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Polymers of α-Substituted Benzyl Methacrylates as a New Type of Electron-Beam Resist

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Summary

Polymer of α-substituted benzyl methacrylate was found to be used as a new type of positive electron-beam resist, which forms methacrylic acid units in the polymer chain on the exposure to electron-beam and can be developed using alkaline solution as a developer. The sensitivity was dependent on the bulkiness of the ester group and the number of β-hydrogen atoms in the ester group. The sensitivity and γ-value of atactic poly(α,α-dimethylbenzyl methacrylate) were improved by a factor of more than three over poly(methyl methacrylate).

Introduction

There has been considerable effort in developing the electron-beam resist of positive type. These resists are mostly the polymers which are degraded on the exposure to electron-beam. The resulting lower molecular weight polymer in the exposed area can be selectively removed by a solvent or a solvent-mixture under certain developing conditions. The development is accomplished by the difference in the rate of dissolution between the exposed and unexposed area, which is a function of the molecular weight of the polymer. Recently a special type of positive resists were reported, which were depolymerized into a volatile monomer by electron-beam and developed without treatment by a developer (WILLSON et al., 1982, HATADA et al., 1982, BOWDEN and THOMPSON 1974).

In this paper we will describe a new type of positive electron-beam resist, which forms methacrylic acid units in the polymer chain on the exposure to electron-beam and can be developed by using alkaline solution as a developer after the exposure. In this case, the structural change in the side group of the polymer effectively alter the solubility property of the exposed polymer, and an excellent contrast between the exposed and unexposed areas was obtained as compared with the case where the decrease of the molecular weight in the exposed area is the most important factor for the efficient development.

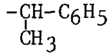
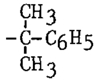
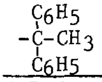
Experimental

Benzyl methacrylate was obtained commercially. α-Methylbenzyl (YUKI et al., 1968) and α,α-dimethylbenzyl (YUKI et al., 1977) methacrylates were synthesized in diethyl ether from methacryloyl chloride and the corresponding alcohols in the presence of triethylamine. α,α-Diphenylethyl methacrylate was prepared from methacryloyl chloride and lithium α,α-diphenylethoxide in tetrahydrofuran (OKAMOTO et al., unpublished). All the methacrylates except for α,α-diphenylethyl methacrylate were purified by the fractional distillation under reduced nitrogen pressure. The monomers thus purified were dried over calcium dihydride and then distilled under high vacuum just before use. α,α-Diphenylethyl methacrylate was purified by recrystallization from hexane.

Poly(methyl methacrylate) was obtained commercially. The polymers of other methacrylates were prepared in toluene with AIBN at 60°C. Isotactic poly(α,α-dimethylbenzyl methacrylate) was obtained with C_6H_5MgBr in toluene at 0°C. Poly(methacrylic acid) was prepared in water by potassium persulfate at 60°C. The properties of polymethacrylates are summarized in Table 1.

Table 1

Polymethacrylates[a] Used for the Electron-beam Resist

Ester group		$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$\frac{M_w}{M_n}$	Tg (°C)	Tacticity(%) I	H	S
$-CH_3$[b]		40.6	12.5	3.25	123	8	37	55
$-CH_2-C_6H_5$		123.6	52.9	2.34	63	5	34	61
 $-\underset{CH_3}{CH}-C_6H_5$		144.1	46.0	3.13	106	5	35	60
 $-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_5$	Atact.	175.5	84.7	2.07	101	10	47	43
	Isot.[c]	5.2	1.5	3.47	85	86	9	5
 $-\overset{C_6H_5}{\underset{C_6H_5}{C}}-CH_3$		14.3	4.3	3.33	98	31	42	27

[a] Polymerization conditions: monomer 10mmol, AIBN 0.1 mmol, polymn temp. 60°C, polymn time 24hr.

[b] Commercial products.

[c] Polymerization condition: monomer 10mmol, C_6H_5MgBr 0.25mmol, polymn temp. 0°C, polymn time 24hr, solvent toluene 5ml.

The polymers except for poly(methacrylic acid) were dissolved in toluene and the solution was spin-coated on a silicon wafer substrate. Poly(methacrylic acid) was used as a pyridine solution. The thickness of the resist films was about 0.3 μm.

The coated silicon wafer was prebaked and then exposed to 20 KV electron-beam. The exposed resist was developed using a mixture of methyl isobutyl ketone (MIBK) and isopropanol (IPA) or a dilute solution of sodium methoxide in methanol and subsequently rinsed with IPA or methanol respectively. The film thickness was measured on a Talystep instrument or by optical interference.

The molecular weights of the polymers were measured with a JASCO FLC-A10 GPC chromatograph with Shodex GPC column A-80M (50cm) with maximum porosity of 5×10^7 using tetrahydrofuran as a solvent. The chromatogram was calibrated against standard polystyrene samples.

Infrared spectra were recorded on the resist film casted on the silicon wafer using a JASCO A-3 spectrometer. The silicon wafer without resist film was placed in the reference beam to balance the silicon absorption bands.

The ^1H NMR spectra were taken on a JEOL JMM-MH-100 (CW) or a JEOL JNM-FX100 (FT) spectrometer at 100MHz.

Glass transition temperature of the polymer was measured with a Rigaku Denki Calorimeter, Model 8001 SL/C, at a heating rate of 10°C/min using an aluminum sample pan with lid.

Results and Discussion

The electron-beam resist behavior was studied on the radically prepared polymers of methyl, benzyl, α-methylbenzyl, α,α-dimethylbenzyl and α,α-diphenylethyl methacrylates at the acceleration voltage of 20 KV. The results are shown in Table 2. When the exposed resist films were developed with a mixture of MIBK and IPA, the sensitivities of these polymers were on the order of 10^{-4} C/cm^2.

Table 2

Electron-beam Exposure Characteristics of Polymethacrylates[a]

Ester group		MIBK/IPA[b]		CH_3ONa/CH_3OH[c]	
		Sens. (C/cm^2)	γ	Sens. (C/cm^2)	γ
$-CH_3$		167×10^{-6}	3.6	126×10^{-6}	—
$-CH_2-C_6H_5$		172×10^{-6}	—	103×10^{-6}	—
$-\underset{CH_3}{CH}-C_6H_5$		250×10^{-6}	2.4	97×10^{-6}	—
$-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_5$	Atact.	85×10^{-6}[d]	4.4	36×10^{-6}[d]	11.3
	Isot.	110×10^{-6}[d]	4.8	28×10^{-6}[d]	7.4
$-\overset{C_6H_5}{\underset{C_6H_5}{C}}-CH_3$		150×10^{-6}[e,f]	—	150×10^{-6}[e]	—

[a] Film thickness 0.3μm, prebake 170°C × 1hr, acceleration voltage 20 KV, development time 30 sec, rinse time 30 sec.

[b] MIBK/IPA = 1/5 (vol/vol). [c] CH_3ONa/CH_3OH = 1/20 (wt/vol).

[d] Prebake 142°C × 1hr. [e] Prebake 120°C × 1hr.

[f] Developer MIBK/IPA = 1/1 (vol/vol).

When a dilute solution of sodium methoxide in methanol was used as a developer, the sensitivity was enhanced as compared with the former case, and increased with an increase in the bulkiness of the ester group of the polymer except for poly(α,α-diphenylethyl methacrylate). The sensitivity of poly(α,α-dimethylbenzyl methacrylate) was improved by a factor of more than three over poly(methyl methacrylate).

In Figure 1 are shown the exposure characteristics of atactic and isotactic poly(α,α-dimethylbenzyl methacrylate) resists with CH_3ONa development together with those for the poly(methyl methacrylate) resist with MIBK/IPA development. The poly(α,α-dimethylbenzyl methacrylate)s showed very good contrast between exposed and unexposed areas and the γ-value of the atactic polymer was about three times γ-value of poly(methyl methacrylate) resist.

Infrared spectra of poly(α,α-dimethylbenzyl methacrylate)s unexposed and exposed to electron-beam are given in Figure 2 together with the spectrum of poly(methacrylic acid). The

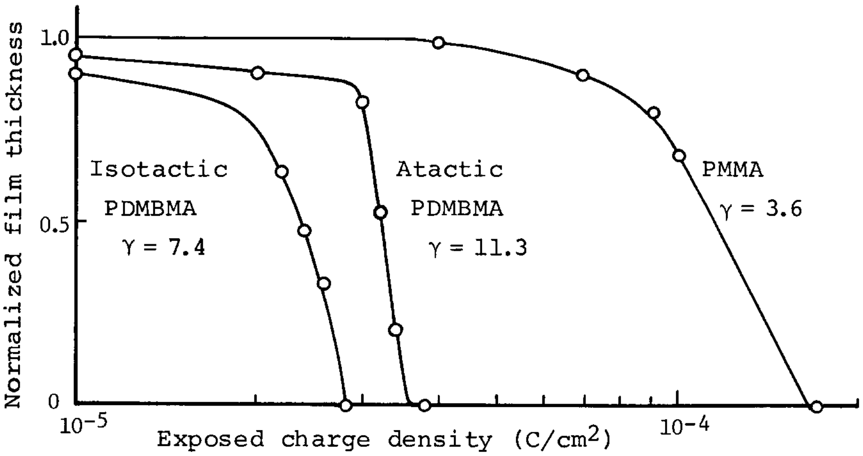


Figure 1. Exposure characteristics of poly(methyl methacrylate) (PMMA), and atactic and isotactic poly(α,α-dimethylbenzyl methacrylate)s (PDMBMA)

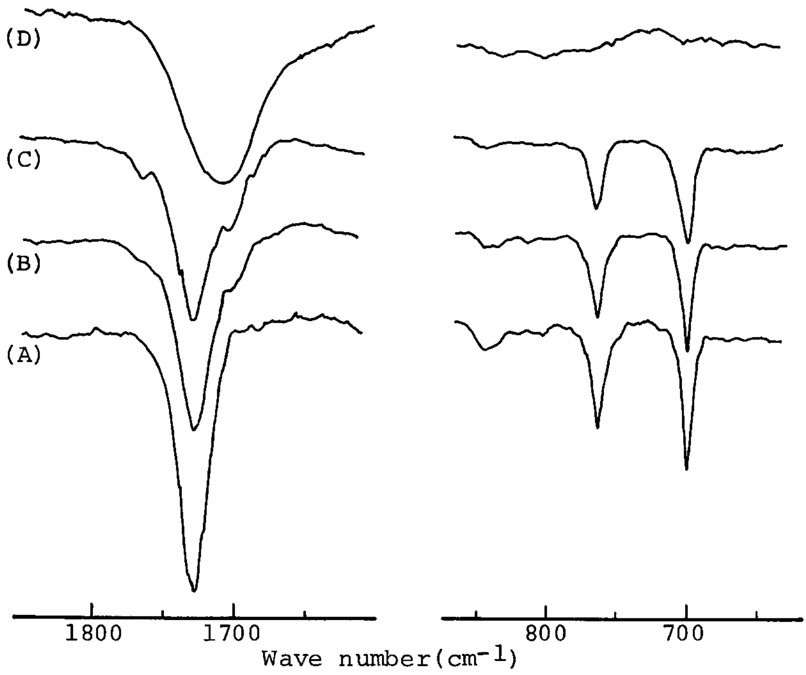
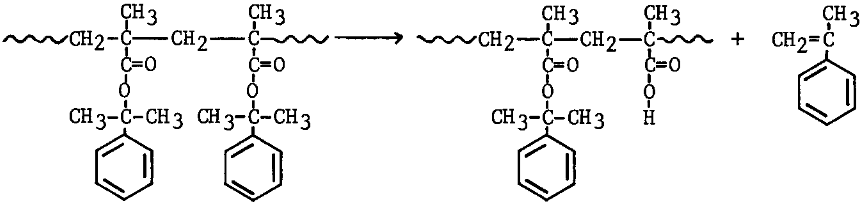


Figure 2. IR spectra of atactic poly(α,α-dimethylbenzyl methacrylate)s unexposed(A) and exposed(B) to electron-beam, isotactic poly(α,α-dimethylbenzyl methacrylate) exposed(C) and poly(methacrylic acid)(D)
Exposure charge density 1.6×10^{-4} C/cm^2, film thickness 0.5 μm, prebake at 142°C

exposure of the polymers resulted in a decrease of the absorption at 1729, 764 and 700 cm^{-1} and the appearance of absorption at 1707 cm^{-1}, which should be the carbonyl stretching band of poly(methacrylic acid). A small shoulder at 1760 cm^{-1} in the spectra of exposed polymers may be due to the formation of acid anhydride group in the polymer chain. When the atactic polymer was heated at 170°C under vacuum for 1hr, it decomposed into volatile and nonvolatile components. The former was found to be α-methylstyrene and the latter poly(methacrylic acid) by ^1H NMR spectroscopy. The results clearly indicate that the enhancement in the sensitivity and γ-value of poly(α,α-dimethylbenzyl methacrylate) resist over poly(methyl methacrylate) is mainly due to the formation of methacrylic acid unit on the exposure to electron-beam. The exposed area, which contains the methacrylic acid unit, easily dissolves in the alkaline developer but the nonexposed area does not. In this case the factor, which determines the resist properties, is not the rate of dissolution in the development process but the change of the solubility characteristics on the exposure. This is the reason why the high sensitivity and contrast are obtained with poly(α,α-dimethylbenzyl methacrylate) resist.



From the comparison of the spectra of atactic and isotactic poly(α,α-dimethylbenzyl methacrylate)s exposed to electron-beam (Fig. 2B and 2C), it is clear that the isotactic polymer forms acid anhydride group as well as acid group more easily than the atactic polymer on the exposure to electron-beam. The easier formation of acid group should enhance the sensitivity of the polymer, but the formation of acid anhydride may depress the dissolution rate of the exposed polymer in the alkaline developer, which results in the decrease of the sensitivity. Consequently, the sensitivity of isotactic polymer is not so different from that of atactic polymer. The easier formation of anhydride group in the isotactic polymer was also reported in the thermal treatment of poly(methacrylic acid) (GEUSKENS et al., 1971).

The carbonyl stretching band in the infrared spectrum of isotactic poly(α,α-dimethylbenzyl methacrylate) prebaked at 142°C for 1 hr indicated the formation of a small amount of acid group during the prebake, while the atactic polymer showed no change in the spectrum at this temperature. This may be the reason why the isotactic polymer showed lower γ-value than the atactic polymer.

The decomposition of the ester group into methacrylic acid unit and the corresponding olefin may occur more favourably when the ester group is bulkier and the number of β-hydrogen atoms in the ester group is larger. The β-hydrogen atom should migrate to the carboxylic group of methacrylic acid unit during the decomposition. With properly bulky ester group and six β-hydrogen atoms, poly(α,α-dimethylbenzyl methacrylate) exhibited the highest sensitivity through the alkaline development among the polymers shown in Table 1.

In the case of poly(α-methylbenzyl methacrylate) the number of β-hydrogen atoms is three, and the intensity of the absorption of acid carbonyl group formed on the exposure to electron-beam was smaller as compared with poly(α,α-dimethylbenzyl methacrylate). The results parallel with the lower sensitivity of this polymer in the development by alkaline solution.

Poly(α,α-diphenylethyl methacrylate) showed no improvement in the sensitivity by alkaline developer as compared with the sensitivity by MIBK/IPA developer. Although this polymer contains the bulky ester group with three β-hydrogen, no formation of acid carbonyl group was observed by infrared spectroscopy when exposed to electron-beam. However, it formed the acid group easily by the heat-treatment at 140°C. The segmental mobility of the ester group of this polymer should be decreased owing to its higher bulkiness, as a result, the decomposition of the ester group does not occur on the exposure to electron-beam at ambient temperature. When α,α-diphenylethyl methacrylate was copolymerized with methyl methacrylate with radical initiator, the resulting copolymer showed higher sensitivity in the alkaline development than both homopolymers (HATADA et al., unpublished). This may be due to the increased mobility of the diphenylethyl group by the copolymerization. The similar improvement of the sensitivity was also observed in the copolymer of α,α-dimethylbenzyl methacrylate and methyl methacrylate (HATADA et al., unpublished). The results will be published in the near future.

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