New thermally crosslinkable electron-beam resists: 3. Prediction of the gel clearing dose

A. F. Miles*, I. J. McEwen and R. Ferguson
Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK
(Received 28 May 1991; accepted 30 July 1991)

A theoretical description of the electron exposure dose required to solubilize the gel fraction of pre-crosslinked positive resists was first proposed by Suzuki and Ohnishi. These authors proposed that the important factors affecting the sensitivity of pre-crosslinked resists are the weight-average molar mass of the primary polymer (M_w°), the main-chain scission efficiency and the average number of crosslinked units per weight-average molecule (δ). In this paper we re-examine these conclusions and show that, for the practical situation, δ and M_w° should not be regarded as independent variables. Using a functional relationship between δ and molar mass, and expressions due to Charlesby for the change in the gel fraction beyond the gel point, equations are developed to predict the critical exposure dose for the cases where degradation occurs (i) exclusively via scission of the crosslinks and (ii) exclusively by scission of main-chain units. Experimental data for pre-crosslinked copolymers of monomethyl itaconate and methyl methacrylate show good agreement with values calculated assuming that degradation of the gel occurs only via main-chain scission.

(Keywords: resist materials; electron-beam lithography; gel degradation; gel clearing dose)

INTRODUCTION

Suzuki and Ohnishi[1] were the first to derive an expression for the highest attainable sensitivity for pre-crosslinked resists. According to these authors, the total number of connected crosslink sites, per unit volume of gel, formed by light or heat treatment, prior to exposure of the resist, is given by $\rho N_A \delta / M_w^\circ$. Here ρ is the polymer density, N_A is Avogadro's number and δ is the crosslinking coefficient, defined by Charlesby[2] as the number of crosslinked repeat units per molecule of primary weight-average molar mass M_w°. During electron exposure the reduction in the number of connected crosslink units following the absorption of ε electronvolts per unit volume is $2G_c P_c \varepsilon/100$. Here G_c is the number of crosslink breakages per 100 eV of absorbed energy (at each breakage the number of connected crosslink units is reduced by 2) and P_c is the ratio of energy absorbed by the crosslinks to that absorbed by the entire system. The gel fraction in the exposed areas of resist was assumed to be reduced to zero when the number of crosslinks per unit volume becomes less than that at the gel point (where from crosslinking theory $\delta = 1$). The condition that the resist becomes completely soluble was written as:

$$\frac{\rho N_A \delta}{M_w^\circ} - \frac{2G_c P_c \varepsilon}{100} \leqslant \frac{\rho N_A}{M_w'} \tag{1}$$

where M_w' is the weight-average molar mass corresponding to $\delta = 1$. Suzuki and Ohnishi further suggested that M_w' may be related to M_w° by adopting Charlesby's expression [2] for the degradation of a Poisson distribution of linear chains, and finally obtained:

$$D_{\text{crit}} \geqslant \frac{200\rho \text{N}_A(\delta - 1)}{G_s A M_w^\circ} \tag{2}$$

A is a proportionality constant between ε and D, where D_{crit} is the areal electron exposure dose (C cm^{-2}) required to destroy the gel. G_s is the number of main-chain scission events per 100 eV of absorbed energy. Values of δ are required in each case, and these were proposed to be estimated from the proportions of sol and gel in each sample. On the basis of expression (2), Suzuki and Ohnishi suggest that there are three ways to improve the sensitivity of pre-crosslinked resists: make M_w° large, make G_s large, and make $(\delta - 1)$ small. Implicit in these conclusions is the suggestion that δ and M_w° are not interdependent. As it stands, expression (2) also has the unfortunate trait of tending to infinity as M_w° tends to zero, which is unrealistic.

In part 2 of this series[3] we have proposed that the assumption that δ is independent of M_w° may be incorrect, and obtained the following functional relationship:

$$\delta = \frac{(M_n^\circ)^2 + M_c^2}{M_c(M_n^\circ + M_c)} \tag{3}$$

where M_n° is the primary (number-) average molar mass and M_c is the (number-) average molar mass between crosslinks. Expression (3) can be combined with:

$$s + \sqrt{s} = 2/\delta \tag{4}$$

first obtained by Charlesby[2] for the growth of the gel fraction, equal to $(1 - s)$, beyond the gel point for molecules having a random or most probable primary molar-mass distribution (*MMD*). This provides a simple method for the modelling of the gel fraction introduced into the resist prior to electron exposure, and from which M_c may be estimated[3].

In this paper we consider the derivation of modified expression for D_{crit} on the basis of the above relationship between δ and M for the limiting situations where degradation occurs (i) exclusively via scission of the

---

* To whom correspondence should be addressed

0032-3861/92/091937-04

crosslinks and (ii) exclusively by scission of connected main-chain units. It will also be shown that the conversion factor A can vary with experimental conditions of accelerating voltage, substrate type and, importantly, resist thickness.

EXPERIMENTAL

Pre-crosslinked resist films were prepared using copolymers of monomethyl itaconate (MMI) and methyl methacrylate (MMA) containing ≈ 10 mol% MMI as described previously[3,4]. Electron-beam exposure of selected samples was performed using a Cambridge Instruments Electron Beam Microfabricator (EBMF-2) using an accelerating voltage of 20 kV. The exposed patterns were forced developed by immersion of the resist in tetrahydrofuran (THF) for 168 h.

RESULTS AND DISCUSSION

Following Suzuki and Ohnishi[1] we adopt equation (1) as a starting point to develop an expression for the critical absorbed energy $\varepsilon_{\text{crit}}$ as a function of primary molar mass. The first term on the l.h.s. of (1) describes the gel crosslink density in terms of the primary polymer molar mass, and thus complies with Charlesby's definition of δ. However, the analogous term (with δ set to unity) forming the r.h.s. of (1) refers δ to the molar mass M'_{w} at the clearing point for the degradation of a phantom network modelled by the primary linear chains. To avoid the need to identify an expression for M'_{w}, we can consider the extreme case in which only crosslink (but not main-chain) scission occurs. Constraining ourselves to this model and assuming that during the exposure of the gel each crosslink is broken once (only), then at the point at which the gel is first destroyed $M'_{\text{w}} = M^{\circ}_{\text{w}}$. Replacing M'_{w} with M°_{w} and substituting (3) for δ leads to:

$$\varepsilon_{\text{crit}} = \frac{100\rho N_{\text{A}}}{2G_{\text{c}}P_{\text{c}}} \frac{M - M_{\text{c}}}{M_{\text{c}}(M + M_{\text{c}})} \qquad (5)$$

This expression sensibly predicts $\varepsilon_{\text{crit}} \rightarrow 0$ as $M \rightarrow M_{\text{c}}$, and asymptotic behaviour at large M.

For case (ii), where the degradation of the gel is assumed to take place exclusively via the scission of connected network chains, the number of main-chain sequences between crosslinks per unit volume of gel may be expressed in terms of δ as $\rho N_{\text{A}}(\delta - 1)/M^{\circ}_{\text{w}}$. Following the absorption of ε electronvolts per unit volume, the number of such sequences destroyed is $G_{\text{s}}(1 - P_{\text{c}})\varepsilon/100$, where G_{s} is the number of chain scissions per 100 eV and $(1 - P_{\text{c}})$ is the proportion of energy absorbed by the connected chains. Assuming that (a) each main-chain sequence is broken only once and (b) at the point where the gel is first made soluble the number of connected main-chain sequences is zero, then:

$$\frac{\rho N_{\text{A}}(\delta - 1)}{M^{\circ}_{\text{w}}} - \frac{G_{\text{s}}(1 - P_{\text{c}})\varepsilon}{100} = 0 \qquad (6)$$

This formalism avoids any statement about the molar mass of the degraded network fragments. It then follows that:

$$\varepsilon_{\text{crit}} = \frac{100\rho N_{\text{A}}}{G_{\text{s}}(1 - P_{\text{c}})} \frac{M - M_{\text{c}}}{M_{\text{c}}(M + M_{\text{c}})} \qquad (7)$$

which differs from (5) only by the factors to be used in the denominator. For lightly crosslinked chains, we suggest that P_{c} can be estimated from $M_{\text{XL}}\delta/M$, where M_{XL} is half the molar mass of a crosslinking unit. Using this, $P_{\text{c}} \sim 10^{-3}$ over a reasonable range of primary molar-mass values.

Expressions (5) and (7) are derived for the particular case where the material to be irradiated consists entirely of gel. For the normal industrial situation, a resist film will consist of a gel fraction plus some residual sol, and thus, where $\varepsilon_{\text{crit}}$ is to be calculated for any real resist film, expressions (5) and (7) should be weighted by $(1 - s)$. *Figure 1* shows $\varepsilon_{\text{crit}}$ as a function of M°_{n} calculated using expression (5), where degradation occurs exclusively via scission of the crosslinks, and also using expression (7) where degradation occurs via the scission of connected chain units. The curves shown are weighted by $(1 - s)$ obtained using expressions (3) and (4) to model the gel fraction as a function of primary molar mass as described[3] in part 2 of this series. Also taken from part 2 is the value of $M_{\text{c}} = 0.5 \times 10^5$ g mol^{-1}, which was found best to characterize this series of MMI–MMA copolymers. M_{XL} was chosen to be 100 g mol^{-1}. Values of $G_{\text{s}} = 2$ and $\rho = 1.195$ g cm^{-3}, characteristic of PMMA, were employed. A value of $G_{\text{c}} = 10$ was chosen as reasonable for a heteroatom-containing linkage. It is apparent from *Figure 1* that $\varepsilon_{\text{crit}}$ is predicted to be several orders of magnitude smaller for the case where degradation of the network is assumed to take place via scission of the connected main-chain sequences. It will be shown below that the values of $\varepsilon_{\text{crit}}$ calculated on this basis are in closer agreement with experimental reality.

Comparison between calculation and experiment

Pre-crosslinked samples of MMI-*stat*-MMA copoly-

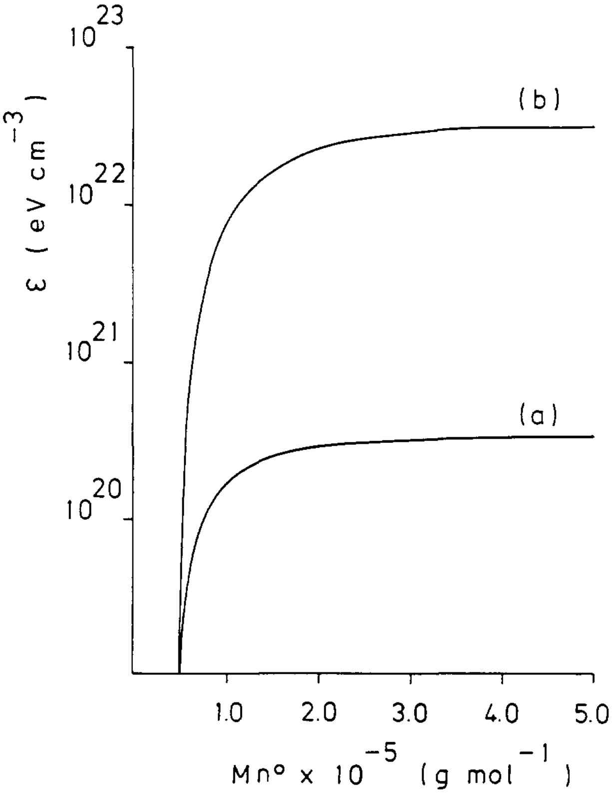

Figure 1 Calculated values of $\varepsilon_{\text{crit}}$ as a function of M°_{n} for a resist material with $M_{\text{c}} = 0.5 \times 10^5$ g mol^{-1}: (a) where network degradation takes place via scission of connected network sequences and (b) where network degradation takes place exclusively via scission of crosslinkages

mers of essentially constant copolymer composition but with increasing M_w° were exposed and the samples developed by immersion in THF for 168 h. This procedure is designed to remove all of the soluble material from the exposed samples. The normalized remaining thickness after development in this manner can be taken as a measure of the gel fraction, and the exposure dose at which the normalized remaining thickness is reduced to zero noted as D_{crit} in μC cm^{-2} (*Figure 2*). Values of D_{crit} thus obtained and corresponding values of ε_{crit} calculated using expression (7) for main-chain scission and weighted by $(1-s)$ are collected in *Table 1*. (Values for M_c, M_{XL}, G_s and ρ as above.)

To provide a direct comparison between the experimental results and calculated values of D_{crit} in μC cm^{-2}, it is necessary to convert ε_{crit} obtained from (7) via the relationship $\varepsilon = AD$ where A is the proportionality constant between ε and D. For a uniform large-area exposure, the incident energy dissipation may be described by an empirical one-dimensional depth–dose model[5–7]:

$$\varepsilon(t) = (D/e)(V_a/R_G)\Lambda(f) \qquad (8)$$

Here $\varepsilon(t)$ is the absorbed energy density (eV cm^{-3}) at depth t (μm); D is the incident exposure dose (C cm^{-2}); e is the charge on the electron; V_a is the accelerating voltage; R_G is the Grun range (μm), given by $0.046V_a^{1.75}/\rho$; and $\Lambda(f)$ is an empirical depth–dose function in terms of normalized depth $f = t/R_G$, conveniently expressed in terms of a polynomial whose terms vary slightly with the atomic number z of the target material. For $5 < z < 12$, Heidenreich *et al.*[7] use:

$$\Lambda(f) = 0.74 + 4.7f - 8.9f^2 + 3.5f^3 \qquad (9)$$

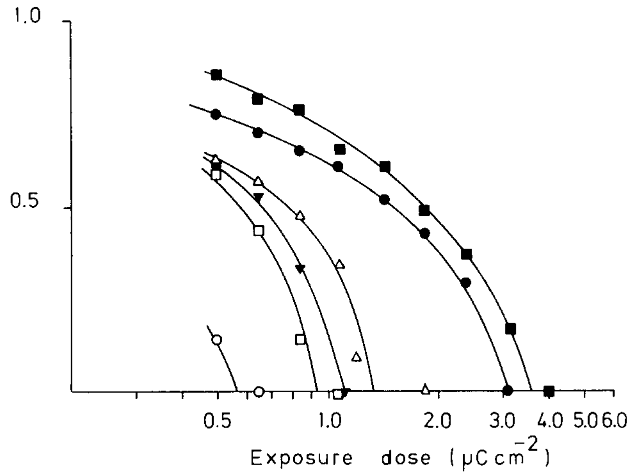

Figure 2 Experimental data showing the normalized remaining thickness *versus* exposure dose for copolymers of MMI–MMA containing ≈10 mol% MMI: (○) $M_w^\circ = 1.31 \times 10^5$ g mol^{-1}; (□) $M_w^\circ = 2.62 \times 10^5$ g mol^{-1}; (△) $M_w^\circ = 2.94 \times 10^5$ g mol^{-1}; (■) $M_w^\circ = 4.36 \times 10^5$ g mol^{-1}; (●) $M_w^\circ = 7.11 \times 10^5$ g mol^{-1}; (▼) $M_w^\circ = 9.32 \times 10^5$ g mol^{-1}

The total energy absorbed by the film in terms of the incident areal exposure dose D is then given by the integral:

$$\varepsilon = \frac{D(1+\eta)V_a}{e}\int_0^f \Lambda(f)\,\mathrm{d}f \qquad (10)$$

where η is an experimentally determined coefficient characterizing the number of back-scattered electrons. For a silicon substrate, using an accelerating voltage of 20 kV, η is approximately 0.17 (ref. 8). Values of $A = \varepsilon/D$ calculated via (10) are presented for the experimental resist films in *Table 1*. Over the range of film thicknesses encountered in this work (0.4–0.9 μm) the value of A can be seen to vary by a factor of ≈2.

Using the appropriate values of A, the entries for D_{crit} shown in *Table 1* are readily obtained, and these show sensible agreement with the experimental data. In fact, the trend in the predicted values, which allow for thickness effects, is mirrored by the experimental D_{crit}, apart from a minor divergence for the sample with $M_w^\circ = 9.32 \times 10^5$ g mol^{-1}. This may be due to the lower MMI content of this sample leading to a lower level of crosslinking. The agreement between the calculated values and the experimental results suggests that it is necessary only to consider the main-chain scission model to describe the solubilization of such lightly crosslinked resist materials. According to this model ε_{crit} is predicted to be zero for $0 < M \leqslant M_c$, and to rise towards an asymptotic value for $M \gg M_c$. Thus the conclusion obtained by Suzuki and Ohnishi—that the gel clearing dose will be reduced for polymers having a large M_w°—appears incorrect. According to this present model, the gel clearing dose will be smallest for polymers with a large value of G_s and with M greater than, but close to, M_c. In a practical sense, however, this may not be appropriate where other requirements such as the thermal stability or reproducibility of the gel fraction introduced into the resist have to be considered.

ACKNOWLEDGEMENTS

This work was completed as part of a cooperative programme, and the authors would like to acknowledge the financial assistance given (to AFM) by the Department of Trade and Industry and the SERC under the Advanced Lithography Research Initiative. Acknowledgements are also due to Dr D. R. Brambley, presently on secondment from GEC–Marconi (Caswell) to the

Table 1 Calculated and experimental values of D_{crit} for MMI–MMA copolymers

MMI (mol%)	$M_w^\circ \times 10^{-5}$ (g mol^{-1})	t (μm)	$\varepsilon_{crit} \times 10^{20}$ (eV cm^{-3})	$A \times 10^{26}$ (eV C^{-1} cm^{-1})	D_{crit} (μC cm^{-2}) Calc.	D_{crit} (μC cm^{-2}) Expt.
9	1.31	0.41	0.68	0.71	1.0	0.6
9	2.62	0.86	2.38	1.69	1.4	0.9
9	2.94	0.74	2.58	1.41	1.8	1.3
9	4.36	0.59	3.06	1.08	2.8	3.6
10	7.11	0.44	3.37	0.77	4.4	3.1
7	9.32	0.51	3.46	0.91	3.8	1.1

Rutherford Appleton Laboratory under the Advanced Lithography Research Initiative, and to Mr R. H. Bennett of GEC–Marconi (Caswell), for their help in the preparation and exposure of the resist films.

REFERENCES

1 Suzuki, M. and Ohnishi, Y. *J. Electrochem. Soc.* 1982, **129**, 402

2 Charlesby, A. 'Atomic Radiation and Polymers', Pergamon Press, Oxford, 1960, pp. 134–158

3 Miles, A. F., Cowie, J. M. G., Bennett, R. H. and Brambley, D. R. *Polymer* submitted

4 Miles, A. F. and Cowie, J. M. G. *Eur. Polym. J.* 1991, **27**, 165

5 Bowden, M. J. *CRC Crit. Rev. Solid State Sci.* 1979, **8**, 223

6 Thompson, L. F. and Bowden, M. J. in 'Introduction to Microlithography' (Eds L. F. Thompson, C. G. Wilson and M. J. Bowden), *ACS Symp. Ser.* 1983, **219**, 16

7 Heidenreich, R. D., Thompson, L. F. and Melliar-Smith, C. M. *J. Appl. Phys.* 1973, **44**, 4039

8 Brewer, G. R. in 'Electron-Beam Technology in Microelectronic Fabrication' (Ed. G. R. Brewer), Academic Press, New York, 1980