Electron-Sensitive Resists. II. Positive Resists Derived from High Polymers of Methyl Methacrylate, Methyl α-Chloroacrylate, and Hexyl Methacrylate

JUEY H. LAI and SURESH SHRAWAGI, *Honeywell Corporate Research Center, Bloomington, Minnesota 55420*

Synopsis

This paper reports the synthesis, characterization, and evaluation of copolymers of methyl methacrylate (MMA) and hexyl methacrylate (HMA) and of HMA and methyl α-chloroacrylate (MCA) and of terpolymers of MMA, MCA, and HMA as electron-sensitive positive resists. The sensitivities of the resists were found to be strongly dependent on the composition. Two of the terpolymers were found to be significantly more sensitive than poly(methyl methacrylate) (PMMA).

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a well-known electron resist and is probably one of the more widely used positive resists.[1] PMMA has adequate resolution and acceptable resist properties, but its sensitivity of $\simeq 5 \times 10^{-5}$ coulomb/cm^2 at 15 kV is inconveniently low.[1,2] In recent years, the search for a more sensitive positive resist has led to the development of other resists such as poly(olefin sulfones),[3] poly(methyl isopropenyl ketone),[4] poly(methyl methacrylate–*co*–isobutylene),[5] and poly(methyl methacrylate–*co*–acrylonitrile).[6] The minimum dose required to pattern these resists is generally lower than 1×10^{-5} coulomb/cm^2 but higher than 1×10^{-6} coulomb/cm^2. Poly(butene-1-sulfone),[3] which appears to be the most sensitive, requires a minimum dose of 1×10^{-6} coulomb/cm^2.

It is well known that degradation of a positive resist occurs through the scission of main chain bonds. Chemical and steric configurations which tend to weaken the main chain stability of a polymer, e.g., a polar substituent at the quaternary carbon or a bulky side group, may also increase the radiation degradation susceptibility of the polymer. Poly(methyl α-chloroacrylate) (PMCA) and the copolymers of methyl methacrylate–methyl α-chloroacrylate [poly(MMA–*co*–MCA)] have been reported recently[7] to be more susceptible to radiation degradation than PMMA, and this has been attributed to an electron withdrawing effect of the chlorine atom on the quaternary carbon. In a previous paper,[8] we reported our studies of PMCA and poly(MMA–*co*–MCA) as electron-sensitive positive resists. We found that both PMCA and the copolymers were more sensitive than PMMA. We also found that crosslinking predominated in PMCA when the electron dose exceeded 6×10^{-4} coulomb/cm^2.

Although increasing the length of the alkyl group in the methacrylate polymer is known to decrease the glass transition temperature of the polymers significantly,[9] its effect on the radiation susceptibility of the polymers has not been fully studied.

In this paper, we wish to report our studies of electron resists derived from copolymers of methyl methacrylate (MMA) and hexyl methacrylate (HMA), copolymers of HMA and methyl α-chloroacrylate (MCA) and terpolymers of MMA, HMA, and MCA.

It has been found that the sensitivity of the resists is strongly dependent on the composition, and two of the terpolymers are significantly more sensitive than PMMA. However, the inclusion of HMA comonomer appears to enhance the crosslinking of the resists in high dose range.

EXPERIMENTAL

Polymer Synthesis and Characterization

The copolymers, poly(hexyl methacrylate–co–methyl α-chloroacrylate) [poly(HMA–co–MCA] and poly(methyl methacrylate–co–hexyl methacrylate) [poly(MMA–co–HMA], and the terpolymers of MMA, HMA, and MCA were synthesized in a chlorobenzene solution at 65°C using AIBN (2,2-azobisisobutyronitrile) as a free-radical initiator. The synthesized polymers were twice precipitated from chlorobenzene with methanol and dried in a vacuum oven at 50°C for 48 hr. Methyl methacrylate, hexyl methacrylate, and methyl α-chloroacrylate were obtained from Polysciences, Inc., Warrington, Pennsylvania.

A Wescan Model 231 recording membrane osmometer was used to measure the osmotic pressures of the polymer solutions. Number-average molecular weight of the polymers, $\overline{M}_n$, were derived from the osmotic pressure-versus-concentration data using the standard method. The molecular weight distribution of the polymers, i.e., dispersity D, were determined by a Water Associates Model 202 gel permeation chromatograph. The glass transition temperature of the polymers was determined by a du Pont 990 differential scanning calorimeter. The values of $\overline{M}_n$, dispersity, and T_g are shown in Table I.

The chemical composition of the copolymers was determined by elemental analysis. The carbon, oxygen, and hydrogen content of each polymer was determined by Galbraith Laboratories, Inc., Knoxville, Tennessee. The composition of the resists is shown in Table I.

Electron Beam Exposure

The polymers were spin coated from solution at 1500 rpm on glass substrates which were coated with a Cr film 0.07 μm thick. Chlorobenzene was used as the spinning solvent. Before electron beam exposure, the polymer films were prebaked in a vacuum oven at 100°C for 30 min. The resists were exposed in a computer-controlled scanning electron microscope with a test pattern that contains a series of rectangles covering a wide range of exposures. The electron energy was 15 kV, and the beam current before and after exposure of the pattern was measured with a Faraday cup. The resist films were developed by spraying a mixture of dimethylformamide and 2-propanol for 30–60 sec. The resist thickness was measured by a Bendix Proficorder.

TABLE I
Characterization of Resists

Resist	Composition, mole %			$\bar{M}_n$	Dispersity	T_g, °C	Scisson sensitivity, coulomb/cm²	Crosslink sensitivity,[a] coulomb/cm²
	MMA	MCA	HMA					
PMMA[b]	100			150,000	2.5	105	4.2×10^{-5}	1×10^{-3}
Poly(MMA-co-HMA)	80	0	20	98,000	1.8	67	2.5×10^{-5}	5×10^{-5}
Poly(HMA-co-MCA)-A	0	64	36	46,000	1.9	77	1.9×10^{-5}	7×10^{-5}
Poly(HMA-co-MCA)-B	0	79	21	119,000	1.8	107	2.8×10^{-5}	9×10^{-5}
Terpolymer-A	29	51	20	125,000	1.9	108	8.0×10^{-6}	8×10^{-5}
Terpolymer-B	11	55	34	151,000	1.8	98	1.5×10^{-5}	1×10^{-4}
Terpolymer-C	40	37	23	236,000	1.7	93	6.0×10^{-6}	2×10^{-4}
PMCA[c]	0	100	0			151	1.2×10^{-5}	

[a] Crosslink sensitivity is the dose above which $I/I_0 > 0$.
[b] Elvacite 2021 from du Pont Co.
[c] See reference 8.

RESULTS AND DISCUSSION

The results of our exposure studies are shown in Figures 1–3. In these figures, the ratio of l/l_0 is plotted against electron dose, where l and l_0 are, respectively, the film thickness of exposed and unexposed areas after development. A value of l/l_0 equal to zero means the resist is fully developed. Development of the resists was carried out by spraying the spinning resist films with mixtures of dimethylformamide/2-propanol. To compare the sensitivity of the resists, the resists were developed by suitable solvent mixtures which did not dissolve more than 20% of unexposed resist after 30–45 sec of spraying. The sensitivity of the resists is shown in Table I.

It is known that both molecular weight and molecular weight distribution have a significant effect on the sensitivity of a positive resist.[1,9] Since both molecular weight and molecular weight distribution are different in resists, a quantitative statement regarding the effect of composition on the sensitivity of the resists cannot be derived precisely. However, the results shown in Table I and Figures 1–3 indicate that two of the terpolymers, terpolymer-A and terpolymer-C, are significantly more sensitive than PMMA, and both copolymers, poly(HMA–co–MMA) and poly(HMA–co–MCA), are slightly more sensitive than PMMA.

The exposure applied in the present work ranged from 1.0×10^{-7} to 3.2×10^{-4} coulomb/cm². In this range, it has been found that poly(methyl α-chloroacrylate) (PMCA) is more sensitive than PMMA and crosslinking predominates in PMCA when the electron dose[8] exceeds 6×10^{-4} coulomb/cm². It also has been found that the presence of comonomer methyl methacrylate has the effect of reducing the crosslinking rate in PMCA and resulting in a more sensitive copolymer. The copolymers with 30–50 mol-% MCA are much more sensitive than either PMCA or PMMA.[8]

An important finding in the present study is that while the presence of MMA appeared to reduce the rate of crosslinking, the presence of comonomer hexyl methacrylate in PMCA appeared to enhance the rate of crosslinking in the copolymer. It is seen from Figure 2 that the applicable exposure range for both poly(HMA–co–MCA)-A and -B as positive resists is extremely narrow, and the
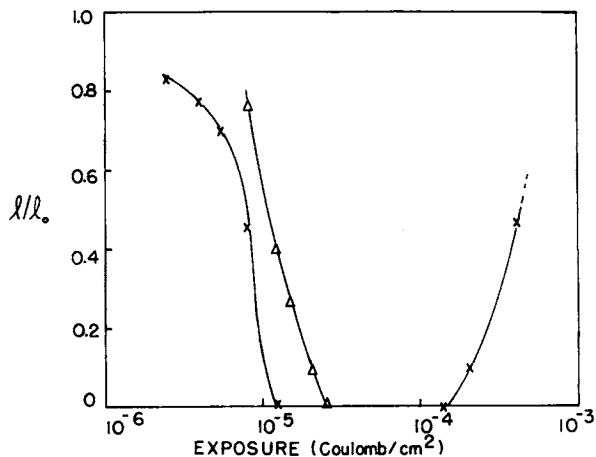

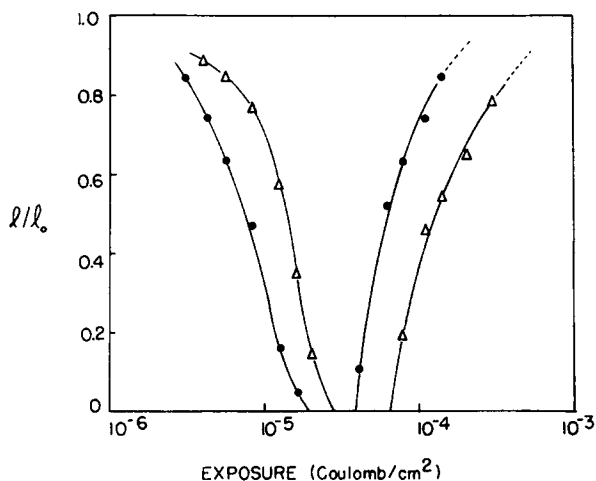Fig. 1. Experimental development curves for poly(MMA–co–HMA) (△) and PMCA (×).

Fig. 2. Experimental development curves for poly(HMA–co–MCA)-A (●) and poly(HMA–co–MCA)-B (△).

crosslinking becomes important at a lower exposure dose, being 5×10^{-5} and 7×10^{-5}, respectively, for poly(HMA–co–MCA)-A and -B.

It is not totally clear how the presence of hexyl methacrylate in the copolymer would enhance the rate of crosslinking in the polymer. It is well known, however, that the properties of n-alkyl methacrylate polymers depend critically on the length of the alkyl group. The glass transition temperature T_g of the methacrylate polymers, for example, decreases with increasing length of the n-alkyl group. The temperatures of the mechanical and dielectric α relaxations similarly decrease with increasing length of the n-alkyl group. An explanation occasionally given for these observations is that as the length of the side group increases, neighboring chains are pushed further apart, thus decreasing the hindrance to chain backbone motions.[10] It can be seen from Table I that T_g of both copolymers poly(HMA–co–MCA)-A and -B are significantly lower than T_g of
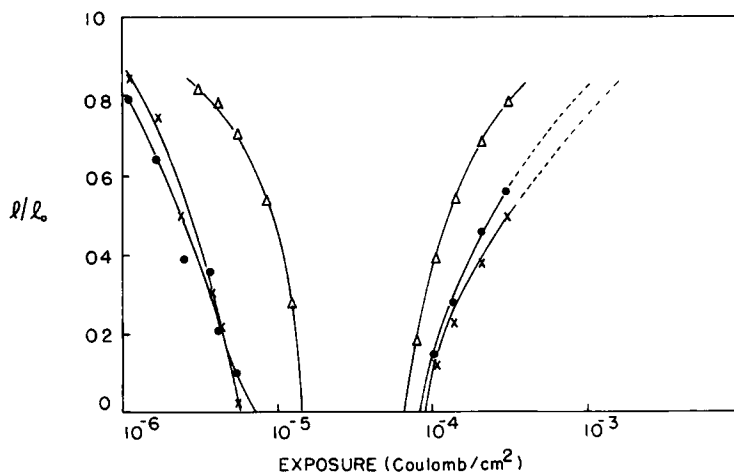

Fig. 3. Experimental development curves for terpolymer-A (●), terpolymer-B (△), and terpolymer-C (X).

PMCA. If the explanation given above is plausible, then the "internal plasti-cization" effect of hexyl methacrylate could result in an increase in the main-chain backbone motion of the copolymers. The increase in the main-chain backbone motion could lead to an increase in the probability of the combination of two polymer radicals, thereby increasing the rate of crosslinking. The observation that poly(HMA–co–MCA)-A, which has a higher content of HMA (therefore lower T_g) than poly(HMA–co–MCA)-B, also exhibits higher sensitivity to crosslinking in a high dose range is consistent with this explanation. We have not carried out the exposure studies on poly(hexyl methacrylate) because of its low glass transition temperature, $-5°C$.

It may be simply that in the present exposure range (1.0×10^{-7} to 3.2×10^{-4} coulomb/cm^2), poly(hexyl methacrylate) is more susceptible to radiation-induced crosslinking. However, the presence of comonomer hexyl methacrylate is not seen to enhance the rate of crosslinking in PMMA. On the contrary, poly(MMA–co–HMA) is seen to be slightly more sensitive than PMMA. Although the n-hexyl group is substantially longer than the methyl group, the alkyl group in the methacrylate polymer is still separated from the backbone chain by three single bonds. The steric strain in the main-chain backbone caused by the hexyl ester group is probably not much larger than the one exerted by the methyl group because the strain could be partially relieved through C—C bond rotation. It is perhaps not surprising that poly(HMA–co–MMA) is only slightly more sensitive than PMMA.

The most sensitive resist found in the present study is terpolymer-C. The sensitivity of terpolymer-C is 6.0×10^{-6} coulomb/cm^2, which is about the same as the most sensitive copolymer, poly(MMA–co–MCA)-C, reported previously.[8] The inclusion of hexyl methacrylate apparently does not significantly increase the overall sensitivity of the copolymer. However, the glass transition temperature of the terpolymer is significantly lower, and the adhesion of the terpolymer may be superior to that of the copolymers. Further studies on the resist properties of the terpolymer are underway and will be reported in a future communication.

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