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Novel Chemically Amplified Imaging Materials Containing Malonate Pendant Groups.

A new chemically amplified polymeric imaging system based on polymers containing t-butylmalonate pendant groups has been demonstrated. Both the homopolymer of di-t-butyl (vinylbenzyl)benzylmalonate and its copolymer with styrene have been tested in coatings containing a photoacid generator. The materials exhibit very high sensitivity when exposed to deep-UV light but their application as resists for microlithography is limited by their relatively low glass transition temperature

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Summary

A new chemically amplified polymeric imaging system based on polymers containing *t*-butylmalonate pendant groups has been demonstrated. Both the homopolymer of di-*t*-butyl (vinylbenzyl)benzylmalonate and its copolymer with styrene have been tested in coatings containing a photoacid generator. Imaging experiments confirm that the materials have very high sensitivities when exposed to UV radiation near 250nm.

Introduction

A large number of polymeric materials useful as imaging materials have been designed in recent years, with a number gaining acceptance in the semiconductor industry.[1-4] Many of these new resists implement the concept of chemical amplification[5], first disclosed[6-11] by Fréchet, Willson and Ito in 1982, where the initiation of one active species results in a cascade of chemical events. Of particular interest have been a number of acid-catalyzed processes, in which acid is generated by irradiation of a photoactive substance contained within a polymer film causing its modification via a catalytic process. By far the best known acid-catalyzed, chemically amplified, systems today are resists based upon poly(4-*tert*-butyloxycarbonyloxystyrene)[8-11] or similar structures[12-16] where photochemically generated acid and the subsequent postbaking step result in the catalytic removal of the 4-*t*-butyloxycarbonyl (*t*-BOC) protecting groups. This chemical change results in a profound change in the solubility of the exposed resist, allowing for the formation of images after development.

Other similar resists have been designed incorporating *tert*-butyl substituted pendant groups,[5-10,16-19] such as poly(*t*-butyl methacrylate) and other comparable structures. *Tert*-butyl esters can readily undergo cleavage under acidic conditions via the $A_{AL}1$ mechanism, as proposed by Ingold,[20] due to the relatively stable *t*-butyl carbocation formed in this hydrolysis. These materials show good sensitivities to deep-UV irradiation when used with photoacid generators such as onium salts, and small feature sizes are generally obtainable due to minimal swelling by developers.

Under acidic conditions, malonates produce a carboxylic acid, carbon dioxide and an alcohol , and are used as synthetic precursors to substituted carboxylic acids.[21] The mechanism of this reaction proceeds via two distinct steps, with hydrolysis of the malonic ester, followed by decarboxylation of the resulting malonic acid via a six-membered transition state,[22] in a similar fashion to the decarboxylation of β-keto acids,[23] resulting in an enol which rapidly tautomerizes to the carboxylic acid.[24] This structural modification should lead to great changes in solubility, which could translate into a unique, highly sensitive imaging material.

Experimental

Deep-UV exposures were performed using an Optical Associates Inc. exposure system comprising of a low pressure mercury lamp with a shutter system, an intensity controller, and an exposure timer. Photon flux was measured using an Oriel Merlin radiometer equipped with a silicon detector head. The output of the mercury lamp was filtered through a 254 nm narrow bandwidth filter from Oriel Corporation. Film thickness measurements were performed using a Tencor Alphastep 200 profilometer. The resist samples were spin-coated onto silicon or quartz wafers, with a usual film thickness of 1 μm. Unless otherwise indicated, the films were prebaked at 120°C for 3 minutes after coating and were postbaked at 120°C for 2 minutes after exposure. Development was carried out for 15s in 5% aqueous tetramethylammonium hydroxide. E-beam exposures were performed on a Leica/Cambridge EBMF-10.5/CS electron beam lithographic system at 20 kV, with a current of 1 nA and a beam diameter of 83 nm.

Di-*tert*-butyl malonate and sodium hydride (as a 60% dispersion in mineral oil) were obtained from Aldrich, and were used without further purification. Vinyl benzyl chloride, a mixture of 3- and 4-substituted isomers, was obtained from Dow and was used without further purification. Tetrahydrofuran was obtained from Fischer, and was distilled over sodium and benzophenone before use. Benzyl chloride, obtained from Aldrich, was dried over $MgSO_4$ and distilled. Azobisisobutyronitrile (AIBN) obtained from Kodak was recrystallized from methanol. Toluene was obtained from Fischer, and was distilled over calcium hydride. Styrene, obtained from Aldrich, was distilled under reduced pressure. AZ312MIF, a 0.54N aqueous solution of tetramethyl ammonium hydroxide, was obtained from Hoechst Celanese, and was diluted with deionized water as needed. Triphenylsulfonium hexafluoroantimonate was obtained from General Electric and used without further purification.

Di-tert-butyl benzyl malonate (1)

A slurry of sodium hydride (1.849 g, 46.2 mmol) in THF (30.0 mL) was stirred under nitrogen for 5 minutes at 0°C. Di-*t*-butyl malonate (10.000 g, 46.2 mmol) was then added dropwise with rapid stirring. Benzyl chloride (5.853 g, 46.2 mmol) was added dropwise, and the reaction mixture was then heated to 65°C for 22 hours. The mixture was quenched with 15 mL of deionized water, and then extracted with diethyl ether (3x25mL). The combined extracts were washed with water and dried over $MgSO_4$. Evaporation under reduced pressure yielded a pale yellow liquid. The crude product was purified by distillation *in vacuo*, followed by flash chromatography using a 3:2 mixture of hexane and methylene chloride. The purity of the final product was confirmed using HPLC. 7.724 g (57%) of a clear liquid was obtained. Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.39; H, 8.35. IR(NaCl): aromatic C-H stretch at 2979 cm^{-1}; aliphatic C-H stretch at 2934 cm^{-1}; C=O stretch at 1728 cm^{-1}; and sym. and antisym. C-O stretches at 1250 and 1139 cm^{-1}. ^1H-NMR: δ($CDCl_3$) 7.33-7.21 (5H, m, ar H); 3.50 (1H, t, $C\underline{H}$); 3.15 (2H, d, $C\underline{H}_2$); and 1.43 ppm (18H, s, $C\underline{H}_3$). ^{13}C-NMR: δ($CDCl_3$) 168.1 ($\underline{C}$=O); 138.2 (ar C); 128.8 (ar C); 128.2 (ar C); 126.4 (ar C); 81.3 (quaternary C); 55.4 ($\underline{C}H$); 34.5 ($\underline{C}H_2$); and 27.7 ppm ($\underline{C}H_3$).

Di-t-butyl (vinyl benzyl) benzyl malonate (2)

A slurry of sodium hydride (0.821 g, 20.5 mmol) in THF (20.0 mL) was stirred under nitrogen for 5 minutes at 0°C. Di-*t*-butyl benzyl malonate (6.000 g, 20.5 mmol) was then added dropwise with rapid stirring. Vinyl benzyl chloride (3.132 g, 20.5 mmol) was added dropwise, and the reaction mixture was then heated to 65°C for 12 hours. The mixture was quenched with 10 mL of deionized water, and then extracted with diethyl ether (3x20mL). The combined extracts were washed with water and dried over $MgSO_4$ to give a pale yellow liquid after evaporation of solvents under reduced pressure. The crude product was purified by flash chromatography using a 1:1 mixture of hexane and methylene chloride, giving 8.392 g of a pale yellow liquid (97%). Anal. Calcd for $C_{27}H_{34}O_4$: C, 76.75; H, 8.11. Found: C, 76.62; H, 7.98. IR(NaCl): aromatic C-H stretch at 2978 cm^{-1}; aliphatic C-H stretch at 2934 cm^{-1}; C=O stretch at 1746 cm^{-1}; C=C stretch at 1603 cm^{-1}; and sym. and antisym. C-O stretches at 1276 and 1175 cm^{-1}. ^{1}H-NMR: $\delta(CDCl_3)$ 7.33-7.15 (9H, m, ar H); 6.68 (1H, m, $CH_2=C\underline{H}R$); 5.60 (1H, m, $C\underline{H}_2=CHR$); 5.22 (1H, m, $C\underline{H}_2=CHR$); 3.21 (4H, d, $C\underline{H}_2$); and 1.41 ppm (18H, s, $C\underline{H}_3$). ^{13}C NMR: $\delta(CDCl_3)$: 170.2 ($\underline{C}=O$); 136.6 ($CH_2=\underline{C}HR$); remaining peaks in range 137.3-124.6 (aromatic C); 113.6-113.2 ($\underline{C}H_2=CHR$); 81.3 (*t*-butyl quaternary C); 60.2 (quaternary C); 38.9-38.6 ($\underline{C}H_2$); and 27.8 ppm ($\underline{C}H_3$).

Poly(di-t-butyl (vinyl benzyl) benzyl malonate) (3)

A solution of di-*t*-butyl (vinyl benzyl) benzyl malonate (2.094 g, 4.96 mmol) and azobisisobutyronitrile (0.0210 g) in toluene (2.0 mL) under a nitrogen atmosphere was heated to 65°C for 22 hours. The solution was then precipitated into methanol, filtered, redissolved in THF and finally reprecipitated into methanol. 1.577 g of a white solid (79%) was obtained after drying *in vacuo*. TG/DTA: 36.9% weight loss at 229°C. Tg: 73.1°C. GPC: Mn=1.9x10^5, Mw/Mn=4.1. ^{1}H-NMR: $\delta(CDCl_3)$ 7.1 (5H, ar H), 6.8 (2H, ar H), 6.3 (2H, ar H), 3.0 (4H, CH_2), 1.6 (2H, CH_2), 1.2 (18H, CH_3).

Poly(styrene-co-di-t-butyl (vinyl benzyl) benzyl malonate)

Sample 1 (4)

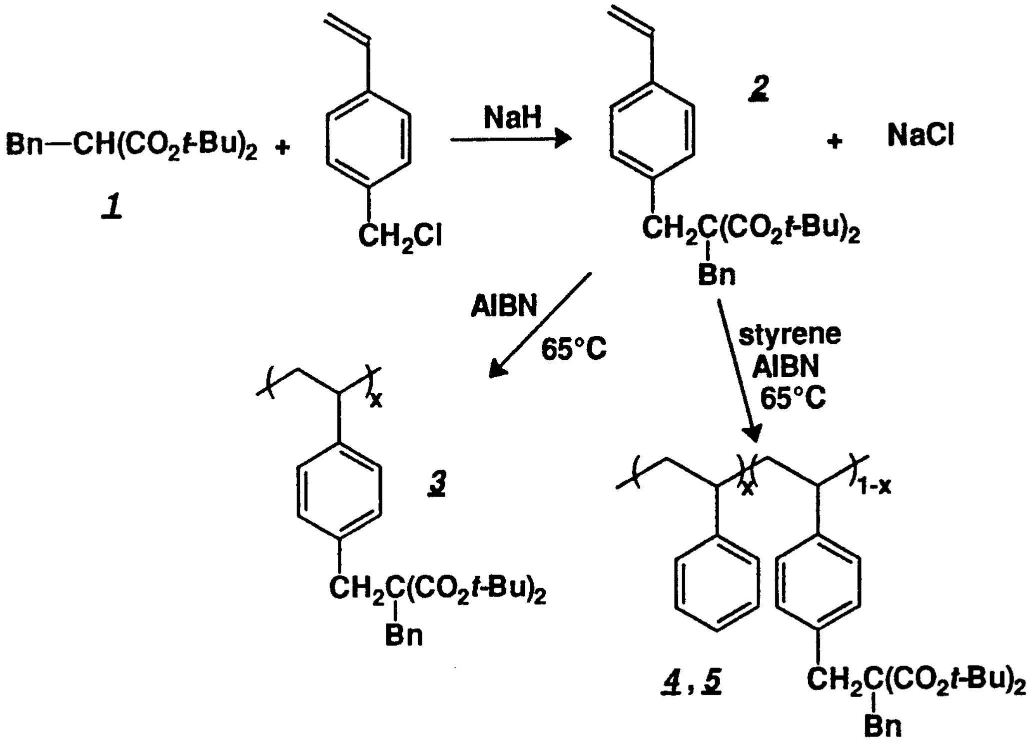
A solution of di-*t*-butyl (vinyl benzyl) benzyl malonate (1.298 g, 3.07 mmol), styrene (1.362 g, 13.08 mmol) and azobisisobutyronitrile (0.0266 g) in toluene (2.7 mL) under a nitrogen atmosphere was heated to 65°C for 24 hours. The solution was then precipitated into methanol, filtered, redissolved in THF and finally reprecipitated into methanol. 1.925 g (72%) of a white solid was obtained after drying *in vacuo*. TG/DTA: 17.8 % weight loss at 238°C. Tg: 91.8°C. GPC: Mn=3.8x10^3, Mw/Mn=2.1.

Sample 2 (5)

A solution of di-*t*-butyl (vinyl benzyl) benzyl malonate (2.310 g, 5.47 mmol), styrene (0.190 g, 1.82 mmol) and azobisisobutyronitrile (0.0250 g) in toluene (2.5 mL) under a nitrogen atmosphere was heated to 65°C for 16 hours. The solution was then precipitated into methanol, filtered, redissolved in THF and finally reprecipitated into methanol. 1.024 g (41%) of a white solid was obtained after drying *in vacuo*. TG/DTA: 32.6% weight loss at 227°C. Tg: 85.1°C. GPC: Mn=7.5x10^3, Mw/Mn=7.2.

Results and discussion

The polymers used in this study were synthesized via the route shown in Scheme 1.



Scheme 1.

The synthesis of a malonate monomer was first attempted through the direct addition of vinyl benzyl chloride to di-*t*-butyl malonate, without the prior addition of a protecting group. However, it was very difficult to completely separate the disubstituted product from the desired mono-vinylbenzylated product, which lead to insoluble polymeric materials. Thus benzyl chloride was first added to di-*t*-butyl malonate as a protecting group to give **1**, which was rigorously purified to remove any remaining starting material prior to the addition of vinyl benzyl chloride.

Homopolymers of **2** were obtained via free-radical polymerization initiated by AIBN. These polymers were found to be soluble in organic solvents, and insoluble in the aqueous base developers commonly used for development in microlithography. Thermogravimetric analyses were performed on these polymers in order to observe their thermal decomposition behaviors. **3** showed a weight loss of 36.9% at 229°C, due to ester cleavage and decarboxylation (expected weight loss = 37.0%).

The glass transition temperature of the homopolymer was found to be fairly low (Tg = 73.1°C), which affects imaging properties and makes the achievement of very small feature sizes very difficult or impossible. Therefore copolymers of **2** with styrene were prepared, in order to raise the glass transition temperature closer to 100°C. The copolymers were easily obtained via free-radical polymerization in toluene using AIBN as the radical initiator.

Table 1: Data on polymers containing **2**

Polymer	Mn	Mw/Mn	Tg (°C)	mol% **2**	mol% styrene	Sensitivity (mJ/cm^2)
3	$1.9x10^5$	4.1	73.1	100	0	0.7
4	$3.8x10^3$	2.1	91.8	19	81	n/a
5	$7.5x10^3$	7.3	85.1	65	35	5.0

Two copolymers containing differing amounts of **2** were prepared. Data on these copolymers is contained in Table 1. The relative molecular weights of these copolymers, as determined via GPC, were found to be lower than that of the homopolymer obtained under analogous conditions. Thermogravimetric analyses were used to determine the exact amount of malonate monomer incorporated into each copolymer. The percent weight loss during hydrolysis and decarboxylation is directly proportional to the percentage of malonate repeat units contained in each copolymer, with styrene repeat units making up the remaining mass. DSC analysis confirmed that a modest improvement in glass transition temperature was achieved by copolymerization.

Films containing 5 wt% triphenylsulfonium hexafluoroantimonate photoacid

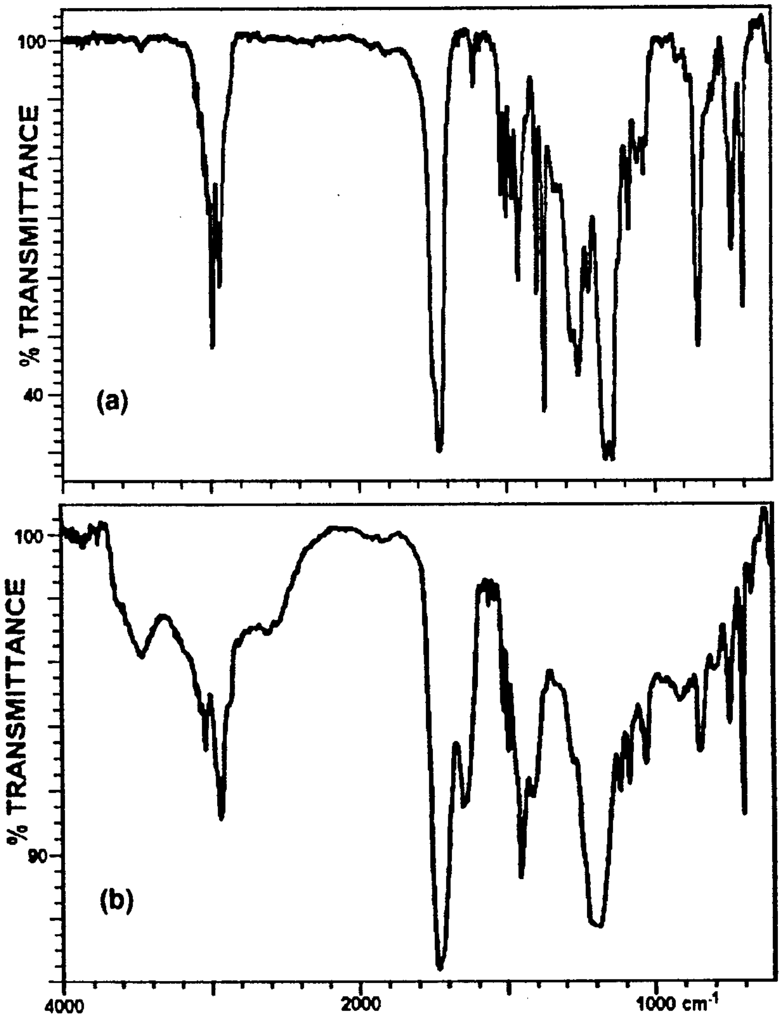
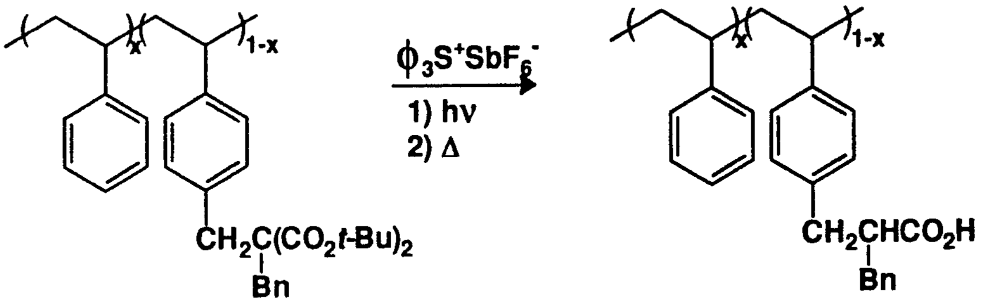


Figure 1. IR spectra a) before and b) after irradiation and postbaking.

generator (PAG) and the homopolymer **3** were analyzed spectroscopically to verify chemical changes in the film composition after irradiation and postbaking. Figure 1 illustrates the changes observed in the IR spectra for resists containing **3** and PAG before and after exposure to 254 nm UV light at a dose of 100 mJ/cm^2 and postbaking for 3 minutes at 120°C. Hydrolysis and decarboxylation are confirmed by the appearance of characteristic acid peaks in the IR spectrum of the irradiated and postbaked film. These included a broad O-H stretching absorbance at 3400 cm^{-1}, a new C=O stretch centered at 1650 cm^{-1}, as well as the loss of the C-O stretching bands at 1150 and 1275 cm^{-1}. This decarboxylative process (Scheme 2) occurs as a result of the photogeneration of protons within the exposed areas of the film, which are then free to catalyze the thermal decarboxylation upon heating to 70°C in the postbaking step. This was confirmed through a control experiment in which no onium salt was added to the resist formulation. In the absence of acid, no changes were observed in the resist film, even after baking at 120°C for 10 minutes.



Scheme 2.

*Imaging and sensitivity of the films derived from polymers containing **2***

The sensitivity curves obtained from films containing **3** or **5** and 5 wt% PAG are shown in Figure 2. As can be seen in this figure, the sensitivity of the homopolymer at 254 nm is extremely good, at approximately 0.7 mJ/cm^2. Films made from the copolymers of **2** and styrene showed lower sensitivities than **3**. The copolymer **4**, which incorporated only 19 mol% **2**, did not function as a resist because the unexposed film was also soluble in the aqueous base developer. Copolymer **5**, containing 65 mol% **2**, showed a sensitivity of 5 mJ/cm^2. E-beam sensitivity experiments were performed on **3**, and films of 0.75 µm thickness showed a sensitivity of 1.0 µC/cm^2 at 20 kV. This curve is also included in Figure 2.

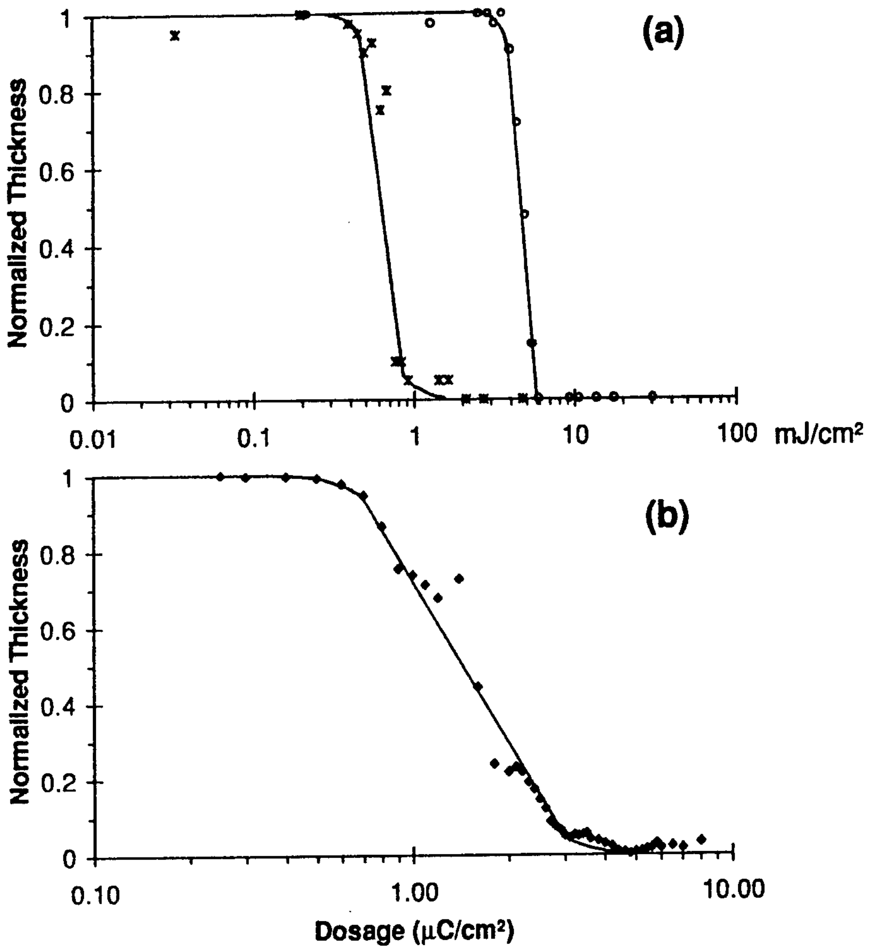


Figure 2. Sensitivity curves for films containing polymers with pendant malonate groups: (a) sensitivity curves for films exposed to 254nm irradiation (*= 95% **3**, 5% PAG; O = 95% **5**, 5% PAG), (b) e-beam sensitivity curve for film containing 95% **3**, 5% PAG.

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