

Synthesis and Evaluation of Methyl Methacrylate Copolymers and Terpolymers as Electron-Beam Resists.

I. Poly(methyl Methacrylate–Methacrylic Acid–Methacryloyl Chloride)*

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Synopsis

Terpolymers of methyl methacrylate with methacrylic acid and methacryloyl chloride [poly(MMA–MAA–MAC)] were synthesized with high yields by slow radical polymerization. The influence of the temperature of prebaking on the changes in the chemical composition and the molecular weight characteristics of poly(MMA–5%MAA–5%MAC) was studied by infrared spectroscopy and gel permeation chromatography. It was found that resists containing terpolymer with molecular weight (\bar{M}_w) of 41,000, which were prebaked at 100°C, were able to produce high contrast images ($\gamma = 3.3$) at doses of 16 $\mu\text{C}/\text{cm}^2$.

INTRODUCTION

In the last decade an enormous amount of experimental material has been accumulated concerning the use of polymers and copolymers with different structure, composition, and molecular weight characteristics as electron-beam resists (EBRs). Although poly(methyl methacrylate) was the first polymeric material tested as EBR,¹ it is still widely used. It possesses medium sensitivity, but fairly good resolution. On the other hand, the contemporary trends in microelectronics require an improvement over this polymer in both sensitivity and thermal stability.

In the present work an attempt is made to meet the above stated requirements by synthesis and evaluation of a terpolymer of methyl methacrylate (MMA) with methacrylic acid (MAA) and methacryloyl chloride (MAC). Terpolymers of the same composition have been mentioned in the patent literature without any details.² Similar systems have been described by several research groups.^{3–5} The synthetic routes for obtaining these materials have some disadvantages: synthesis of two copolymers, poly(MMA–MAA) and poly(MMA–MAC), and their mixing³; thermal treatment and filtration of crosslinked copolymers⁴; etc. In this study an effort is made to avoid these disadvantages by slow radical terpolymerization with simultaneous introduction of the co-

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monomers. The composition of the terpolymer could be selected in a way ensuring that the excellent resolution of polyMMA and its resistance to wet etching combines with good sensitivity, thermal stability and adhesion of MAC and MAA polymers, respectively (Table I).

The technological characteristics for each EBR have practical value only if they correspond to the available electron-beam system. In order to achieve the desired final parameters for the lithographic process, it is of crucial importance to establish the influence of the preexposure conditions on the incipient chemical and physical alterations taking place in the resist (polymer) layer.

The aim of the present investigation is to study the changes occurring in the chemical structure and the molecular weight characteristics of poly(MMA-MAA-MAC) during the stages preceding exposure. These stages predetermine to a large extent the final results of the microlithographic process.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN) (Fluka AG) was recrystallized in ethyl alcohol. MMA, MAA, and MAC (Fluka AG) were distilled twice before use. Methyl isobutyl ketone (MIBK) (Merck) was dried over molecular sieve 3 Å and distilled prior to use.

Polymerization

In glass ampoules, to a 1 mol/L (overall) monomer solution in MIBK 0.5 mol % AIBN was added. After twofold evacuation under freezing in liquid nitrogen, the vacuum-sealed ampoules were heated at 60°C for a definite time. The terpolymers formed were precipitated in diethyl ether and dried under reduced pressure. The yields exceeded 90%.

Methods

The molecular weight characteristics of the terpolymers (weight average molecular weight \bar{M}_w and molecular weight distribution MWD) were determined via polystyrene standards by gel permeation chromatography (GPC) using

TABLE I
Technological Characteristics of MMA, MAA, and MAC Polymers,
Copolymers, Terpolymers, and Their Mixtures

Polymer	Sensitivity ($\mu\text{C}/\text{cm}^2$)	Contrast	Reference
PolyMMA	50.0-100	1.7-2.0	6
PolyMAC	5.4	—	7
Poly(MMA-MAC)	0.5-20	—	8
Poly(MMA-MAA)	2.0-10	—	9
Poly(MMA-MAC) + Poly(MMA-MAA)	8.0-40	—	3
Poly(MMA-MAA-MAC)	0.5-20	—	2

Waters 244 apparatus equipped with an automatic injector WISP 710B, Ultrastyrigel linear column, and Waters 840 chromatography control and data station. Tetrahydrofuran was used as eluent, the flow rate being 1.0 mL/min. The temperature was maintained at 45°C. The molecular weights of the terpolymers were in the range from 30,000 up to 80,000.

The content of MAC in the terpolymers was determined using the well-known method of Vollhard. The content of MAA was established by titration of the acetone solution of the terpolymer with 0.1N NaOH and phenolphthalein as indicator.

The overall chemical composition of the isolated terpolymers was estimated by infrared spectroscopy (IRS) using UR20 equipment (Karl Zeiss, Jena, GDR). The polymer products were cast on KBr plates from tetrahydrofuran solutions. The purified terpolymers were dissolved in a mixture of xylene, *n*-butyl acetate, and cellosolve acetate and spin-coated on the substrates.

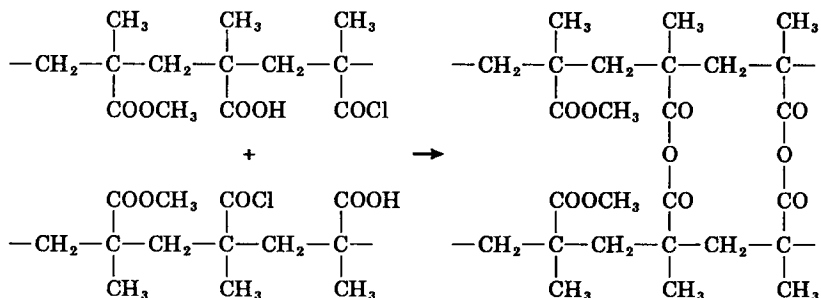
The viscosity of the resist was tightly controlled and maintained within 15 and 17 cP enabling the formation of a smooth layer on the substrate surface with area 12.5 × 12.5 cm. The thickness of the resist layer formed was 5000 Å with a deviation of less than 100 Å.

After spin coating, the wafers were thermally treated at 100 and 120°C in a nitrogen atmosphere for 60 and 45 min, respectively. The changes occurring in the polymer during the thermal treatment were followed by GPC and IRS of the stripped layer. The substrates were irradiated after prebake by electron vector-scanning system at 20 kV with doses ranging from 3 to 20 μC/cm². The exposed wafers were developed by spraying with MIBK at 23°C and subsequently rinsed in isopropyl alcohol.

RESULTS AND DISCUSSION

For the investigation of the influence of the prebake conditions on the molecular weight characteristics and the chemical composition of the resist film, a terpolymer having molecular weight (M_w) of about 40,000 was chosen. The initial composition of this product before thermal treatment was 90% MMA, 5% MAA, and 5% MAC. When coated on the substrate, this polymer formed the smoothest layer.

The mechanism of action for resists containing polymers or copolymers of MMA, MAA, and MAC is based on the formation of intermolecular anhydride linkages in the polymer film during prebaking at different temperatures³⁻⁵:



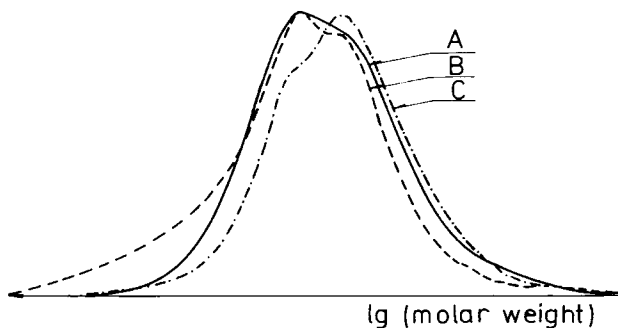


Fig. 1. GPC traces of poly(MMA-5%MAA-5%MAC) stripped from wafers after prebaking at different temperatures (A) 23°C; (B) 100°C/60 min; (C) 120°C/45 min.

These linkages are destroyed during exposure leading to formation of a positive image. This mechanism supposes a strong dependence of the final results upon the temperature of prebaking which determines the degree of dehydrochlorination. It has been established that prebaking at temperatures between 100 and 120°C gives the highest values of contrast and sensitivity for the copolymer MMA-itaconic acid.¹⁰ The same temperatures are used in the present investigation.

The GPC and IRS analyses of the polymer layers stripped from wafers baked at different temperatures demonstrate explicitly the interdependence of temperature with degree of crosslinking (Fig. 1 and Table II). From the results obtained, an approximate estimate can be deduced for the degree of anhydride formation during the prebaking stage. At 100°C the molecular weight and MWD increase more than two times in comparison to the initial values. The major part of the polymer film on the wafer could be stripped by tetrahydrofuran used as a solvent for GPC. The IRS studies show an increased content of anhydride linkages in the soluble fraction ($\nu = 1815$ and 1761 cm^{-1}). At 120°C the molecular weight of the soluble fraction surprisingly does not change substantially. The alterations in MWD are smaller in comparison to the prebaking at 100°C. The content of anhydride linkages in this fraction amounts only to 28.5%, but

TABLE II
Influence of the Prebake Temperature on the Composition of Poly(MMA-5%MAA-5%MAC) Films and Their Molecular Weight Characteristics

Temperature (°C)	Time (min)	Soluble fraction ^a				Gel fraction ^b (%)
		% Content of anhydride groups (%)		\bar{M}_w (GPC)	MWD (GPC)	
Ambient	—	100	0	41,000	1.9	0
100	60	85	24	112,000	4.8	15
120	45	62	28.5	43,000	2.9	38

^a Soluble in tetrahydrofuran.

^b Insoluble in tetrahydrofuran.

the content of carboxylic groupings ($\nu = 1715 \text{ cm}^{-1}$) exceeds the theoretical value of the initial terpolymer ($[\text{MAA}]_0 = 5\%$; $[\text{MAA}]_{120^\circ\text{C}} = 21\%$). The quantity of the insoluble fraction amounts to 38%. These results show that at 120°C the crosslinking proceeds more fully in the polymer layer on the wafer. Probably due to the interaction with moisture available in the system, part of the MAC units in the terpolymer turns into MAA units, which explains their increased content in the soluble fraction. MAA and its derivatives are also capable of forming anhydride bridges,^{4,5,10} but via dehydration which requires higher pre-baking temperatures.

The technological evaluation shows that, with the available electron-beam system, it is more rational to use a material with lower degree of crosslinking. The characteristic curve of resist prebaked at 100°C is shown in Figure 2. The achieved values of sensitivity and contrast are $16 \mu\text{C}/\text{cm}^2$ and 3.3, respectively.

The chemical composition of the terpolymer investigated determines its relative instability during a longer period of storage. Indeed, the GPC analyses of the same solution immediately after its preparation and 14 months later show that the monomodal MWD of poly(MMA-5%MAA-5%MAC) turns into a bimodal one (Fig. 3). The molecular weight, however, does not change very considerably. Probably the MAC units in the terpolymer turn partially into MAA units due to the interaction with the moisture present. This assumption is confirmed by IRS. The spectroscopic study proved that the content of carboxylic groups increases with time ($[\text{MAA}]_0 = 5\%$; $[\text{MAA}]_{14 \text{ months}} = 18\%$). The resulting terpolymer has slightly different chemical composition, which alters its hydrodynamic volume in the tetrahydrofuran solution. The different size of part of the macromolecules causes the appearance of a shoulder in the terpolymer peak [Fig. 3(B)].

CONCLUSIONS

The results obtained show that the synthesized poly(MMA-5%MAA-5%MAC) behaves quite similarly to the known copolymer mixtures with the

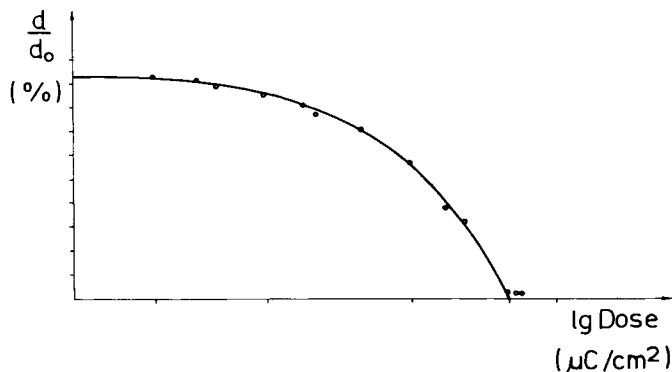


Fig. 2. Characteristic curve of poly(MMA-5%MAA-5%MAC) after electron-beam irradiation at 20 kV. D = dose of irradiation; d_0 and d = thickness of the resist layer before and after electron-beam exposure; $d_0 = 5700 \text{ \AA}$.

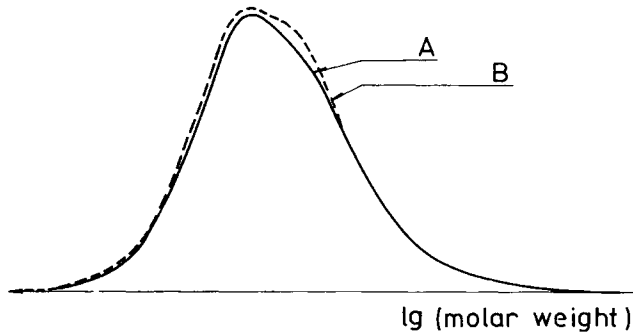


Fig. 3. Changes in the molecular weight and molecular weight distribution of poly(MMA-5%MAA-5%MAC) with time: (A) initial terpolymer; (B) the same polymer product after 14 months storage in solution.

same chemical composition.³ It is established that the temperature of prebaking influences to a great extent the chemical alterations in the composition and structure of the terpolymer. It determines the final results obtained with this system. An advantage of the terpolymer investigated is the lower prebake temperature required to obtain well-resolved images. At the chosen conditions of preexposure treatment, the achieved values of sensitivity and contrast guarantee a reasonable productivity for some practical purposes (mask fabrication) at good resolution. However, the synthesized terpolymer is relatively unstable and EBRs containing this material must be consumed within 12 months.

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