New thermally crosslinkable electron beam resists: 2. Monomethyl itaconate–methyl methacrylate copolymers

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The lithographic evaluation of monomethyl itaconate (MMI) and methyl methacrylate copolymers as thermally crosslinkable electron beam resists is described. Their properties were investigated as a function of copolymer composition and primary molar mass in order to determine an optimum formulation for the preparation of high resolution resist patterns. Line and space test patterns with features $<0.5\ \mu m$ have been prepared using copolymers containing 10 mol% MMI with lithographic sensitivity of $\sim 80\ \mu C\ cm^{-2}$ and resist contrast of $\sim 4\ cm^2\ \mu C^{-1}$ when developed in a mixture of n-butyl acetate and n-hexyl acetate. In accordance with previously published results, the electron exposure dose required to first destroy the pre-crosslinked fraction of the resist has been found to be very much less than the electron exposure dose required for the preparation of high resolution resist patterns. The results obtained in this work are compared to a theory of gel degradation originally developed to describe the solubilization of lignin from plant tissue, whereby the breakdown of the gel can be modelled using the statistics for random network formation, except applied in reverse.

(Keywords: resist materials; electron beam lithography; monomethyl itaconate copolymers; gel degradation)

INTRODUCTION

Thermally crosslinkable electron beam resists were first proposed by Roberts[1,2] as a modification to existing poly(methyl methacrylate) resist materials. Although the sensitivity of pre-crosslinked resist materials is now generally inferior to other types of positive acting resists[3], pre-crosslinked materials offer advantages for high resolution direct-write lithography, including high thermal stability, wide processing latitudes and good adhesion to a variety of substrates[4]. The major disadvantages are a relatively poor sensitivity (materials generally require an areal exposure dose in the range of $5-100\ \mu C\ cm^{-2}$), difficulty in the reproducibility of the level of crosslinking introduced prior to electron exposure and difficulty in removing the resist during 'lift-off' processing. Following the disclosure by Roberts, many other types of pre-crosslinked polymers have been reported, and a review of methacrylate- and acrylate-based systems has been provided by Moreau[4].

Some progress towards an understanding of the factors affecting the reproducibility of behaviour in these materials has been made by Roberts[5], who reported that, for a mixture of two copolymers, poly(methacryloyl chloride-*stat*-methyl methacrylate) and poly(methacrylic acid-*stat*-methyl methacrylate), the lithographic sensitivity (defined as the electron exposure dose D_o required for the complete removal of resist from an exposed area under given development conditions) is dependent upon the cure temperature used during resist pre-baking, and upon the proportion of crosslinking sites introduced into the copolymers. For copolymers containing 10–15 mol% of reactive functional groups, Roberts reported that the lithographic sensitivity is most reproducible for cure temperatures in the range of 150–200°C and that the cure temperature should be maintained within 1°C of its intended value for optimum results. Experience with the same copolymer mixtures[6] has shown that accurate control of the relative humidity during pre-baking is also important.

In the first publication of this series[7] we described a new range of thermally crosslinkable resist materials based upon copolymers of itaconic anhydride (IT.ANH) and methyl methacrylate (MMA) which were found to exhibit a general variation in D_o and resist contrast (γ) with copolymer composition. An acceptable balance of D_o and γ was obtained for copolymers containing $\sim$46 mol% IT.ANH, and resist patterns with feature sizes $<0.5\ \mu m$ were prepared using a copolymer containing 46 mol% IT.ANH and with number average molar mass $(M_n^o) = 5.30 \times 10^5\ g\ mol^{-1}$. D_o was found to pass through a minimum with variation in primary molar mass for the particular range of copolymer samples that were investigated.

Other studies of pre-crosslinked resists have been made by Asmussen and co-workers[8] and by Suzuki and

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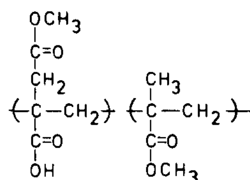
Ohnishi[9]. The former authors noted that the complete destruction of the crosslinked fraction of the polymer is a necessary requirement for the successful development of the resist by solvent developers, and that this is accomplished only if the absorbed electron dose exceeds a critical value. Below this critical threshold some part of the irradiated resist will remain.

A more detailed attempt to predict the critical exposure dose D_{crit} required for the the destruction of the gel fraction was made by Suzuki and Ohnishi[9]. A theoretical formula obtained by these authors was found to give values of D_{crit} in approximate agreement with the experimentally determined values for certain pre-crosslinked resist materials, although the predicted variation in D_{crit} with primary molar mass values has not been thoroughly tested. This aspect of the behaviour of pre-crosslinked resists is the subject of a subsequent paper.

Relevant to this present study are previous results for monomethyl itaconate (MMI) and MMA copolymers made by Anderson[10]. This author deliberately used a low pre-bake temperature of 120°C in order to minimize thermal crosslinking and thereby favour improved lithographic sensitivity. In a separate study, Anderson and Rodriguez[11] determined the radiation chemical yield for main chain scission of MMI–MMA copolymers containing 19 and 39 mol% MMI, obtaining values of 1.7 and 2.2 scissions per 100 eV absorbed energy respectively (compared with 0.8 for PMMA). The use of MMI-*stat*-MMA copolymers



as thermally crosslinkable resist materials is reported here with particular emphasis on the variation in resist properties with copolymer composition and primary weight average molar mass (M_w^o). The behaviour is compared with previously published work in which it was proposed that processes of random network degradation can be modelled using the statistical theories developed for the random crosslinking of polymer chains, but applied in reverse.

EXPERIMENTAL

Full details of the preparation and characterization of the polymers used in this work have been presented elsewhere[12]. Samples of copolymers containing ~10 mol% MMI were separated by fractional precipitation using a 60:40 toluene and acetone mixture as solvent and petroleum ether as precipitant. Fraction molar masses were determined as polystyrene equivalents using gel permeation chromatography in tetrahydrofuran (THF). Details are given in *Table 1*.

Resist films were prepared by spin coating from 5 to 10 w/v% solutions in 2-methoxyethyl acetate onto silicon substrates (76 mm diameter) using a Headway Research photoresist spinner. Following resist coating, all samples were pre-baked at 170°C for 1 h in a glove box with a nitrogen atmosphere. Lithographic evaluation of selected resist samples was carried out as reported previously[7]. The gel fraction following pre-baking was estimated from measurement of the normalized film thickness remaining following removal of the soluble fraction by immersion of the sample in THF or acetone for 140–168 h.

Table 1 Resist films prepared from MMI-*stat*-MMA copolymers

Copolymer composition (mol% MMI)	$M_w^o \times 10^{-5}$ (g mol^{-1})	$\overline{M_w^o}/\overline{M_n^o}$	Film thickness (μm)	Gel fraction after baking[a] A	B
5	–	–	0.47	–	–
9	1.31	1.5	0.41	0.53	0.47
8	1.65	1.4	0.53	0	0
9	2.28	1.7	0.74	–	0.54
9	2.62	1.7	0.86	0.83	–
9	2.94	1.3	0.74	0.93	0.88
9	3.56	1.7	1.12	0	0
8	4.22	1.3	0.97	0.91	–
9	4.28	1.3	0.73	0.96	–
9	4.36	1.5	0.59	0.98	0.98
10	7.11	1.3	0.44	0.91	0.88
7	9.32	1.5	0.51	0.98	0.98
20	–	–	0.44	–	–
35	–	–	0.40	–	–
54	–	–	0.63	–	–

[a] A, soluble material extracted using acetone, 168 h; B, THF, 168 h

RESULTS AND DISCUSSION

Variation in resist performance with composition. Plots of normalized remaining thickness *versus* exposure dose for samples containing 5–54 mol% MMI are presented in *Figure 1*. All samples were developed for 90 s plus a further 30 s in a 7:3 mixture of methyl isobutyl ketone (MIBK) and isopropanol (IPA). Values of D_o and γ are presented as a function of copolymer composition in *Table 2* where a gradual trend of reducing lithographic sensitivity (increasing D_o) and increasing γ is observed with increasing MMI comonomer content. Examination of the developed resist test pattern using scanning electron microscopy suggested that high resolution resist features could be prepared using copolymers containing ~10 mol% MMI and so further work was concentrated at this composition.

Selection of solvent developers. Plots of normalized remaining thickness *versus* exposure dose for a copolymer containing 9 mol% MMI, with $M_w^o = 2.62 \times 10^5$ g mol^{-1} and developed in various solvents, are presented in *Figure 2*. As in the case of the series of IT.ANH-*stat*-MMA copolymers investigated previously[7], it is found that D_o can be reduced significantly with the selection of an appropriate solvent developer, although this is generally accompanied by a reduction in resist contrast and more rounded resist profiles. Interestingly, reasonable results were obtained using a 4:1 mixture of isopropanol and water although the feature definition appeared slightly inferior to that obtained using a 4:1 mixture of n-butyl acetate and n-hexyl acetate which was selected as the preferred developer. *Figures 3* and *4* are scanning electron micrographs of test patterns prepared in a copolymer containing 10 mol% MMI developed in 4:1 n-butyl acetate and n-hexyl acetate.

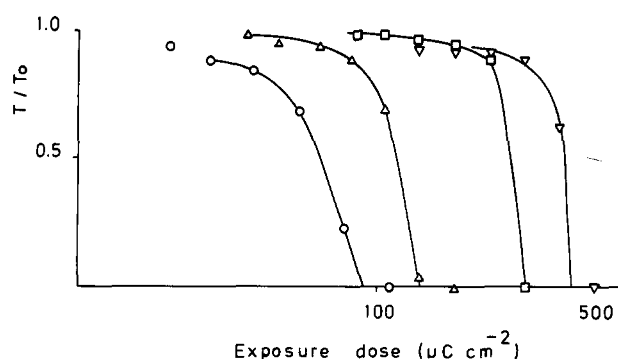


Figure 1 Normalized remaining thickness *versus* exposure dose for copolymers containing 5–54 mol% MMI: (○) 5 mol%; (△) 20 mol%; (□) 35 mol%; (▽) 54 mol%

Table 2 Values of D_o and γ for MMI-*stat*-MMA copolymers

Copolymer composition (mol% MMI)	D_o (μC cm^{-2})	γ (cm^2 μC^{-1})
5	90	4
20	138	6
35	300	10
54	420	16

Developer = 7:3 methylisopropylketone and isopropanol

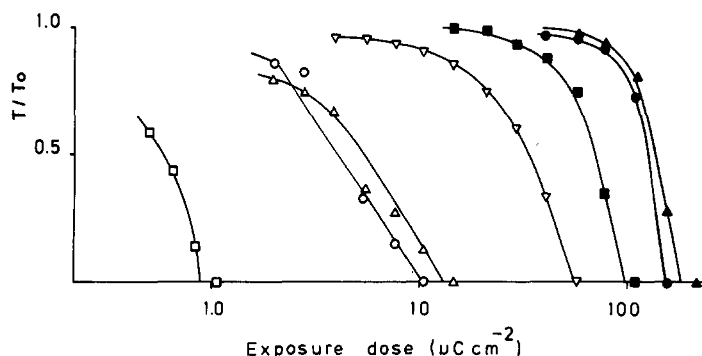


Figure 2 Normalized remaining thickness *versus* exposure dose for copolymer containing 9 mol% MMI, $M_w^o = 2.62 \times 10^5$ g mol^{-1}. Developers: (○) 4:1 ethyl acetate and isopropanol; (△) 2-methoxyethyl acetate; (▽) 4:1:1 n-butyl acetate and n-hexyl acetate and 2-methoxyethyl acetate; (■) 4:1 n-butyl acetate and n-hexyl acetate; (●) 4:1 isopropanol and water; (▲) isoamyl acetate; (□) forced developed THF, 168 h

Variation in resist performance with primary molar mass. Samples of copolymers were exposed using a standard test pattern and the samples developed using a 4:1 mixture of n-butyl acetate and n-hexyl acetate in order to investigate the variation in resist performance with primary molar mass. Measurements of D_o as a function of M_w^o for this developer system are presented in *Figure 5* where, contrary to the results obtained for IT.ANH–MMA copolymers[7], D_o can be seen to pass through a maximum at $M_w^o = 2.6 \times 10^5$ g mol^{-1}. The results of this type of experiment thus appear to be dependent upon the particular resist material and the solvent developer used. As with the IT.ANH–MMA copolymers, D_o has been found to vary significantly with the primary molar mass suggesting that this must be considered if the lithographic response of the resist is to be reproducible.

Formation of the gel fraction. Theoretical treatments of the crosslinking of linear polymers were first published by Flory[13] and by Stockmayer[14]. The basic assumptions of these treatments are that all reactive sites have an equal probability of reacting and that all finite molecules

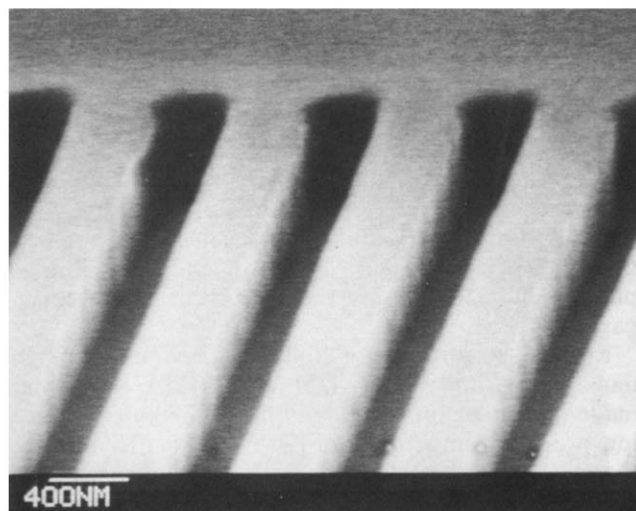


Figure 3 Line and space test patterns with 750 nm pitch prepared in copolymer containing 10 mol% MMI. Exposure dose = 215 μC cm^{-2}

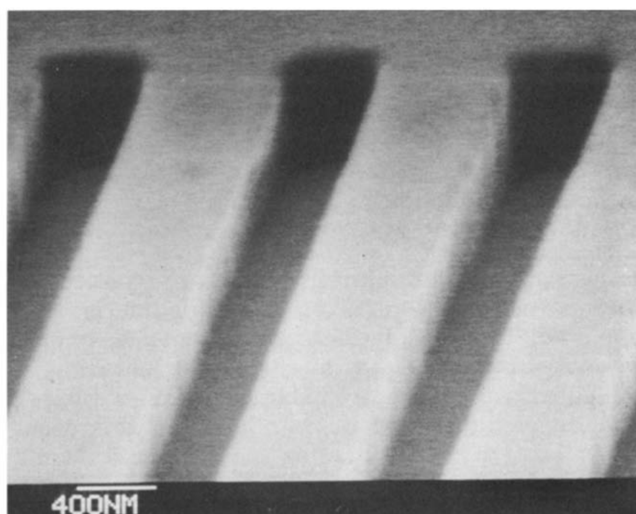


Figure 4 Line and space test patterns with 1125 nm pitch prepared in copolymer containing 10 mol% MMI. Exposure dose = 215 μC cm^{-2}

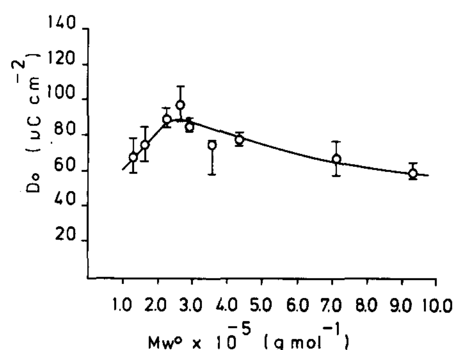


Figure 5 Lithographic sensitivity D_o *versus* M_w^o for copolymers containing ~10 mol% MMI. Developer = 4:1 n-butyl acetate and n-hexyl acetate. Error bars represent uncertainty in the extrapolation of normalized remaining thickness *versus* exposure dose data

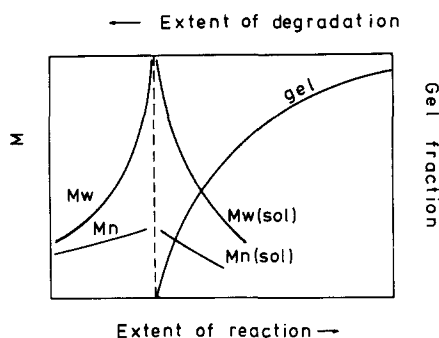


Figure 6 Schematic illustration showing the variation in molar mass averages and the gel fraction in the vicinity of the gel point for the crosslinking of primary molecules and during the random degradation of the gel fraction (see text)

are 'tree-like', i.e. there are no intramolecular cyclization reactions[15]. During crosslinking five main stages can be identified:

1. Increase in the average molar mass and in the polydispersity of finite chains
2. Formation of a gel, or non-soluble fraction, at the gel point
3. Increase in the gel fraction with preferential incorporation of the longer than average molecules into the gel phase
4. Reduction in the average molar mass of finite species (beyond the gel point)
5. Increase in the degree of crosslinking and elastic properties of the gel.

A schematic illustration of these changes is shown in *Figure 6*.

Expressions for the calculation of the variation in number and weight average molar mass values, and for the growth of the gel fraction, due to Flory and Stockmayer are not generally amenable to simple calculation. However, Charlesby[16] has provided explicit expressions for the proportions of sol (s) and gel $(1-s)$ beyond the gel point for particular cases of the generalized Schultz–Zimm type of primary molar mass distribution (*MMD*) in terms of the crosslinking coefficient δ (defined as the number of crosslinked repeat units per molecule of primary weight average molar mass). For molecules having a uniform or monodisperse primary distribution

$$(1-s) = -\ln(s)/\delta \tag{1}$$

while, if the original distribution is of the random or most probable type

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

The quantitative characterization of the species within a network has been addressed by Flory[15], who suggested that the structure of a random network can be described by two quantities: the proportion of repeat units engaged in connected chains between crosslinks; and the proportion of free chain ends. Accordingly the weight fraction of free chain ends S_f is given by

$$S_f = \frac{2M_c}{(M_n^o + M_c)} \tag{3}$$

where M_c is the (number) average molar mass between crosslinks and M_n^o is the primary number average molar mass. The weight fraction of connected chains is thus $(1-S_f)$ and this provides the basis for a functional relationship between δ and M_n^o. For a generalized distribution the crosslinking coefficient can be expressed as

$$\delta = \left[\frac{(1-S_f)M_n^o}{M_c}\right] + 1 \tag{4}$$

noting that $M_w^o = 2M_n^o$ for a most probable distribution. Expressions (3) and (4) then lead to

$$\delta = \frac{M_n^{o2} + M_c^2}{M_c(M_n^o + M_c)} \tag{5}$$

Using expressions (1) or (2), this definition of δ may be applied to the practical situation in which a resist formulation of fixed composition is pre-crosslinked by baking for a specified time and temperature. From the Flory–Stockmayer analysis the gel fraction introduced into the resist is a function of both the weight average molar mass and primary molar mass distribution. However for a series of polymers where the distributions are similar, the gel fraction may appear to depend on primary molar mass only. Data for MMI-*stat*-MMA copolymers showing this behaviour are presented in *Figure 7*. Also shown is the calculated variation in gel fraction with primary molar mass according to equation (2) (for molecules having a most probable primary *MMD*) using the proposed relationship between δ and molar mass given by equation (5). On the basis of the general agreement between the predicted and experimental trends, this simplified treatment of the statistical theory of crosslinking appears to be a useful description of gel formation in resist materials, and a value of $M_c = 0.5 \times 10^5$ g mol^{-1} best characterizes this series of copolymers for the baking regime used.

The figure also highlights that the gel fraction displays a significant dependence on M_w^o for $M_w^o < 5 \times 10^5$ g mol^{-1} and, where the gel fraction introduced prior to electron exposure is a consideration (for example when thermal distortion of the resist pattern during subsequent processing or where the thinning of unexposed areas of resist is important), then the primary molar mass of the primary polymer must be carefully controlled.

Degradation of the gel fraction. Following pre-baking, resist materials of the type described here can be expected to consist of two major components: a soluble fraction, made up of linear or branched molecules of finite size not connected to the crosslinked network; and a gel

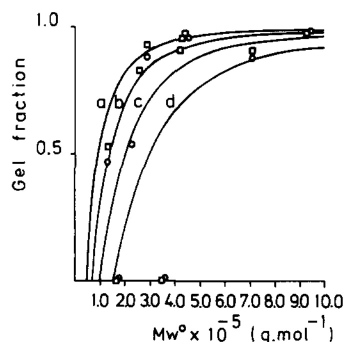


Figure 7 Calculated and experimental values of the gel fraction $(1-s)$ *versus* M_w^o for copolymers containing ~10 mol% MMI pre-crosslinked by baking for 1 h at 170°C: (□) experimental gel thickness following extraction of soluble material in acetone, 168 h; (○) THF, 168 h. Calculated full lines for: (a) $M_c = 0.25 \times 10^5$; (b) $M_c = 0.35 \times 10^5$; (c) $M_c = 0.5 \times 10^5$; (d) $M_c = 0.75 \times 10^5$

fraction, typically consituting 0.6–1.0 volume fraction of the resist material. The fate of the molecules constituting the soluble fraction of the resist during irradiation was discussed earlier[7] where it was concluded that the linear or lightly branched molecules can be expected to undergo chain scission with a reduction in average molar mass, finally to yield species having the most probable molar mass distribution.

The breakdown of a network fraction by random scission events has received some attention largely as a result of its possible significance in the industrially important process of the solubilization of the natural polymer lignin. Argyropoulos *et al.*[17–21] have investigated the proposal first made by Szabo and Goring[22] that random network degradation can be treated by the mathematical expressions contained in the Flory–Stockmayer theory of network formation, except applied in reverse. Argyropoulos *et al.* provide a significant body of evidence supporting the proposition of Szabo and Goring, confirming, at least in a qualitative sense, the correctness of these proposals for a number of model networks. According to this theory, during the initial stages of degradation only low molar mass fragments are cleaved from the network. As degradation proceeds the size of the species released progressively increases as scission of the network becomes more effective in freeing larger molecules. At the same time the *MMD* of fragments released into the sol is predicted to broaden. The general trends in M_w and M_n for the sol are illustrated by the upper arrow shown in *Figure 6*. Here the critical point at which the gel fraction is reduced to zero is represented as the turning point for the sol species distribution, and beyond this the molar mass averages are suggested to follow the reverse path to that predicted for the system prior to gelation.

This picture of gel degradation can rationalize features of the behaviour of pre-crosslinked resists, notably that the critical exposure dose required to destroy the insoluble fraction of the resist is normally very much less than the exposure dose required for the preparation of high resolution resist patterns. *Figure 2* shows that where the resist pattern is forced developed in THF for 168 h the reduction in normalized remaining thickness for the residual gel intersects the exposure dose axis to give a value of D_{crit} one to two orders of magnitude smaller than the lithographic clearing dose D_o. Following the description above, at D_{crit} the average molar masses of the degraded gel fragments obtain their maximum value and thus, although the gel is destroyed, the relatively high molar mass averages preclude the dissolution of the irradiated material using common developing solvents with short developing times.

The observation that a relatively wide range of D_o and γ values can be obtained with variation in developer type, or time of development, can also be rationalized as being due to the varying abilities of the developers to selectively remove polymer of different average molar mass values and *MMD* within the given development time.

CONCLUSIONS

MMI-*stat*-MMA copolymers have been found to operate as thermally crosslinkable positive acting electron-beam resists. A range of copolymer compositions has been investigated and a useful resist formulation containing 10 mol% MMI has been identified. Resist patterns with $<0.5\ \mu$m resolution and good edge acuity have been prepared on silicon substrates with $D_o \sim 80\ \mu$C cm^{-2} and $\gamma \sim 4$ cm$^2\ \mu$C^{-1} using a 4:1 mixture of n-butyl acetate and n-hexyl acetate as developer. D_o has been found to pass through a maximum with variation in M_w^o.

From the Flory–Stockmayer analysis for the random crosslinking of primary chains, the gel fraction introduced into a pre-crosslinked resist is predicted to be a function of both M_w^o and the *MMD* of the primary polymer. Making certain simplifying assumptions a useful model for the gel fraction introduced into the resist can be obtained on the basis of M_w^o alone. From this, the number average molar mass between crosslinkages for the series of copolymers investigated here has been estimated to be 0.5×10^5 g mol^{-1} for the particular conditions of pre-bake time and temperature used. This analysis also suggests that where the gel fraction introduced into the resist prior to electron exposure is an important consideration then the primary molar mass (and possibly the *MMD*) of the primary polymer must be carefully controlled.

By treating gel degradation as the reverse process of random network formation certain aspects of the lithographic behaviour of pre-crosslinked resists may be rationalized.

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