2-Phenylallyl-ended Poly(α -Methylstyrene): A New Positive Electron-Beam Resist

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1. Introduction

The miniaturization of microelectronic devices has been progressing rapidly for the last twenty years. For example, the accumulation of integrated circuits in an ultra-large-scale-integration (ULSI) increases four times every 3 - 4 years.[1] For the fabrication of such an integrated pattern, a high performance resist polymer must be developed. The primary demand for the high performance resists is, of course, to improve resolution. One of the important factors to improve resolution is the kind of irradiation source that can be utilized on the resist. In other words, a resist having a high sensitivity toward a rather narrower beam (UV $\rightarrow$ deep UV $\rightarrow$ X-ray, EB) is suitable for the integrated pattern.

One of the other important points to improve the resist performance is to investigate a novel polymeric system which is susceptible to the irradiation sources as stated above. For the higher performance resist, both negative and positive type resists must be created for versatile purposes. We have recently been studying the synthesis of organosilicon-containing polymers for a negative EB-resist having a high RIE resistivity.[2] One of the organosilicon-containing polymers prepared so far, poly[4-bis(trimethylsilyl)methylstyrene] showed extremely a high resolution parameter having moderate sensitivity.[3] Very recently, we have started a new molecular design for the creation of a high performance positive EB-resist.[4]

Polymers having a low ceiling temperature (T_c) have been investigated for the positive type resist utilizing their depolymerization characteristics.[5] For example, poly(phthalaldehyde) (PPHA), which shows a T_c of ca. -40 °C, can be depolymerized by acid treatment due to the high sensitivity of acetal repeating units. Thus the PPHA film can be a positive photo-resist when it is coupled with a photo-acid generator.[6] Poly(α -methylstyrene) (PMS) is one of the other well-known polymers which induces depolymerization at ambient temperature due to the low T_c (ca. 0 °C).[7] PMS is suitable for a resist because of its low perturbation due to its high glass transition temperature (T_g = 130 °C). Since there is no susceptible group in the PMS skeleton, however, its sensitivity against EB-exposure is not enough. Ito and his coworkers pointed out the easier depolymerization of PMS, which was prepared by cationic polymerization, by subsequent acid treatment than that obtained by the anionic polymerization technique.[8] They explained that such an easier depolymerization tendency of the cationically synthesized PMS was attributable to the end double bond formed by the proton transfer reaction during the cationic polymerization process.[9] However, the extent of the double bonds at the end of the polymer chain should not be quantitative in the cationic polymerization process.[9] Our idea was to synthesize a uniform size PMS possessing an EB-susceptible double bond at the end of the polymer chain through the

anionic polymerization technique. According to this idea, we prepared several types of uniform size PMS with an end reactive group such as the 2-phenylallyl group, 2-tolylallyl group and 2-phenyl-3,3-difluoroallyl group.[10] The end-reactive PMS derivatives thus prepared were susceptible against certain stimuli such as heating, acid and base treatments. For example, the on-set temperature of the thermal degradation of PMS derivatives with a 2-phenylallyl end group was more than 50 °C lower than that of the hydrogen-terminated polymer.[11] Therefore, PAMS can be promising as a positive type EB resist. This paper communicate the EB resist characteristics of PAMS.

2. Experiments

2.1. Materials: Purifications of commercial THF (Wako), and α -methylstyrene (MS; Wako) were described in our previous paper.[10] sec-Butyllithium (sec-BuLi; Aldrich; in cyclohexane) was used as received, the concentration of which was determined by a gas chromatography technique, viz, sec-BuLi was reacted with 1,1-diphenylethylene (DPE), then the unreacted DPE was quantified by GC. 2-Phenylallyl bromide (PAB) was prepared according to the literature. [12] Other materials were used as received.

2.2. Polymerization Procedure: A typical anionic polymerization was performed in a 100-mL round-bottomed flask with a 3-way stopcock. The reactor was first carefully washed with a hexane solution of butyllithium, then THF (6.6 mL), MS (1.18 g; 10 mmol) and sec-butyllithium (0.34 mL; 0.26 mmol) were added via a syringe at -78 °C. The color of the mixture immediately turned brownish red. The reaction was allowed to continue for 20 min. For an end-modification reaction, a 2 - 5 times excess molar amount of the end coupling agent, PAB, was added to the living polymer solution and allowed to react for a further 20 min. The resulting mixture was analyzed by gel permeation chromatography (GPC) and then poured into a large excess of methanol. The precipitate was purified by 3-fold successive reprecipitations from THF solution. The polymer obtained was freeze-dried with benzene to remove the solvents employed.

2.3. Degradation experiments: Thermal analysis was conducted by thermogravimetric analysis. For a basic degradation, 0.2 mL of n-BuLi was added to a THF (1 mL) solution of the polymer sample (50 mg) and stirred for 1 h. The mixture was analyzed by GPC.

2.4 Resist Processing: To prepare a resist film, a THF solution of the polymer sample was prepared with a 10 wt.% concentration. The prepared solution was spin-coated at 1,500 r.p.m. for 30 sec on a silicon wafer surface. The thickness of the resist film thus obtained was about 0.25 μm and EB was exposed using a JEOL JSM-5200 scanning electron microscope (SEM) equipped with a Tokyo Technology L & S Pattern Generator LSPG1-1S at probe currents of 10 pA and accelerating voltages of 20 kV. A dose that ranged from 10 - 1,000 $\mu\text{C cm}^{-2}$ was employed. The exposed film was developed by soaking in methanol/methylisobutylketone (2:3) for 4 minutes, then the remaining film thickness was measured with a Tencor ALPHA STEP 300.

The sensitivity and resolution parameters were calculated from the sensitivity characteristic curve as the D_g^i and γ values, respectively. The D_g^i value denotes the minimum dose at the detectable remaining film on the wafer.[13] The γ value was calculated from the following equation.

$$\gamma = [2 \log(D_g^{50}/D_g^i)]^{-1}$$

where D_g^{50} denotes the dose at half remaining film thickness after development.[14]

2.5. Analytic methods and instruments were described elsewhere.[11]

3. Results and discussion

3.1. Preparation of End-Functionalized Poly(α -methylstyrene)

It is well known that MS can be polymerized by the anionic polymerization technique without any side reaction such as termination and chain transfer reactions.[15] In our previous paper, we revealed that the organosilicon-containing α -methystyrene derivative, 4-bis(trimethylsilyl)methyl- α -methylstyrene (SMS), can be polymerized in the same manner as that of MS to form the living polymer.[10] The end-modification of the living polySMS by 2-phenylallyl bromide proceeded almost quantitatively.

The anionic polymerization and the end modification of MS by PAB proceeded similar to that of SMS. From a GPC analysis, it was found that the obtained PMS exhibited a very low molecular weight distribution factor ($M_w/M_n = 1.06$) even for the sample after the end modification reaction. It should be noted that the end modification agent, PAB, possesses both carbon-halogen and carbon-carbon double bonds in the same molecule, which has several possibilities of side reactions such as dimerization of the prepolymers and oligomerizations of the coupling agent with the

Scheme 1

prepolymers when it is treated with the prepolymer. The molecular weight of the obtained polymer was 19,000.

The extent of the end-modification factor was evaluated by analysis of its ^1H NMR spectra. The two singlet signals appearing at 4.9 and 5.3 ppm were assignable to the two olefinic protons at the end of the polymer. By comparison of these signals vs. phenyl protons in each repeating unit, the 2-phenylallyl group was introduced almost completely to the PMS end.

3.2. Degradation Tests of PAMS

The degradation behavior of the 2-phenylallyl-ended PMS, PAMS, was investigated. Thermal degradability of PAMS was investigated by thermogravimetric analysis (TGA). The hydrogen-terminated PMS started to degrade at 310 °C. When the 2-phenylallyl group was introduced at the end of the polymer chain, the onset temperature of the degradation shifted to the lower temperature side. This fact can be explained in the following way. The high temperature induced the cleavage reaction of the end-double bond to form a radical species, which initiated the depolymerization reaction of the poly(α -methylstyrene) derivatives as shown in Scheme 1. The whole TGA profile of PAMS shifted to the lower temperature range, indicating a quantitative end-modification of the polymer which agreed well with the NMR data.

The increased susceptibility of the end 2-phenylallyl group was also confirmed by the alkaline treatment. When PAMS was mixed with *n*-BuLi in THF at ambient temperature, almost all of the polymer disappeared as shown in Fig. 1. A low molecular weight oligomeric mixture was observed instead of the starting polymer. This is in sharp contrast to the hydrogen-terminated polymers, which almost completely remained after the reaction

with *n*-BuLi.[11] This result indicates that butyllithium adds to the double bond at the end of the polymer chain to form the active carbanion, followed by the depolymerization reactions.

Fig. 1. GPC of PAMS before and after butyllithium treatment

3.3. Evaluation as EB resist

Since each PAMS thus prepared quantitatively possesses a 2-phenylallyl end group and it is susceptible to both heating and alkaline treatments, it is anticipated to show high sensitivity against EB exposure. Figure 2 shows the sensitivity characteristic curve for PAMS with an EB-dose. As can be seen in the figure, the remaining film thickness decreased with increasing EB dose, indicating the positive character of PAMS. The fact can be explained by the facile depolymerization which took place from the 2-phenylallyl group at the end of the polymer chain due to the easier formation of active species by the EB exposure

as compared to the hydrogen terminated PMS. Actually, no remarkable decrease in film thickness was observed in the case of the PMS film under the same EB exposure conditions.

Fig. 2. Sensitivity characteristic curves

The D_g^1 and γ values for PAMS were found to be $420 \mu\text{C cm}^{-2}$ and 4.2, respectively. A fairly higher contrast parameter (γ) than the common resists ($\gamma = 1 - 1.5$) may be attributable to the very narrow molecular weight distribution of the polymer. Further studies on PAMS homologues as electron-beam resists will be published elsewhere.

4. Conclusions

Utilizing the anionic living polymerization technique, the 2-phenylallyl group was quantitatively introduced at the end of poly(α -methylstyrene) chain. The obtained polymer was susceptible not only heating but also alkaline treatment to induce degradation to the monomer and/or oligomeric mixture. In the same manner, micropatterning can be obtained by the EB exposure. The typical lithographic parameters, D_g^1 and γ values for PAMS were found to be $420 \mu\text{C cm}^{-2}$ and 4.2, respectively. Thus PAMS can be regarded as a positive PMS resist with high sensitivity against EB exposure.

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