## **Supporting Information**

The preparation of novel polymeric sulfonium salt photoacid generator and its application for advanced photoresists

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## 1. The GPC data of polymers

In the reported literatures, polymeric PAGs for CA resist were generally synthesized by free radical copolymerization of monomer with PAG units and other monomers. The direct chemical modification on polymer chain as in this work was seldom reported. The direct chemical modification methodology offers advantages over polymerization way. The starting material PHS is easily available commercial product used in Deep-UV resists. The molecular weight distribution of the raw material PHS is 1.6 which is shown in Figure 1. After the introduction of sulfonium salt group, the molecular weight distribution became 1.8. Because of the bad solubility of polymer **a** (PHS-sulfonium chloride, the intermediate product of the reaction) in THF, the GPC curve was not measured.

The molecular weight distribution of polymer  $\mathbf{c}$  is 2.1, which is a little wider than polymer  $\mathbf{b}$ . That's properly because the protection of the hydroxyl group by the t-BOC group and the protection ratio is an average distribution.





Figure 2. the GPC curve of polymer b (PHS-S- $C_4F_9SO_3$ )



Figure 3. the GPC curve of polymer c (PHS-S-BOC)

## 2. The IR spectrum of the acid-catalyzed decomposition of the t-BOC protection

The photoacid generating of the polymeric PAG can be confirmed by the acidcatalyzed decomposition of the t-BOC protection. Taking the 55 mol% protected sulfonium nonaflate as an example (sulfonium amount: 16%), a film of the polymeric PAG was formed on a KBr slice and FTIR spectra of the film were recorded before and after exposed to a low pressure mercury lamp (254 nm)



Figure 4. the IR spectra change of polymer c film (1) without exposure; (2) with flood

exposure (dose=400 mJ/cm<sup>2</sup>) following by post exposure bake (PEB) at 130 °C for 2 min. Only the region from 4000 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> is shown.

## 3. The molecular structure of ester acetal polymer p(APA-CHDDE)



Figure 5. the structure of polymer p(APA-CHDDE)