum $G(x)$ is observed for the copolymer with a 50% methylstyrene composition, or for the chlorinated polymethylstyrenes with about one chlorine per monomer unit (where about 50% of the pendant methyl groups are chlorinated). In addition, when the polymethylstyrenes are highly chlorinated, the alpha and beta hydrogens are replaced by chlorine atoms which reduces the number of hydrogens available for abstraction and further decreases the likelihood of crosslinking. Tanigaki et al.²³ estimated that the active chlorine atoms abstract alpha hydrogen in about a 5:4 ratio compared to pendant methyl hydrogens for an equimolar mixture of methylstyrene and chloromethylstyrene. The lack of available hydrogens on either a pendant methyl group or on the alpha carbon could account for the very low $G(x)$ value determined for the chloromethylated poly(α -methylstyrene).

The variations in $G(s)$ values are not as readily explained, as scission products have not been investigated. While previous authors¹⁶ expected an increase in chain scission as backbone chlorination increased, the opposite effect is observed here. This aspect of the resist mechanism clearly merits further investigation.

CONCLUSIONS

Radiation chemical yields may be determined from electron beam exposure curves for resists with a general Poisson distribution. This represents an extension of the Charlesby-Pinner technique, which is applicable only to

polymers with a polydispersity of 2. $G(x)$ and $G(s)$ values have been determined for several different chlorine containing styrene based resists. The radiation yields, particularly $G(x)$, agree well with the lithographic sensitivity trends for these negative acting resists, and may be explained based on recent mechanistic studies. An optimal resist composition was shown to consist of both para-chloromethylstyrene and para-methylstyrene. Chlorination of the polymer backbone should be avoided.

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