

polymer reports

Excited-state charge-transfer interactions in electron-beam resists based on styrene copolymers*

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Halogenated derivatives of polystyrene that are known to perform as single-stage crosslinking electron-beam resists, such as copolymers of styrene or a methylstyrene with a chlorostyrene or chloromethylstyrene, and similar structures formed by chloromethylation of polystyrene or chlorination of a polymethylstyrene, are shown in general to function through parallel non-interacting radiation-induced crosslinking mechanisms. One of these is the same radical mechanism that would operate within the homopolymers of the constituent comonomers. The other mechanism is characteristic of the systems being copolymers and arises from intramolecular excited-state charge-transfer interactions between adjacent chlorine-containing and non-chlorine-containing units of the polymer chains. Pulse radiolysis studies demonstrate the formation of a transient intermediate in poly(*p*-methylstyrene-*stat-p*-chlorostyrene), the spectrum of which is consistent with that of a methylstyryl radical-cation. The radiation chemical yields for crosslinking derived from the lithographic sensitivities of a range of such systems, are modelled in terms of these mechanisms and the variation with copolymer composition is shown to be in excellent accord with experimental observation.

(Keywords: chlorinated styrene copolymers; radiation-induced crosslinking; exciplex; electron-beam resists)

INTRODUCTION

The use of substituted polystyrene derivatives as negative-working electron-beam resists has been well established for more than a decade. Polystyrene itself was demonstrated to be a high resolution resist when the technology was comparatively young, but it lacks sensitivity to the electron beam and does not display the high lithographic contrast obtainable from comparably sensitive positive-working resists based on poly(methyl methacrylate). However, their sensitivity is markedly increased by partial halogenation, and since the aromatic structure imparts a high dry-etch durability to resists of this class, this, together with their good film-forming capability, has led to their use in the manufacture of application-specific VLSI devices and in mask-making to endure.

It is intended that the copolymers of the title should embrace all the halogenated derivatives of polystyrene, but the most important examples of this class of resist are polystyrenes or poly(methylstyrene)s that have been partially ring-substituted with chloromethyl groups. These include chloromethylated polystyrenes^{1,2}, chlorinated poly(methylstyrene)s^{3,4} and copolymers of a methylstyrene with chloromethylstyrene^{5,6}. The last materials carry the advantage that the content of chlorine-containing units can be varied from 0 to 100% without backbone chlorination; however, the molecular

weights and polydispersities are confined to those attainable through free radical polymerization, which limits the resist contrast. Nonetheless, copolymerization has been advocated by Ledwith *et al.*⁵ for achieving substituent positional specificity in investigations of the radiation chemistry of such resist materials, and the ready availability of all of the isomers of chlorostyrene has expedited studies of the kind reported in this paper.

Ready explanations for most of the experimental observations of the lithographic properties of these resist materials have been found in terms of theories of radiation chemistry of polymers⁷⁻⁹, or in terms of radical reactivities¹⁰. The subject of this paper is the variation of lithographic sensitivity with chlorine content and, in particular, the sharp increase in sensitivity that follows from the incorporation of only a small amount of halogen, for which satisfactory explanations have not been forthcoming, even though the effects are central to the successful exploitation of these resists. This paper demonstrates that it is possible to explain, correlate and model these variations with composition, in terms of the radiation chemical yield for crosslinking (G_x) based on parallel non-interacting radiation-induced crosslinking mechanisms for these and all similar copolymer systems.

EXPERIMENTAL

Materials

Styrene (S), 4-methylstyrene (*p*-methylstyrene, *p*MS), 3-methylstyrene (*m*-methylstyrene, *m*MS), 2-methylstyrene (*o*-methylstyrene, *o*MS), 4-chlorostyrene (*p*-chlorostyrene,

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*p*CS), 3-chlorostyrene (*m*-chlorostyrene, *m*CS) and 2-chlorostyrene (*o*-chlorostyrene, *o*CS) were supplied by Lancaster Synthesis Ltd. Chloromethylstyrene (vinyl benzyl chloride, VBC) and 4-*tert*-butylstyrene (*p*-*t*-butylstyrene, *pt*BS) were supplied by Polysciences Inc. The monomers were distilled at 40–50°C under reduced pressure prior to use. Polymerizations were carried out in stoppered boiling tubes. A total of 6 ml of monomers together with 10 ml of dry toluene and an appropriate amount of 2,2'-azobisisobutyronitrile were deaerated with dry argon for 15 min before the tubes were immersed for approximately 5 h in a water bath maintained at 70°C. Polymers were precipitated by addition to a large excess of methanol, reprecipitated from toluene solution, filtered and dried at 80°C.

Apparatus and procedures

Copolymer compositions were established from ¹³C n.m.r. spectra obtained using a Jeol JNM-GX270 spectrometer operating at 67.8 MHz. Chemical shifts were relative to tetramethylsilane. Peak area measurements were achieved using inverse-gated decoupling with a 5 s pulse delay. Monomer reactivity ratios were estimated by curve fitting to the feed composition–polymer composition data using non-linear regression analysis in accordance with the 'terminal' model of monomer reactivity. Table 1 presents the reactivity ratios for the free radical copolymerizations of relevance to the present studies.

Molecular weights were obtained as linear polystyrene equivalents using high performance liquid chromatography equipment supplied by Polymer Laboratories Ltd and equipped with a 5 μm PL gel dual column bank of 10⁴ and 500 Å porosity.

Thin films of the polymers, approximately 0.5 μm thick, were spin-coated from 10% solutions in chlorobenzene onto 76 mm silicon wafers using a Headway EC-101 spinner and prebaked at 120°C for 30 min. The wafers were cut into quadrants for lithographic assessments of the resists. Film thicknesses before and after exposure were measured using a Taylor Hobson Talystep.

Lithographic assessment was accomplished using a Cambridge Instruments EBMF-2 electron-beam lithography tool operating at 20 kV accelerating potential. Exposed resists were developed in methylisobutylketone (MIBK) for 60 s, rinsed in isopropanol for 30 s and dried in a stream of nitrogen. Sensitivities were estimated as

the dose corresponding to 50% thickness remaining after development ($D_n^{0.5}$). All thicknesses were normalized to the original spun thickness.

Radiation chemical yields for crosslinking (G_x) and chain scission (G_s) were determined in accordance with the method described by Hartney⁹, using the approximations to radiation dose and gel fraction developed by Novembre and Bowmer¹¹, in a best fit of lithographic data to Inokuti's equation¹².

Polymer samples for pulse radiolysis studies were prepared as 5 mm diameter glassy cylinders with their faces polished to an optical quality. Pulse radiolyses of the samples with 50 or 100 ns duration pulses of 2.5 MeV electrons were generated by a High Voltage Engineering (Europa) KS-3000 Van de Graaff accelerator. The estimated dose per pulse was 1.8 krad. The analysing light beam for absorption measurements was a flash of 5 ms duration from a nominally 250 W xenon arc lamp briefly pulsed to about 100 times normal brightness. Photodetectors used were an EMI 9781 photomultiplier with 6 ns rise-time (240–600 nm wavelength range), a Hamamatsu S1722-0.2 silicon photodiode with 2 ns rise-time (400–1100 nm wavelength range) and a Barnes Engineering A-100 indium arsenide photodiode with 80 ns rise-time (900–1500 nm wavelength range).

RESULTS AND DISCUSSION

It has been suggested^{13,14} that lithographic sensitivity, $D_n^{0.5}$, varies with composition in a linear fashion between the limits set by the homopolymers of the component comonomers. It is clear from Figure 1, which depicts the variation of intrinsic sensitivity ($1/R^{0.5}\overline{M}_w$)* with composition for the representative copolymers of *p*MS and VBC (Figure 1a) and of *o*MS and *p*CS (Figure 1b), that this suggestion is erroneous. Indeed, it is our experience and that of others, that non-linearity of such plots is the rule rather than the exception. With the exception of one *p*CS/*o*MS copolymer of low *p*CS content, the intrinsic sensitivities of all of the copolymers of that

* $R^{0.5}$, the absorbed dose in Mrad, is derived from $D_n^{0.5}$ (ref. 11) and \overline{M}_w is the weight average molecular weight of the polymer. This is by far the most useful way of expressing sensitivity for this class of resist as not only does it take account of the variation of sensitivity with the molecular weight of the polymer but it is also a parameter that increases with increasing sensitivity

Table 1 Copolymerization reactivity ratios and G_x curve parameters

Monomer A	Monomer B	r_A	r_B	$r_A r_B$	K	A	B
<i>p</i> CS	<i>o</i> MS	1.406	0.353	0.496	5.44	0.35	0.05
<i>p</i> CS	<i>p</i> MS	0.919	0.543	0.499	8.36	0.31	0.09
<i>p</i> CS	S	0.924	0.697	0.644	6.44	0.48	0.04
VBC	<i>p</i> MS	0.997	0.426	0.425	17.84	1.89	0.09
<i>o</i> CS	<i>p</i> MS	1.422	0.616	0.876	7.84	-0.01	0.09
<i>o</i> CS	<i>o</i> MS	1.678	0.466	0.782	2.84	0.03	0.05
<i>m</i> CS	<i>p</i> MS	0.939	0.455	0.427	8.00	0.32	0.09
<i>p</i> CS	<i>m</i> MS	1.061	0.757	0.803	9.60	0.43	0.09
<i>p</i> CS	<i>pt</i> BS	0.988	0.596	0.590	1.44	0.49	0.03
VBC	<i>p</i> CS	0.970	0.810	0.785	~0	1.95	0.30
VBC	<i>o</i> CS	1.108	0.870	0.964	~0	1.95	0.30
VBC	<i>m</i> CS	0.881	0.699	0.616	~0	1.95	0.30

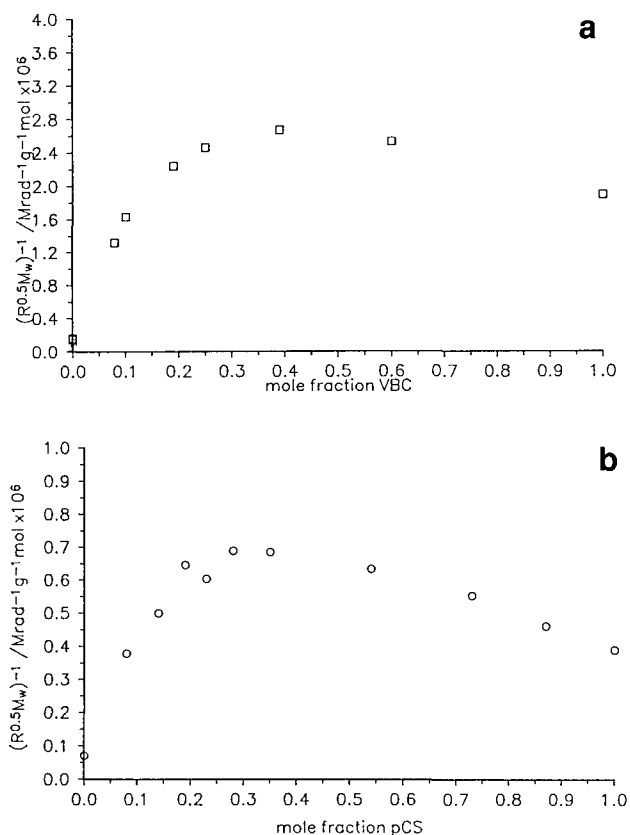


Figure 1 Variation of intrinsic sensitivity with composition for (a) poly(pMS-stat-VBC) and (b) poly(oMS-stat-pCS)

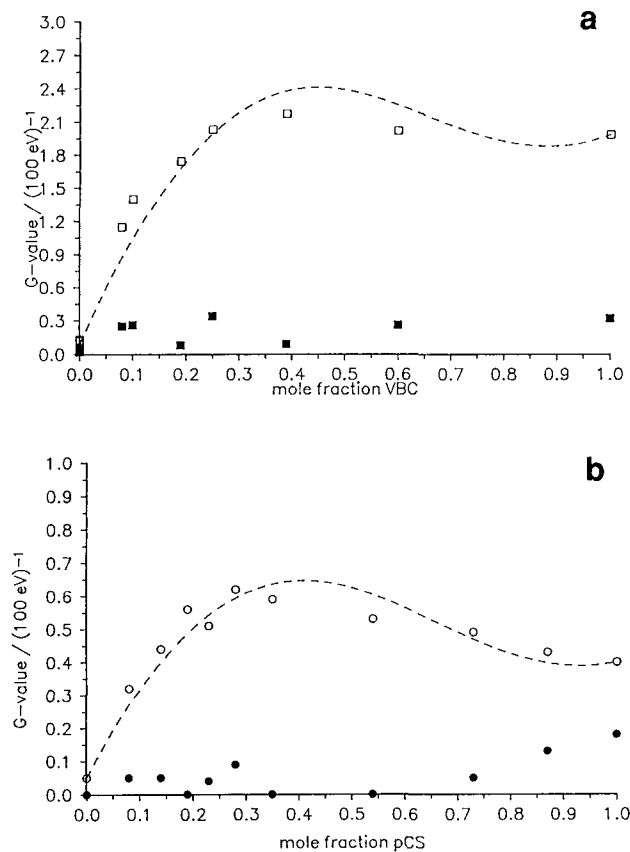


Figure 2 Variations of radiation chemical yields for crosslinking and chain scission with composition for (a) poly(pMS-stat-VBC) and (b) poly(oMS-stat-pCS): \square , \circ , G_x ; \blacksquare , \bullet , G_s

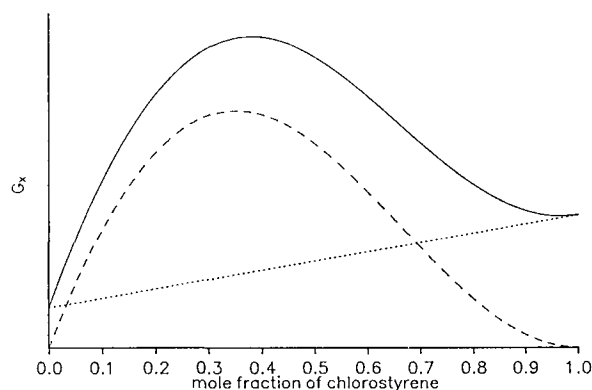


Figure 3 Representation of the contributions of the crosslinking mechanisms to G_x : type 1; ----, type 2; —, total

series are greater than those of either of the relevant homopolymers. A similar effect has been reported by Whipps¹⁵ for copolymers of styrene and pCS.

It can be seen from Figure 2 that intrinsic sensitivities essentially follow the variations determined by G_x in these systems in which G_s is generally negligible. In either case the plots are asymmetric, with maxima at compositions corresponding to a pCS content of between 25 and 35%. The sketch of Figure 3 shows that the variations of Figure 2 can be considered to be compounded from (1) a linear variation of G_x with the mole fraction of the chlorine-containing monomer in the copolymer between the limits set by the homopolymers, and (2) an independent variation with composition that reaches a maximum at some intermediate value and which arises solely because the resist systems are copolymers rather than blends of homopolymers. The first variation is readily attributable to the proportional contributions to the crosslinking from the mechanisms that would be prevalent in the homopolymers; these are presumed to be by combinations of radicals formed by simple radiation-induced homolytic bond fissions. However, the second variation has to be attributed to mechanisms that arise uniquely from adjacency of the two different monomers in the copolymers, which are thus dependent on copolymer sequence distributions. Typically this might arise if an intramolecular excited-state charge-transfer complex were involved in the copolymer radiation-induced crosslinking process.

Figure 4 shows the transient spectra that result from the pulse radiolysis of samples of poly(pMS), poly(pCS) and a copolymer of the two with a composition corresponding approximately to the maxima in Figure 2 at about 30 mol% of the chlorine-containing monomer. The copolymer displays transient absorption bands characteristic of those found for the homopolymers, possibly of precursor species to those that might be responsible for the linear variations of type (1) above, although the absorption at 1300 nm for poly(pCS) is thought to be a vibrational overtone. It also displays an entirely new band at 970 nm, which is in the spectral region commonly associated with aromatic radical cations. Toluene, which may be considered as a low molecular weight analogue of the non-chlorinated component of these copolymer systems, shows a strong absorption at about 1000 nm when it is γ irradiated in a glass at 77 K; this has been attributed to the tolyl radical cation¹⁶.

On the basis of the above observations, the crosslinking mechanism of *Scheme 1* (represented for an MS/CS system) is proposed to explain the variations of type 2 above, for those copolymers for which an excited-state charge-transfer interaction would be expected (it is thought that crosslinks would be the product state of the third reaction, but for clarity it is not represented). Such interactions would not be expected if the component monomers of the copolymer were both electron acceptors (or electron donors). Poly(CS-*stat*-VBC)s are such cases and the variations of G_x with composition for these copolymers are shown in *Figure 5*. Consistent with these arguments, only the linear variations that would be

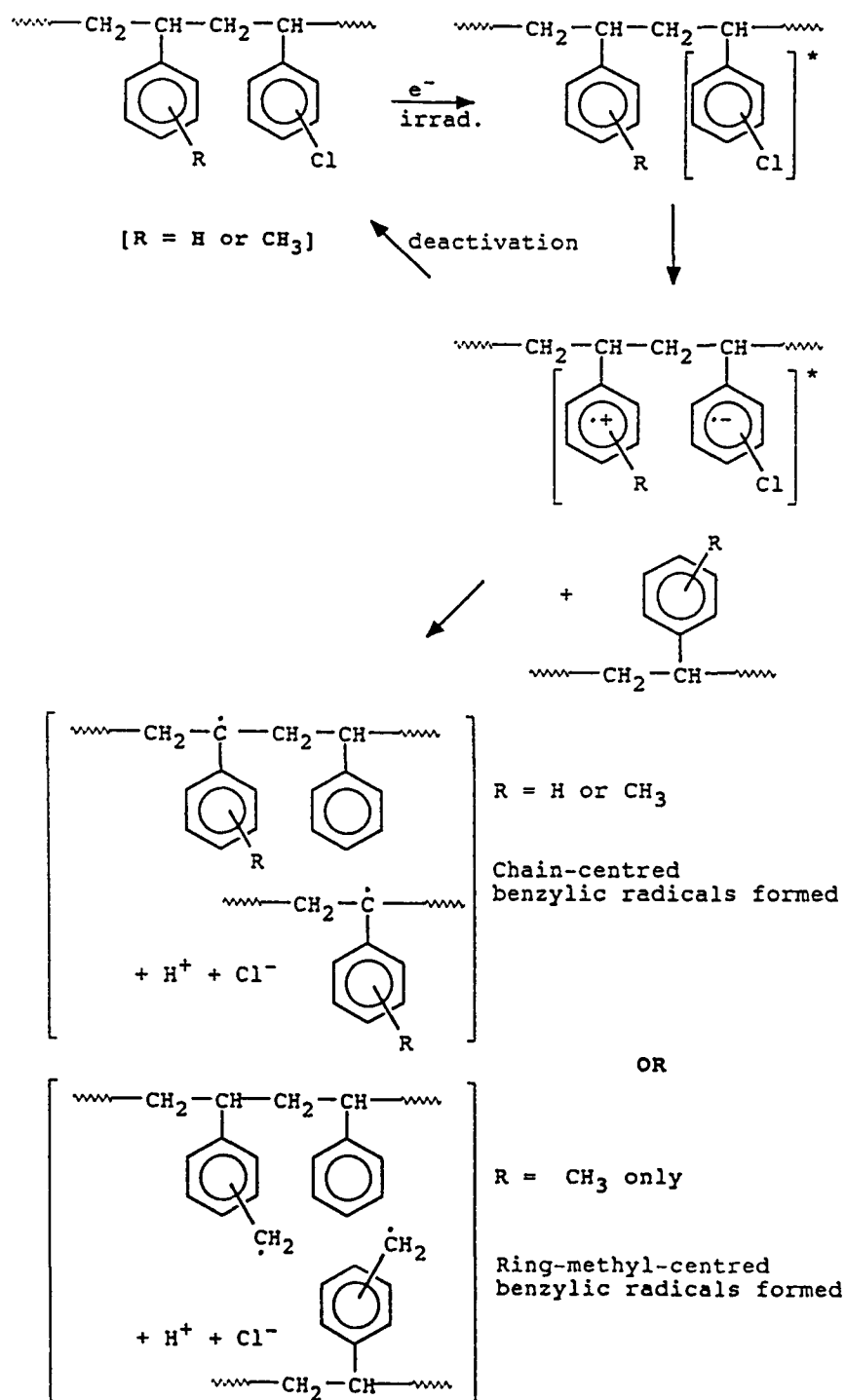
expected to arise from the mechanisms of type 1 are evident.

We have previously shown that the probability of crosslinking, P , by this mechanism can be represented by an expression of the form:

$$P \propto \frac{4m_A m_B^2}{1 + [1 + 4m_A m_B (r_A r_B - 1)]^{1/2}} \quad (1)$$

where m_A and m_B are the mole fractions of CS and MS in the copolymer, respectively, and r_A and r_B are the corresponding copolymerization reactivity ratios¹⁷.

Assuming that the crosslinking mechanism inherent to the homopolymers leads to a linearly varying



Scheme 1

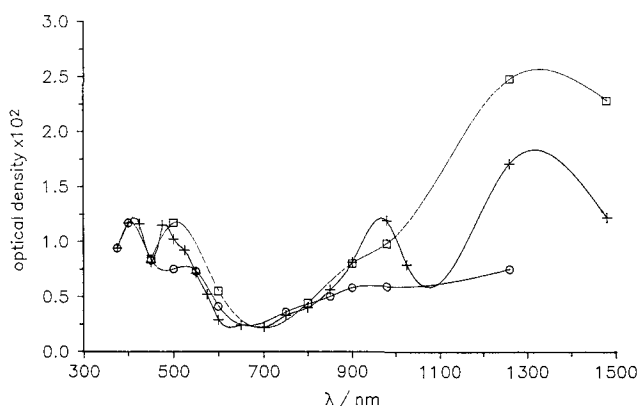


Figure 4 Absorption spectra of transients generated by pulse radiolysis of polymer samples: +, poly(*pMS-stat-pCS*); O, poly(*pMS*); □, poly(*pCS*)

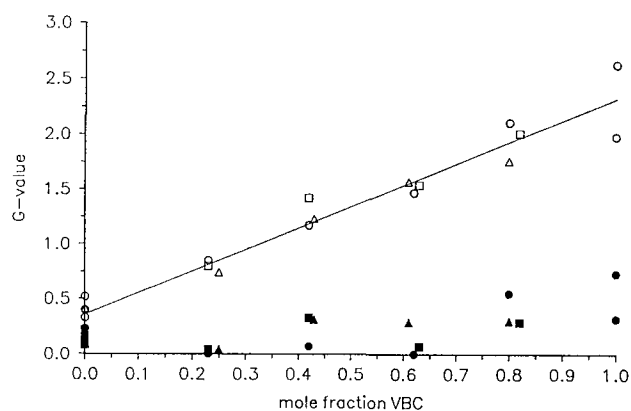


Figure 5 Variations of radiation chemical yields for crosslinking and chain scission with composition for poly(*CS-stat-VBC*): ●, G_s , *pCS/VBC*; ○, G_x , *pCS/VBC*; ■, G_s , *oCS/VBC*; □, G_x , *oCS/VBC*; ▲, G_s , *mCS/VBC*; △, G_x , *mCS/VBC*

contribution to G_x over the whole composition range, then G_x will be given by:

$$G_x = \frac{K m_A m_B^2}{1 + [1 + 4 m_A m_B (r_A r_B - 1)]^{1/2}} + A m_A + B \quad (2)$$

where K , A and B are constants.

For the *oMS/pCS* system, by inspection, $A=0.35$ and $B=0.05$. It is thus possible to determine optimum values of K by the application of a least-squares fitting routine to the data of Figure 2b. The lines represented on Figure 2 have been determined in this way. The fit is quite acceptable for both systems, but it is particularly so for the *pCS/oMS* system, for which the data points are abundant.

The parameter, K , gives a measure of the combined probabilities of the three forward processes for a given system. The variations of lithographic sensitivity with composition have been investigated in this way for a number of systems and the resulting K values are

represented in Table 1. It is clear that the larger values are observed for those systems in which the donor-acceptor interaction is perceived to be greater and in which the product state is driven by the intermediacy of benzylic radicals. The particularly large value of K for the *pMS/VBC* system explains the sharp increase in lithographic sensitivity which is observed when only 5% of VBC is incorporated in the copolymer, or when similarly low levels of chlorine are achieved by chlorination of poly(*pMS*). Furthermore, it is important to note that the crosslinking mechanism of Scheme 1 is by far the most dominant of the various crosslinking mechanisms that have previously been reported or proposed for optimum resist formulations of halogenated polystyrene derivatives.

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