The effect of radiation on comb block copolymers

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(Received 18 February 1986; revised 15 October 1986; accepted 17 October 1986)

In order to increase the plasma etch resistance of photoresists, comb-shaped block copolymers have been prepared with radiation resistant sidechains and radiation sensitive backbones. The sidechains were polystyrene, and the backbones were poly(methyl methacrylate) or poly(alkene sulphones). It was found possible to synthesize these block copolymers with up to 50% of the radiation resistant sidechains by anionic grafting for poly(methyl methacrylate). In the case of the polysulphones, an initial polystyrene containing a terminal alkene group was synthesized. This was copolymerized with the alkene and sulphur dioxide by a radical reaction. The radiation sensitivity of the copolymers was then studied.

(Keywords: comb block copolymers; irradiation; plasma etch resistance; photo resists)

INTRODUCTION

The use of polymers in photolithography frequently requires polymer properties which tend to be mutually opposed[1]. For example, photoresists of high molecular weight are desirable to maximize the effect of chain scission on molecular weight, whilst the resulting high viscosity of the polymer solution presents difficulties in obtaining levelling during spin coating. Also, the required high sensitivity to radiation presents difficulties if it is wished to plasma etch the substrate after development. It is possible that a compromise might be effected by using comb shaped block copolymers in which a radiation sensitive high molecular weight backbone polymer is combined with many comparatively short, radiation resistant, side chains. Then, rapid molecular weight decrease might be achieved in irradiated areas for subsequent solvent development, but the residual polymer in non-irradiated areas could retain high etch-resistance. Moreover because comb shaped polymers with side chains that are short compared with the backbone have a solution viscosity governed mainly by the length of the backbone, for a given overall molecular weight the viscosity would be lower than for a linear polymer of comparable molecular weight.

To pursue this concept two types of comb block copolymers have been prepared and studied; first, poly(methyl methacrylate) (PMMA) with polystyrene (PS) side chains, and secondly poly(alkene sulphones) with PS side chains (*Figure 1*). The first polymer was prepared by reacting an anionically prepared PMMA with the living ends of anionically prepared PS, the method used by Rempp *et al.*[2] to prepare a series of well-characterized graft copolymers. The second were prepared by first preparing by anionic polymerization a PS containing a 1-butene endgroup, then copolymerizing this polymer into a poly(alkene sulphone) by the radical copolymerization of sulphur dioxide with either 1-butene or cyclohexene. This is following the technique used by several previous workers who have established that the presence of the polymer chain has minor effects on the reactivity of the end group[3-5].

EXPERIMENTAL

The monomers and solvents for the anionically prepared polymers were purified as described before[6,7] with all manipulations performed under vacuum. The cyclohexene, 1-butene and sulphur dioxide were dried with drierite and stored on a vacuum line.

The PMMA was prepared in THF solution at $-78°C$ using cumylcaesium as the initiator[8]. The cumylcaesium was prepared by the action of caesium on cumyl methyl ether at room temperature. The solution was cooled to $-78°C$ to precipitate the methoxide and then filtered through a fitted disk and subdivided into a number of breakseal fitted tubes. The methyl methacrylate in THF solution was added rapidly to the THF solution of the initiator with vigorous agitation. The reaction was left for 30 min to go to completion before adding the living PS at $-70°C$[2]. The solution was then allowed to come to room temperature and left overnight. The solution slowly decoloured over this period as the styryl carbanions reacted. Finally a little methanol was added. The isolated polymer showed only a single peak in the g.p.c. with no evidence for homopolystyrene. The percentage of PS measured by u.v. and n.m.r. was in reasonable agreement with the calculated amount.

The living polystyrene was prepared in benzene solution using 2-butyllithium as the initiator at room temperature. The PS containing the 1-butene endgroup ($M_w \sim 9000$) was also prepared in benzene but using 4-lithio butene-1 as the initiator with a little THF (*ca.* 0.5%) added to speed up the initiation. This initiator was prepared by the action of lithium dispersion on the corresponding mercury compound prepared from the Grignard reagent of 4-chlorobutene-1 and mercuric chloride. The sulphone polymers were prepared after the methods of Ivin *et al.*, using either u.v. initiation or silver nitrate as initiator[9].

0032-3861/87/060881-04$03.00

The γ-irradiations were done in a cobalt 60 cell with a flux of 1.2 Mrad/hour. The samples of polymer were freezedried and sealed under vacuum, except for the non PS containing sulphones, which were used as precipitated powder under vacuum. The u.v.-irradiations were made in air on films spun usually on quartz discs, although a few were done on silicon wafers. The u.v. source (254 nm) was a low pressure mercury arc. The radiation dose was restricted to that which would be lithographically useful.

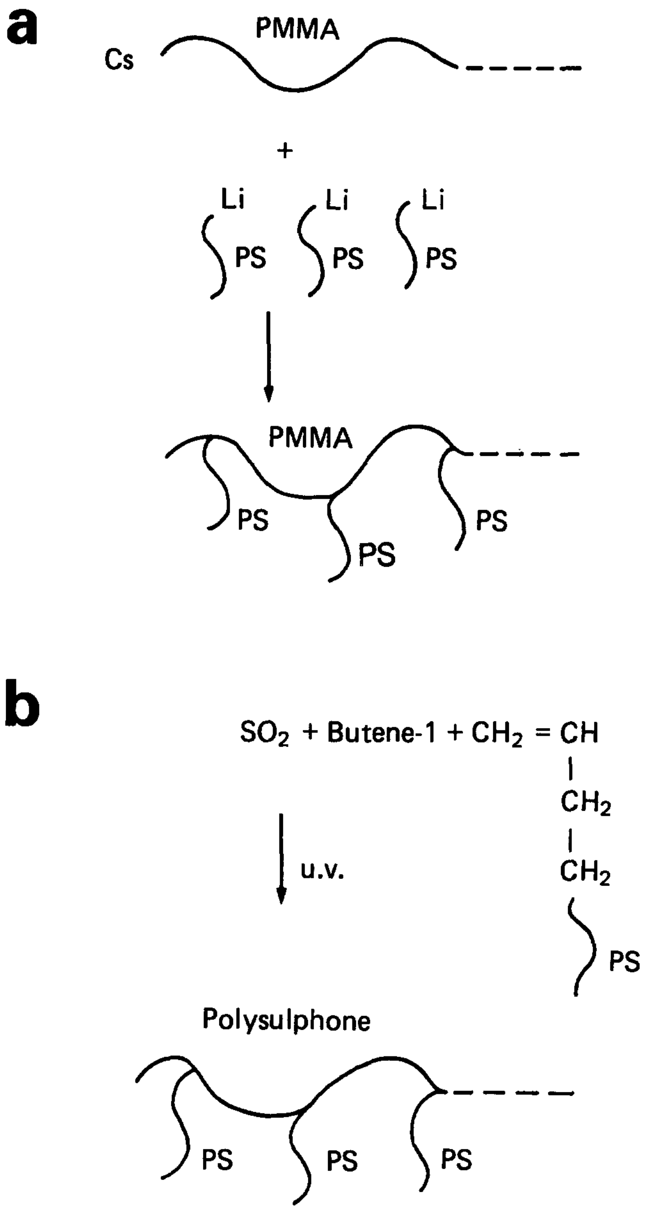

Figure 1 Schemes for the preparation of (a) PMMA-graft PS; (b) polysulphone-graft PS

RESULTS

The PMMA backbone prepared in this fashion showed a reasonably monodisperse molecular weight distribution when studied by g.p.c. on a set of Styragel columns. The M_w/M_n ratios were in the range 1.15 to 1.23 uncorrected for column broadening compared to 1.14 for a monodisperse PS standard. The PS/PMMA comb copolymer retained the same profile on the high molecular weight side of the g.p.c. trace, but a low molecular weight tail developed and the uncorrected M_w/M_n ratio increased to about 1.4 (*Table 1*). It appears that in grafting the polystyrene chains on the PMMA backbone some scission of the backbone occurs. The actual values which were calculated for the molecular weight using a polystyrene calibration, although fairly satisfactory for PMMA, are probably doubtful when applied to a comb shaped block copolymer, because hydrodynamic volumes appear to change little with comparatively short chain branching[10]. This is reflected, as anticipated, in the solution viscosity of these polymers, which changes little as the branching increases (*Table 2*).

The sulphone polymers had a broad distribution. It was found that the butene-1 end group of the polystyrene had a low reactivity compared to butene-1 itself. In general the reactivity ratios of alkenes change little unless there are two substituents on one carbon of the double bond[11]. Hence one could expect the polymeric endgroup to be equally as reactive as the butene-1, in which case the polymeric monomer and the butene-1 could be expected to be incorporated into the polymer in the same ratio as the weight feed. The rate of incorporation found was only half this[3,4]. Cyclohexene was also found to give a similar effect, but as the ceiling temperature for this material is only 24°C the temperature also had a large effect on the incorporation of the polystyrene. However, to obtain polymers of high molecular weight it was necessary to work at temperatures well below the ceiling temperature.

Irradiation

The PMMA copolymers were found to be sensitive to both γ-rays and u.v.-irradiation, but the behaviour to the two types of radiation differed greatly. Studies on PMMA have indicated similar radicals produced by u.v. and γ-

Table 1 Characterization of copolymers[a]

% Styrene	PS[b] $M_w \times 10^{-3}$ g.p.c.	PMMA[b] $M_w \times 10^{-5}$ g.p.c.	Copolymer[b] $M_w \times 10^{-5}$ g.p.c.	Copolymer M_w/M_n g.p.c.	$G_{(s)}$[c]
66	4.7	1.06	1.87	1.40	–
56	3.7	4.16	4.24	1.87	0.5
43	3.1	3.94	4.66	1.63	0.7
45	22	1.62	2.02	1.36	0.5
22	3.8	3.81	3.99	1.47	–
22	4.5	1.30	1.50	1.36	–
10	3.2	3.92	4.27	1.36	0.7

[a] Backbone all PMMA, branches all PS

[b] G.p.c. weight-average molecular weight assuming a PS calibration with no correction for broadening. PS values are the molecular weights of the individual branches

[c] Found for PMMA 0.9

Table 2 Viscosity of polymers

PMMA		Copolymer	
M_w $\times 10^{-5}$	Viscosity (cP)	% Styrene	Viscosity (cP)
1.3	0.42	22	0.43
3.8	0.86	22	0.82
3.94	–	43	0.83
4.16	–	56	0.70

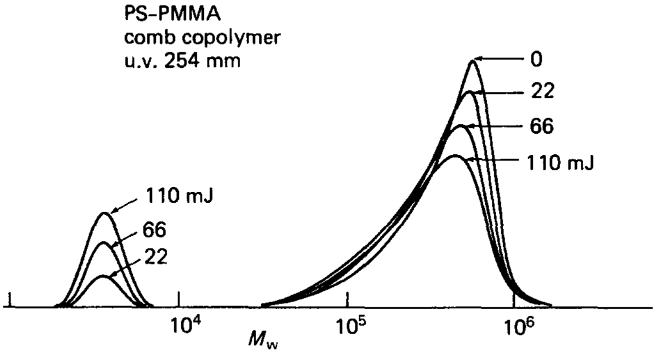

Figure 2 Effect of u.v. irradiation of 1 μm films of PS/PMMA comb copolymers in air. G.p.c. traces of the initial polymer and after irradiation at 254 nm. The peak at M_w 5000 corresponds to the initial polystyrene

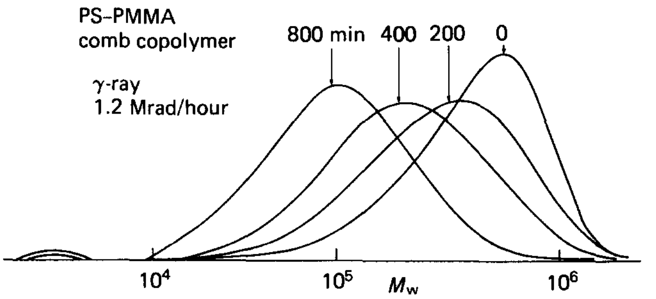

Figure 3 Effect of ^{60}Co γ-ray irradiation of PS/PMMA comb copolymer powder under vacuum. G.p.c. traces of the initial polymer and after 200, 400 and 800 min irradiation

ray irradiation, and perhaps similar ratios of backbone chain cleavage and sidechain elimination would have been expected[12]. The major scission reaction for the u.v. was to remove the PS side chains (*Figure* 2), with only moderate cleaving of the backbone. The PS is attached to the PMMA via a carbonyl group, and it is possible that as the polystyrene is the major u.v. absorber in the copolymer, the energy absorbed in this chain is transmitted along the chain to the sensitive carbonyl linkage to cause excess rupture at this link point.

With γ-rays, however, the main reaction was backbone scission with only minor elimination of side chains (*Figure 2*). It is difficult to find an appropriate way in which to calculate *G* values for these irradiations because of the problem in ascertaining meaningful molecular weights, particularly when substantial sidechain elimination results in a mixture of products. However the γ-irradiation of these PMMA–PS combs gave a reasonably homogeneous product and $G_{(s)}$ values were calculated. ($G_{(s)}$ and $G_{(x)}$ are the yields of scission and crosslinking products.) There appears to be a small reduction in $G_{(s)}$ when polystyrene branches are introduced. $G_{(x)}$ was calculated also but was small, in the region of 0.03 (*Figure 3*).

U.v.-irradiation of the sulphone PS block copolymers left the polymer virtually unchanged as expected from the lack of u.v. sensitive groups in the backbone polymer. γ-irradiation did, however, produce marked degradation (*Table 3*). In the case of 1-butene based copolymer, main chain cleavage was the major reaction, although some of the polystyrene chains were liberated. The polymer with PS sidechains appears to have a slightly lower rate of breakdown of the backbone polysulphone compared with the normal polysulphone, as was found for the PMMA case.

The γ-irradiations were performed at 35°C, the temperature of the cobalt cell cavity, about 10°C higher than the ceiling temperature of the poly(cyclohexene sulphone). When this polymer was irradiated chain cleavage was accompanied by depolymerization of the chain and considerable weight loss to the polymer occurred (*Table 4*). Because of the unzipping of the backbone chain a considerable amount of the polystyrene was liberated, and at the same time there was a marked reduction in the molecular weight of the residual copolymer, *Figure 4*. It appears once again that the

Table 3 γ-Irradiation effects on poly(1-butenesulphone)

Polymer	Dose (Mrad)	Backbone cuts per 10^6 M_w
Polybutene	1.2	0.8
Sulphone	3.6	5.3
$M_w = 3.96 \times 10^6$	6.0	12.8
Polybutene	1.2	1.6
Sulphone/PS	3.6	4.6
$M_w = 4.74 \times 10^5$	6.0	8.3
39% PS		

Table 4 γ-Irradiation effects on poly(cyclohexenesulphone)

Polymer	Dose (Mrad)	Backbone cuts per 10^6 M_w	Wt. loss (% of total)
	1.2	5.6	–
Polycyclohexene	3.6	29.0	36
Sulphone	6.0	35.9	–
	1.2	1.9	–
Polycyclohexene	3.6	6.6	30
Sulphone/PS	6.0	9.8	–
51% PS			

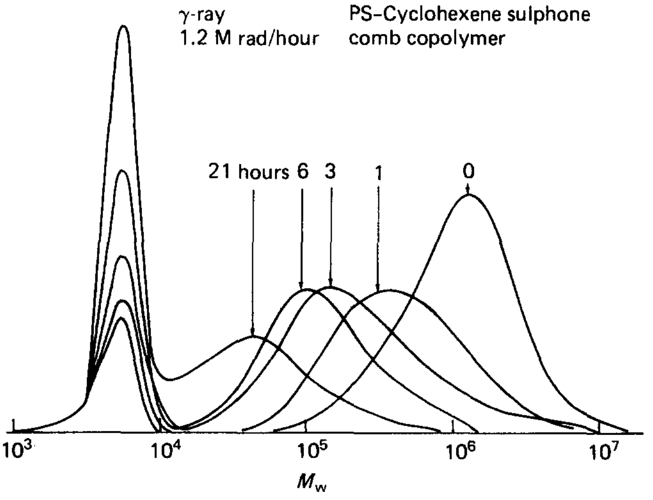

Figure 4 Effect of ^{60}Co γ-ray irradiation of PS/poly(cyclohexene-sulphone) comb copolymer powder under vacuum. G.p.c. traces of the initial polymer and after irradiation. The peak at $M_w = 5000$ corresponds to the initial polystyrene

polystyrene affords some protection to the polysulphone as the rate of loss of molecular weight of the pure cyclohexene–sulphone copolymer was more rapid.

In conclusion, it seems that it is possible to build these comb shaped block copolymers, which are sensitive to radiation, but which, due to their high polystyrene content, should have better etch-resistance. The use of backbone polymers with low ceiling temperatures is also seen to be an advantage, by the principle of chemical amplification[13].

ACKNOWLEDGEMENT

The authors would like to thank Professor J. M. J. Frechet of the University of Ottawa for the use of some of his facilities, and for useful discussion.

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