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Evaluation of halomethylated poly(methylphenylsilane)s as electron-beam resists

Simon J. Holder, Richard G. Jones* and Julian J. Murphy

Centre for Materials Research, Department of Chemistry, University of Kent at Canterbury, Kent, UK CT2 7NH

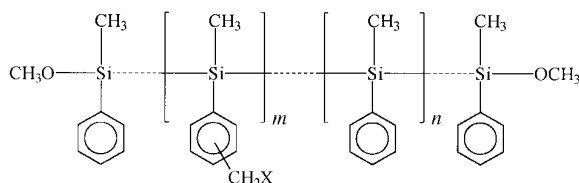
Polysilane analogues of halomethylated poly(styrene)s, chloromethylated and bromomethylated poly(methylphenylsilane), have been prepared from the parent polymer by reaction with the appropriate halomethyl methyl ether. The polymers undergo a single-stage crosslinking reaction when irradiated with 20 kV electrons. As electron beam resists they operate in negative-working mode but their performance is poor in comparison to the corresponding poly(styrene) derivatives. The low lithographic sensitivities and attainable contrasts are shown to arise as a consequence of a competitive chain scission reaction which in the case of the bromomethylated system increases with increasing bromomethyl content. The radiation chemistries of the systems are rationalised in terms of modifications of the crosslinking and scission mechanisms that are thought to operate in the corresponding resists based on poly(chloromethylstyrene-*stat*-styrene).

Since the discovery of tractable poly(diorganosilanes) in the 1970s,^{1,2} a number of potential applications have been proposed. Interest in these unique polymers stems not only from the catenated silicon backbone which has led to one of their most important commercial applications, namely as ceramic precursors,³ but also from the unusual conjugation of the σ -bonds of the backbone which gives rise to electron delocalisation. This has resulted in the polymers being assessed for a number of electrical and optical applications.^{4,5}

Arising from the direct photosensitivity of the silicon backbone of polysilanes, one of their most promising potential uses is as positive-working resists in microlithography. An important advantage that they possess over carbon-based polymers for such applications is a high silicon content, imparting the O_2 plasma and reactive-ion etch resistance required in multilayer microlithographic processing. Accordingly, a large number of organopolysilanes have been tested as photoresists although none have found wide application.⁶ However, future generations of very large scale integrated (VLSI) circuitry will require microlithographic resolutions that are beyond those that can be attained using conventional resists and photo-processing. Typically, resolutions of less than 0.25 μm will have to be routinely achieved. To this end electron-beam (e-beam) lithography finds increasing application in the production of application specific integrated circuitry (ASIC) and photomasks with target resolutions down to 0.1 μm .⁷ Thus, it is as electron beam resists that polysilanes might find a useful role if they can be tailored to suit the requirements of this imaging technique, which must be performed with structures which would not release silicon-containing fragments to the gas phase, that might contaminate the writing tool, during the lithographic process.

Poly(methylphenylsilane) (PMPS) is the cheapest tractable homopolysilane available in relatively high yields from the Wurtz-type condensation polymerisation of dichloroorganosilanes. However, positive-working behaviour (*i.e.* polymer chain degradation) with only a very low sensitivity has been previously observed for this polymer upon e-beam exposure, disqualifying its use as a possible resist in an unmodified form.⁸ The introduction of chloromethyl groups onto the pendant phenyl of poly(methylphenylsilane)-*co*-(dimethylsilane) has been shown to result in a marked increase in the sensitivity of this polymer towards negative-working behaviour.⁹ Arising from its structural similarity to polystyrene, the trivial name poly(silastylene) has been coined for poly(methylphenylsilane)-*co*-(dimethylsilane). It follows that its chloromethylated derivatives might reasonably be compared to chloromethylated polystyrenes which are examples of the well-characterised class

of so-called CMS negative-working resists.^{10–18} Halogenated resists derived from the homopolymer, PMPS, can be considered no less appropriate for comparison with the CMS structures. Accordingly, in the present study, chloromethylated and bromomethylated poly(methylphenylsilanes) over a range of compositions were synthesised with the intention that their application within e-beam lithography might be assessed, and an understanding gained of the underlying radiation chemical processes that occur within electron beam resists that might be based on PMPS and its derivatives.



Experimental

Apparatus and procedures

The polymer structures were characterised by ^1H , ^{13}C and ^{29}Si NMR, FTIR and UV spectroscopy. FTIR and NMR spectra were obtained using ATI Mattson Genesis Series FTIR and JEOL JNM-GX270 NMR spectrometers, respectively. NMR samples were prepared as solutions in CDCl_3 and chemical shifts are quoted in relation to SiMe_4 . $\text{Cr}(\text{acac})_3$ was used as an internal relaxation agent to record the ^{29}Si NMR spectra. UV spectra were obtained from $ca. 10^{-4} \text{ mol dm}^{-3}$ CH_2Cl_2 solutions using a PU 8740 UV-VIS scanning spectrophotometer. Thermal analyses of the polymer samples were performed under a nitrogen atmosphere on a Perkin-Elmer DSC7 differential scanning calorimeter operating at scan rates of 10 K min^{-1} .

Molecular weights of the polymers were obtained relative to polystyrene standards using HPLC equipment (Polymer Laboratories) with a $30 \text{ cm} \times 10 \mu\text{m}$ PLgel mixed-D column. The eluent was THF and determinations were carried out at a flow rate of 2 ml min^{-1} at ambient temperature using a UV detector. It has been reported⁴ that the molecular weights of polysilanes as determined by size exclusion chromatography relative to polystyrene standards are likely to be too low by a factor of *ca.* 2.3. However, recent studies¹⁹ have indicated that the difference in the hydrodynamic volumes of polystyrene and PMPS is very small. It is also unlikely that relatively low loadings of halomethyl groups would substantially affect the

hydrodynamic volume of the PMPS. Accordingly, it is assumed that the molecular weights as determined by size exclusion chromatography are sufficiently accurate for the purposes of the present study.

Resist solutions were formulated by dissolving the copolymers in chlorobenzene to produce 20% w/v solutions. The solutions were filtered through 0.5 μm Millipore filters and spun directly onto 3 inch silicon wafers using a Headway EC-101 spinner and prebaked at 120 °C for 30 min to produce good quality uniform films with a thickness of approximately 1 μm . Exposure was performed using a Cambridge Instruments EBMF-10.5 electron beam lithography tool operating at 20 kV accelerating potential. Development was accomplished by immersing a wafer fragment in methyl isobutyl ketone (MIBK) for 60 s, followed by a 30 s rinse in isopropyl alcohol (IPA). This development procedure was not optimised but was chosen to follow established practice for the corresponding halomethylated poly(styrene) resists.^{15,16} Developed wafers were dried in a filtered stream of nitrogen. Film thickness measurements before and after exposure were taken using a Nanospec/AFT 210 film thickness system. Sensitivities were estimated as the dose corresponding to 50% thickness remaining after development ($D_n^{0.5}$). All resist thicknesses were normalised to the original spun thickness. Lithographic contrasts (γ) were calculated from $D_n^{0.5}$ and the gel dose (D_n^0) using eqn. (1).

$$\gamma = 1/[2 \log(D_n^{0.5}/D_n^0)] \quad (1)$$

Materials

Polymer syntheses and characterisation. The PMPS samples used for halomethylation were prepared from the Wurtz-type reaction of distilled dichloromethylphenylsilane (Lancaster) using freshly prepared sodium sand in refluxing diethyl ether in the presence of 15-crown-5.²⁰ Fractionation of PMPS was accomplished by washing the broad distribution polymer that is initially prepared with *n*-hexane. Halomethylations of unfractionated PMPS samples were carried out in accordance with published procedures.²¹ Based on the composition range identified as being optimal for the lithographic performance of corresponding copolymers of the CMS series of resists such as poly(styrene-*stat*-chloromethylstyrene), the extents of halomethylation were targeted within the range 15 to 40%. The homopolymer PMPS 1 was prepared by the direct reaction of dichloromethylphenylsilane with molten sodium in the absence of a solvent. Fractionation of this sample by repeated Soxhlet extractions of the sample with hexane gave the fractionated homopolymer PMPS 2.

Representative spectroscopic data are given below for both bromomethylated PMPS and chloromethylated PMPS samples, BPMPs and CPMPs respectively. BPMPs 1 and CPMPs 1 were prepared from PMPS samples that were

different from the remaining halomethylated polymers. Both series of copolymers were isolated from samples of halomethylation reaction mixtures taken at various times during extended reactions. The polymer structural and thermal parameters are given in Table 1.

BPMPs

$\delta_{\text{H}}(\text{CDCl}_3)$ – 1.1 to 0.6 (vbr m, CH_3Si), 3.0 (br m, CH_3O), 4.3 (br s, ClCH_2), 6.0–7.7 (vbr m, aromatic). $\delta_{\text{C}}(\text{CDCl}_3)$ – 8.0, –7.5, –6.9, –6.0 (br m, CH_3Si), 33.5 (s, CH_2Br), 50.5 (s, CH_3O), 126.8, 126.5, 134.2, 135.7 (m, aromatic). $\delta_{\text{Si}}(\text{CDCl}_3)$ – 41.1, –39.9, –39.2 (br t, SiCH_3Ph), 8.7 (s, SiOCH_3), 14.6 (d, SiCl). $\nu_{\text{max}}(\text{thin film})/\text{cm}^{-1}$ 3065, 3046, 3014 (C–H stretch, aromatic), 2958, 2893, 2868 (C–H stretch, aliphatic), 1426 (C–C ring stretch, Si–phenyl), 1394 (CH_2Cl bend), 1245 (C–H bend, CH_3Si), 1095 (C–C ring stretch + Si–C stretch, Si–phenyl), 782, 754, 730, 697, 664 (various C–C ring stretch + Si–C stretch), 605, 619 (Si–Br stretch), 465 (Si–Si stretch). $\lambda_{\text{max}}/\text{nm}$ (ϵ) 239 (5700), 279 (3800), 341 (7900).

CPMPs

$\delta_{\text{H}}(\text{CDCl}_3)$ – 1.2 to 0.6 (vbr m, CH_3Si), 3.0 (br m, CH_3O), 4.4 (br s, ClCH_2), 6.0–7.6 (br m, aromatic). $\delta_{\text{C}}(\text{CDCl}_3)$ – 8.0, –7.3, –6.8, –5.9 (br m, CH_3Si), 46.0 (s, CH_2Cl), 50.6 (s, CH_3O), 126.7, 134.3, 135.8 (m, aromatic). $\delta_{\text{Si}}(\text{CDCl}_3)$ – 41.0, –39.9, –39.1 (br t, SiCH_3Ph), 8.7 (s, SiOCH_3). $\nu_{\text{max}}(\text{thin film})/\text{cm}^{-1}$ 3047, 3012, 2991 (C–H stretch, aromatic), 2958, 2893, 2868 (C–H stretch, aliphatic), 1427 (C–C ring stretch, Si–phenyl), 1394 (CH_2Cl bend), 1259, 1246 (C–H bend, CH_3Si), 1097 (C–C ring stretch + Si–C stretch, Si–phenyl), 781, 754, 730, 698, 664 (various C–C ring stretch + Si–C stretch), 465 (Si–Si stretch). $\lambda_{\text{max}}/\text{nm}$ (ϵ) 239 (6300), 279 (4100), 341 (8600).

Results

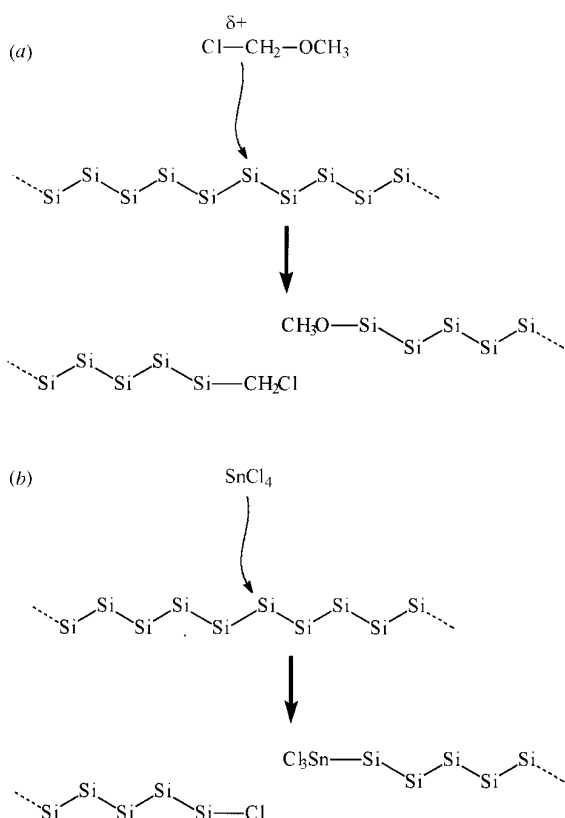
Polymer structure and thermal characterisation

We have previously reported that the halomethylation of PMPS by halomethyl ether prepared *in situ* leads to a substantial degradation of the polysilane backbone as evidenced by size exclusion chromatography.^{21,22} This probably occurs *via* the mechanisms outlined in Scheme 1, as both the SnCl_4 and the halomethyl ethers have been observed to degrade polymers, although it must be emphasised that no conclusive evidence for the formation of terminal SiCH_2X groups ($\text{X} = \text{Br}$ or Cl) has yet been obtained. However, when bromomethyl octyl ether is used in the bromomethylation reaction in place of bromomethyl ether, after several purifications of the product by precipitation, washing and drying under vacuum, a number of alkyl peaks in the region δ 2.0 to 0.5 can be observed in the ^1H NMR spectrum. These are presumed to arise from end-capping of the polysilane chains by octyloxy groups, so provid-

Table 1 Characterisation and lithographic parameters of the homo- and co-polysilanes studied

polymer	M_w	[PD]	CH_2X (%)	DSC		$D^{0.5}/\mu\text{C cm}^{-2}$	γ	G_x	G_s	G_s/G_x
				$T_{\text{peak}}/^\circ\text{C}$	$Q_{\text{peak}}/\text{J g}^{-1}$					
PMPS1	51500	7.5	0	^a	^a	> 300	—	—	—	—
PMPS2	3300	1.4	0	^a	^a	<< 300	—	—	—	—
BPMPs1	15400	2.1	16	—	—	> 300	—	0.32 ± 0.03	0.66 ± 0.09	2.4
BPMPs2	14500	2.3	24	284	–240	135	1.2	0.45 ± 0.03	0.64 ± 0.06	1.4
BPMPs3	12600	2.2	33	295	–290	110	0.9	0.71 ± 0.02	0.93 ± 0.03	1.3
BPMPs4	9900	1.8	38	299	–350	86	0.8	1.36 ± 0.04	0.98 ± 0.05	0.72
CPMPs1	8000	2.4	23	269	–86	137	1.5	0.85 ± 0.02	0.55 ± 0.04	0.65
CPMPs2	14300	2.1	32	303	–260	60	1.7	0.62 ± 0.02	0.38 ± 0.04	0.61
CPMPs3	13900	2.1	33	299	–305	55	1.9	0.64 ± 0.02	0.30 ± 0.03	0.47
CPMPs4	14000	1.9	39	310	–367	46	1.8	0.83 ± 0.03	0.45 ± 0.04	0.54

^a No distinct peak attributable to melting or decomposition observed



Scheme 1 Polymer degradation accompanying the halomethylation of PMPS

ing indirect evidence for the degradation mechanism given in Scheme 1(a). Peaks are always observed in the ^1H , ^{13}C and ^{29}Si NMR spectra corresponding to terminal methoxy groups and also, occasionally, for terminal SiCl groups, the latter most probably remaining from their incomplete conversion to methoxy groups during the isolation and purification of the precursor PMPS.

Contrary to an earlier explanation that these scission reactions occurred at randomly placed siloxy linkages in the polymer chain, it is now believed that they occur at points of conformational disorder that separate the otherwise extended σ -conjugated sequences²³ in PMPS which are known to be on average approximately 40 repeat units long.¹⁹

The extent of halomethylation was calculated from the ^1H NMR spectra. For both the bromomethylated and chloromethylated samples, a general increase in halomethyl content from XPMS 1–4 ($X = \text{Br}$ or Cl) is indicated by NMR spectroscopy. Two structural features that must be emphasised as being of relevance to the subsequent assessment of the copolymers for lithographic applications are as follows: (i) the NMR, FTIR and UV analyses confirm the copolymers to have the expected statistical structures; (ii) the main position of substitution by the halomethyl groups is the *para* position but previous studies²¹ indicate that a small percentage are in the *meta* position.

Data from the thermal analysis of the copolymers are also given in Table 1. A broad exotherm was observed for all of the samples at temperatures in excess of 250°C . The peak temperatures and the energies of these transitions increase with increasing extent of halomethylation and they are accordingly attributed to thermally induced crosslinking processes. No similar exotherms were observed for the homopolymer samples PMPS 1 and PMPS 2. Polymers for application as resists should be robust under the conditions of lithographic pro-

cessing. To this end, they should have glass transition temperatures in excess of 80°C . Weak glass transition temperatures were observed at 113°C for PMPS 1 and at 96°C for PMPS 2. The difficulty of observing a glass transition temperature for PMPS has previously been noted, however our observations are in accordance with previous observations.^{24,25} Even weaker thermal events were observed in the region $90\text{--}100^\circ\text{C}$ for some of the halomethylated polymers. It is therefore on this basis that the copolymers are considered to have thermal properties that are acceptable for application as resists. However, it must be stated that for the solutions in the casting solvent of the BPMPs series of polymers in particular, significant alterations to their molecular weight distributions were observed to occur over a period of days. This would be a most unattractive feature in the lithographic context.

Lithographic assessments

Lithographic contrast curves for PMPS are shown in Fig. 1, and a representative pair of contrast curves for the copolymer systems are shown in Fig. 2. The lithographic parameters are listed in Table 1.

Unfractionated PMPS 1 displays positive-working behaviour with a very low sensitivity when exposed to the electron beam. Over the same dose range, the fractionated PMPS 2, which is of comparable molecular weight to the BPMPs and CPMPs samples, shows considerably less sensitivity to radiation-induced processes. In a recent study of the radiation chemistry of poly(cyclohexylmethylsilane) it was shown that two values for the radiation chemical yield for chain scission, G_s , could be determined.²⁶ For high and low molecular weight polymers the values were 17.4 and 1.8 respectively. This

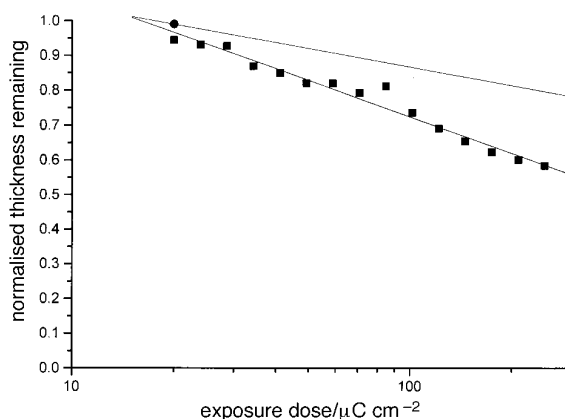


Fig. 1 Representative contrast curves for PMPS: (■) PMPS 1, unfractionated; (●) PMPS 2, fractionated

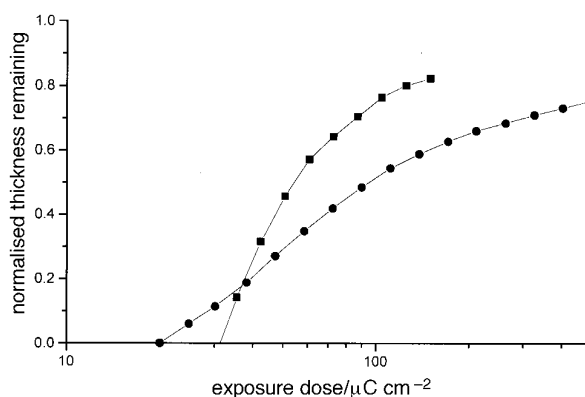


Fig. 2 Representative contrast curves for halomethylated PMPS: (●) BPMPs 3; (■) CPMPs 3

observation accords with the observations of the present study of PMPS and the phenomenon is perhaps more general amongst polysilanes than has previously been recognised. The structures of the high and low molecular weight polysilanes, and in the present context the two PMPS samples, probably differ in one crucial respect. It is likely that the fractionated sample of low molecular weight consists of polymer molecules in which the silicon atoms tend to catenate in all-*trans* sequences, whilst the unfractionated polymer, which has a higher average molecular weight and a bimodal distribution, contains molecules in which the all-*trans* sequences are separated by some linkages that are *gauche*.²⁷ Such linkages continuously translate themselves along the high molecular weight polymer chain when they are in solution and they are considered to be points of weakness in the chain. It is proposed that in the solid state in which these *gauche* linkages are immobilised, they are then the positions that are most vulnerable to scission following electron transfer to the polymer chain such as might occur during irradiation.

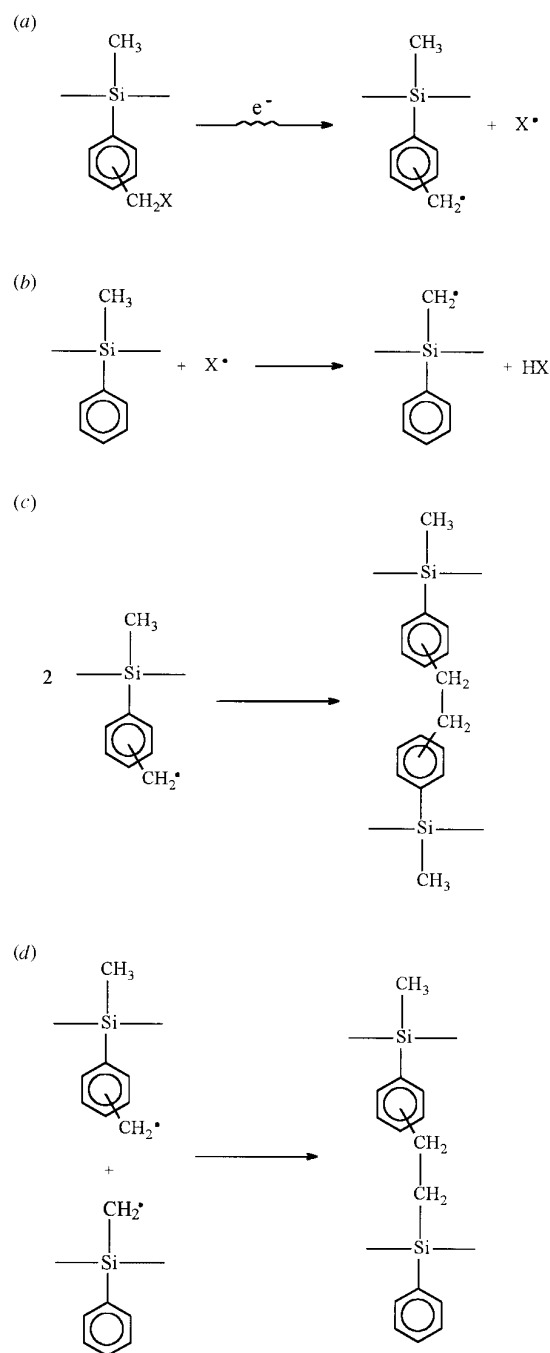
In clear contrast to the positive-working PMPS samples, all the resists of the two copolymer series are negative-working. Although the lithographic sensitivities within each series increase with increasing halomethyl content, the contrasts are low, and are particularly poor for the BPMPS series. The sensitivity variations are to be expected given that the cross-linking sites in these systems are presumed to arise from the halomethyl groups (see Scheme 2) and that scission is expected to remain at a constant level irrespective of halomethyl content, therefore the greater the number of active sites the greater the extent of crosslinking for the same radiation doses. However, it is notable that the BPMPS systems respond more sluggishly than the CPMPS systems and that for both systems the curves tend to normalised thicknesses remaining of only 0.7 to 0.8. This is indicative of a radiation-induced chain scission competing with crosslinking. Furthermore, the contrast curves of Fig. 2 are for bromomethylated and chloromethylated PMPS systems of comparable loadings so it is clear that the replacement of the chloromethyl by bromomethyl groups results in a significantly decreased sensitivity. This is surprising, since the lower bond dissociation energy and the higher reactivity of the C–Br bond when compared with the C–Cl bond (average bond enthalpies at 25 °C of 285 and 339 kJ mol⁻¹, respectively) would be expected to lead to higher lithographic sensitivities for the BPMPS systems. This observation would seem to indicate that the radiation chemistries of the two systems are not directly comparable.

A measure of the relative extents of crosslinking and chain scission can be obtained by plotting the lithographic data for the halomethylated, negative-working systems in accordance with the Charlesby–Pinner equation [eqn. (2)] for radiation-induced crosslinking of polymers with a most-probable (normal) molecular weight distribution.²⁸ From the polydispersities shown in Table 1, the application of the equation is appropriate to the present systems

$$s + \sqrt{s} = G_s/2G_x + 9.65 \times 10^5/M_w G_x r \quad (2)$$

where $s (=1-g)$ is the sol fraction in the exposed region, g being the gel fraction and taken to be equal to the normalised thickness remaining after development, r is the absorbed radiation dose in Mrad and G_s and G_x are the radiation chemical yields for chain scission and crosslinking, respectively.

In Fig. 3 the data points of the representative contrast curves of Fig. 2 are plotted in accordance with eqn. (2). A dose conversion factor of 2 Mrad cm² μC⁻¹ has been applied.²⁹ The values of G_s and G_x , estimated from the slopes and intercepts of these and similar plots for the remaining halomethylated polymers, are listed in Table 1 together with values of the ratio G_s/G_x . Values of G_s/G_x that are at least 4 are usually taken to characterise a potential positive-working resist.³⁰ None of the



Scheme 2 Simple crosslinking mechanism for a halomethylated PMPS (X = Br or Cl)

values in Table 1 even approach this figure but neither are they sufficiently low as to characterise a satisfactory negative-working performance. Taken with the very low sensitivities and poor contrast values, this signifies that on a number of accounts these systems fail as potentially useful electron beam resists. It is nonetheless worthwhile to rationalise the variations of G_s and G_x values with possible radiation chemical mechanisms in order to establish the reasons for the failure of the halomethylated systems in the lithographic context, and to serve that end the variations of the G values with composition are depicted in Figs. 4 and 5. A value of $G_x=0$ is represented for PMPS as it is appears from Fig. 1 that it does not undergo radiation-induced crosslinking.

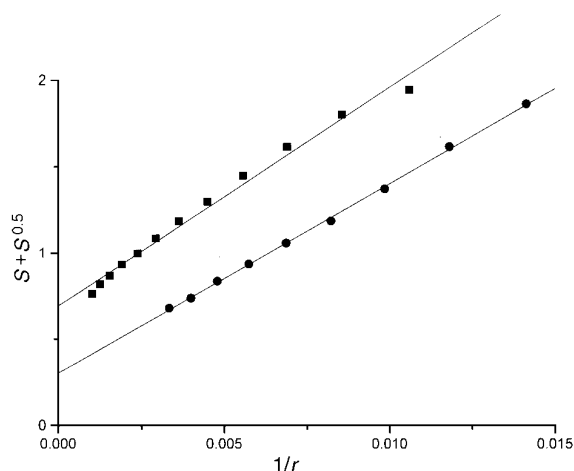


Fig. 3 Charlesby–Pinner plots of the data taken from the contrast curves for BPMPs 3 (●) and CPMPs 3 (■) shown in Fig. 2

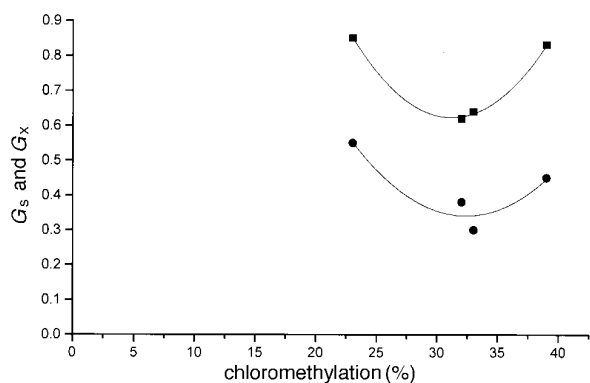


Fig. 4 Variation of the radiation chemical yields for (●) scission (G_s) and (■) crosslinking (G_x) with composition for CPMPs

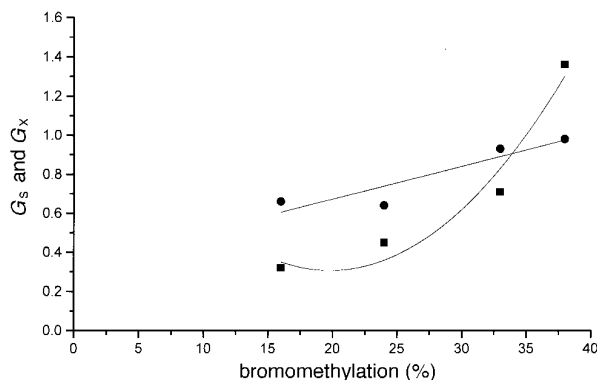


Fig. 5 Variation of the radiation chemical yields for (●) scission (G_s) and (■) crosslinking (G_x) with composition for BPMPs

Discussion

It has previously been shown for the CMS series of resists prepared by statistical copolymerisation of chlorostyrene or chloromethylstyrene with either styrene or methylstyrene, that it is not uncommon for the variation of G_x with composition to display both maximum and minimum values.³¹ The maximum values of G_x in the lithographically useful systems (copolymers of vinyl benzyl chloride and a methylstyrene) are least 2 and they occur in copolymers with chlorine-containing monomer loadings of about 30–40 mol%, at which G_s is effectively zero. Such variations of G_x with composition were

further shown to correlate with a concerted crosslinking reaction of either chain-centred or substituent-centred benzylic radicals which originated from a radiation-induced excited state charge transfer interaction, and evidence for the requisite intermediates was provided from pulse radiolysis studies. This mechanism was assumed to operate over and above the crosslinking mechanism that results from the combination of benzylic radicals formed directly through the radiation-induced scission of carbon–chlorine bonds. Whether or not the details of such processes are accepted, in all the systems studied the optimal values of G_x were found to correlate with copolymer compositions in which there are about 33% halogenated (electron accepting) substituents, the remaining substituents being non-halogenated and therefore electron-donating.

The G_x values of the CPMPs systems display similar variations with composition to those described above but they never attain values that compare favourably with those of the CMS systems. Although only a narrow band of composition has been investigated, it is considered that the composition at maximum G_x , in the region of a 30 mol% chloromethyl loading, is sufficiently close to that found for the CMS systems as to allow the comparison. Within the composition range investigated, the variation of the G_s values with composition appears to follow the G_x values, a feature which might be taken as an indication that scission and crosslinking arise from similar intermediates. This is also the case for those CMS systems in which the two processes, when they occur, can be identified as stemming from chain centred benzylic radicals. It is not possible to identify analogous structures in the CPMPs systems and in the absence of data that are representative of a wider range of compositions it would be unwise to take either these comparisons or the analysis any further, other than to observe that chain scission in the chloromethylated systems is significantly more efficient than in the CMS systems.

There are three reasons why the radiation chemistry of the bromomethylated polymers would differ from that of the chloromethylated polymers: (i) the lesser electronegativity of bromine would not be as favourable as chlorine for excited state charge transfer interactions, (ii) with bromine being a heavier atom than chlorine and the C–Br bond being weaker than the C–Cl bond, there is an increased likelihood of direct scission of the carbon–halogen bond, and (iii) bromine atoms are significantly less reactive than chlorine atoms towards hydrogen atom abstraction.[†] The variation of G values with composition for the BPMPs system are indeed quite different from those of the CPMPs system, though the changes that occur within the narrow composition range investigated are again notable. Whereas both parameters apparently increase linearly up to about 30% bromomethyl content, thereafter G_x undergoes an extremely sharp increase. A $\log_{10}G_x$ versus $\log_{10}[\text{CH}_2\text{Br}]$ plot is shown in Fig. 6 from which it is evident that, whereas G_x varies linearly with bromomethyl content at low values of the latter, at greater values the variation is of a higher order and appears, at the very least, to be in accordance with the square of the bromomethyl content. Any mechanism of radiation-induced crosslinking that is consistent with these observations requires a concerted reaction of increasing probability as the bromomethyl loading is increased. It would be in addition to the crosslinking reaction that follows from the direct formation of benzylic radicals through the radiation-induced scission of carbon–bromine bonds, and it would have to become the dominant crosslinking reaction at high bromomethyl loadings. A possible mechanism is shown in Scheme 3 in which P_{Br} represents a bromomethyl group in the polymer, D represents some kind of proximate association of bromomethyl groups such as a dimer, P is any repeat unit of the

[†] For the reaction $\text{X}^\cdot + \text{CH}_3\text{—H} \rightarrow \text{HX} + \text{CH}_3^\cdot$, the values of ΔH° are estimated to be -4 and -69 kJ mol^{-1} for bromine and chlorine respectively (ref. 28).

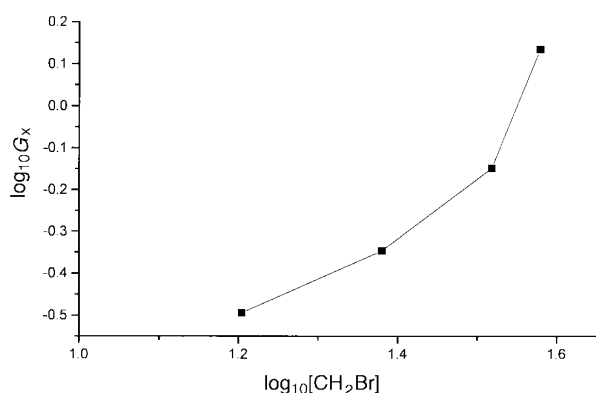
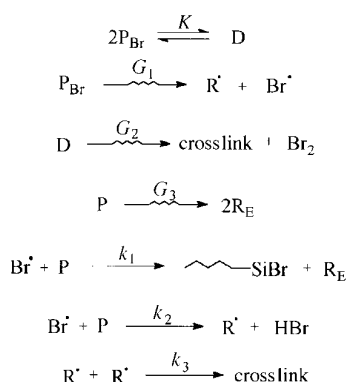


Fig. 6 A log–log plot for the G_x data of Fig. 5



Scheme 3 A representation of a possible mechanism for the radiation chemistry of BPMPS

polymer chain, R' is a substituent-centred benzylic radical or a radical formed by abstraction of a hydrogen atom from a substituent methyl group of the polymer chain, and R_E is a chain end-centred radical resulting from chain scissions. The natures of the other species represented are self evident, and G_1 , G_2 and G_3 are radiation chemical yields for the primary processes represented.

Assuming stationary state conditions for all radical species, it follows that:

$$[Br'] = \frac{G_1 P_{Br}}{k_1 + k_2} \quad (3)$$

so

$$G_x = k_3[R'] + G_2 D = G_1 P_{Br} + k_2 [Br'] P + G_2 D \quad (4)$$

$$= G_1 \{1 + k_1/(k_1 + k_2)\} P_{Br} + G_2 K P_{Br}^2 \quad (5)$$

and

$$G_s P = G_3 P + k_1 [Br'] P = G_3 P + \frac{k_1 G_1 P_{Br} P}{k_1 + k_2} \quad (6)$$

so

$$G_s = G_3 + \frac{k_1 G_1 P_{Br}}{k_1 + k_2} \quad (7)$$

The requisite variations of G_x and G_s are represented in eqns. 5 and 7. At low bromomethyl loadings when the first term of eqn. 5 dominates, G_x is directly proportional to $[P_{Br}]$, but as the loading increases and the probability of bromomethyl groups being in close proximity increases, in accordance with observation the second term assumes a greater importance until it eventually dominates. Also in accordance with observation, eqn. 7 shows G_s varying linearly with P_{Br} and from the

intercept of Fig. 5 the G_s value for PMPS can be estimated to be about 0.3.

Some of the reactions depicted in Scheme 3 are as likely to apply to the CPMPS series as to the BPMPS series of copolymers. The most notable of these is the halogen atom induced chain scission reaction. The apparent greater efficiency with which chain scissions occur in the BPMPS series can be attributed to the bromine atoms being ineffectual at abstracting hydrogen atoms from the methyl substituents of the polymer chain. Without this alternative reaction pathway the bromine atoms are bound to induce chain scissions, *i.e.* $k_1 > k_2$. As indicated above, hydrogen abstraction by chlorine atoms is significantly more exothermic so if chlorine atoms are formed within the CPMPS resists, they have the choice of two reaction pathways. It is reasonable to assume that in this case $k_1 < k_2$.

Conclusion

It is evident that the halomethylated PMPS series of resists are more susceptible to chain scission than their polystyrene counterparts and this can be attributed to halogen atom attack on the polymer backbone in a reaction that is particular to the polysilanes. Chain scission in the CMS series of resists arises from a β -scission reaction following the abstraction of a main chain hydrogen atom from the substituted carbon atom. The polysilanes do not have main chain hydrogen atoms, but the Si–Si bond is weaker than the C–H bond[‡] and is readily susceptible to radical attack. Furthermore, the halomethylated PMPS resists do not undergo crosslinking with comparable efficiency to the chloromethylated polystyrenes or poly(methylstyrenes). For the CPMPS series, in which the effects of chain scission appear to be confined, G_x values of 0.8 would at best make them comparable to the chlorostyrene–methylstyrene copolymer resists. Though greater values of G_x may well be accessible for the BPMPS series of resists at higher bromomethyl contents, not only would the enhanced chain scission reactions preclude their application in e-beam lithography, but so also would their shelf life. Notwithstanding the high silicon content which lends them a high resistance under the conditions of oxygen reactive-ion etching, simple derivatives of PMPS are most unlikely to ever make useful negative-working electron beam resists.

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[‡] The Si–Si bond dissociation energy in $Me_3Si-SiMe_3$ is 337 kJ mol⁻¹ (ref. 32) whilst that of the C–H bond in Et–H is 410 kJ mol⁻¹ (ref. 33).

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