*IOSR Journal of Applied Chemistry (IOSR-JAC)*
*e-ISSN: 2278-5736.Volume 19, Issue 4 Ser. I (April. 2026), PP 42-44*
*www.iosrjournals.org*

# Synthesis Of Chemically Amplified Positive Photoresist

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***Abstract:***
*4-(4'- sulfonato butoxy) styrene sodium was synthesized by the treatment of 4-hydroxyl styrene and 1, 4-butane sultone in presence of 50 wt% aqueous solution of sodium hydroxide and tetrabutyl ammonium bromide in the solvent medium of DMSO heated at 125$^0$c for 6h. Triphenylsulfonium salt of 4-(4'-sulfonato butoxy) styrene was synthesized by the treatment of 4-(4'-sulfonato butoxy) styrene sodium with 50% aqueous solution of triphenylsulfonium chloride stirring at room temperature for overnight, and extracted with dichloromethane. The organic layer was dried over magnesium sulfate. The solvent was removed and the product was dried under vacuum. Polymerization was carried out in presence of AIBN as a free radical initiator (5 mol% to the monomer) in the solvent medium of anhydrous tetrahydrofuran and acetonitrile at 65$^0$c for 24h . The polymer solution were precipitated into a large amount of diethylether and dried in vacuum. The product were redissolved in THF and precipitated with petroleum ether and dried in vacuum for 24h.*

***Keywords:*** *4- (4'- sulfonato butoxy) styrene sodium, triphenyl sulfonium salt, polymerization, UV -light.*

Date of Submission: 09-04-2026 Date of Acceptance: 19-04-2026

## I. Introduction:

The chemical amplification concept was invented at IBM research and quickly brought into use in the production of dynamic random access memory devices in the company. It has remained as an important foundation for the design of advanced resist systems for use in short-wavelength (less than 300 nm) lithographic technologies. We are perhaps in the most exciting era of microelectronics technology. The home computer market is growing rapidly in quantity and quality. Furthermore, the microlithographic technology, the core technology of semiconductor device manufacture, is drastically changing as the minimum feature size of electronic devices is shrinking to less than 0.25µm.

Since the resolution is proportional to the exposing wavelength and inversely proportional to the numerical aperture of the lens, higher resolutions are achieved by increasing the numerical aperture or by reducing the exposing wavelength. The most dominant approach to resolution enhancement has been to shift from the G-line (436nm) to I-line (365nm) and then to increase the NA of the I-line step-and-repeat exposure tools. Another approach is to move to much shorter wavelengths. The shift from the near-UV (436-365 nm) to the mid-UV region (300 – 350 nm) required modification of the diazonaphthaquinone / novolac resist to improve its absorption characteristics at the shorter wavelength. Further reduction of the wavelength the deep - UV regions (254 nm) was sought at IBM in the late 1970s, which necessitated the development of a revolutionary resist system. The classical near-UV positive resist consisting of a novolac resin and a photo active diazonaphthaquinone dissolution inhibitor does not perform adequately because of its excessive unbleachable absorption to the deep-UV region. Several attempts to overcome the problem were only partially successful.

Furthermore, phenolic resins were believed to be too absorbing for use in the deep-UV region, prompting serious research activities to utilize deep-UV transparent methacrylate polymers in the new lithographic technology. However, low resist sensitivity and poor dry etch resistance precluded the use of methacrylate resists in semiconductor manufacture. In fact sensitivity enhancement was a major research subject for many years, but the achievement was only incremental and too marginal to support the new high-resolution technologies. The resist systems based on photochemical events that require several photons to generate one useful product have inherently limited sensitivities.

In order to circumvent this intrinsic sensitivity limitation and to dramatically increase the resist sensitivity, the concept of chemical amplification was proposed in 1980 and reported in 1982. In chemically amplified resist systems, a catalytic species generated by irradiation induces a cascade of subsequent chemical transformations, providing a gain mechanism. The original chemical amplification scheme included (1) cross-linking through ring -opening polymerization of pendant epoxide groups for negative imaging (2) cleavage of pendant groups to induce a polarity change for dual–tone imaging (3) depolymerization for self-developing positive imaging. These three systems are all acid-catalyzed. The chemical amplification concept was considered as a laboratory curiosity when reported. However, as the value of this totally new system became apparent, it was used in production of 1 Mb dynamic random access memory (DRAM) chips by deep-UV lithography in the mid-1980s. Although the use of acid as a catalyst has eventually become the major foundation for the entire family of advanced resist systems, and the semiconductor industry is currently moving steadily toward deep-UV lithography based on chemical amplification resists. IBM already had a long history of DRAM production by deep-UV lithography, made possible by the availability of chemical amplification resists.

## II. Experimental:

**synthesis of 4 – (4’-sulfonato butoxy) styrene sodium:**

To a stirred mixture of 4–hydroxy styrene ( 1.44 g , 12 m mol ) and 60 ml of DMSO under nitrogen were added tetrabutyl ammonium bromide ( 80 mg ) and 5 ml of a 50 wt % aqueous solution of sodium hydroxide . 20 ml DMSO solution of 1, 4-butane sultone (2g, 14 m mol) was added dropwise to the mixture. The reaction mixture was heated at $125^0$c for 6h. The reaction mixture was cooled and precipitated into 500 ml of acetone. The resulting product was collected by filtration and recrystallized from acetone.

**synthesis of triphenyl sulfonium salt of 4 –(4’- sulfonato butoxy) styrene sodium :**

4 - (4’-sulfonato butoxy) styrene sodium was reacted with triphenyl sulfonium chloride 50 % aqueous solution in water at room temperature overnight. The product was refined with dichloromethane and hexane. The product was obtained as a colourless crystal.

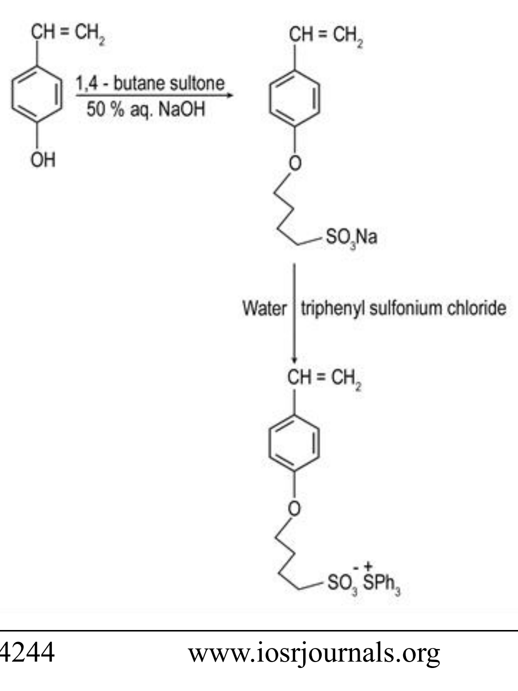
**Polymerization :**

Polymer was prepared by free radical polymerization in sealed pressure vessel Triphenyl sulfonium salt and azobis isobutyronitrile (AIBN) (5 mol % to the monomer) were dissolved in freshly distilled anhydrous THF and acetonitrile. Polymerization was performed at $65^0$c for 24 h. The polymer solution were precipitated into a large amount of diethyl ether and dried in vacuum, the product was then redissolved in THF and precipitated with petroleum ether and then dried in vacuum.

## III. Result And Discussion:

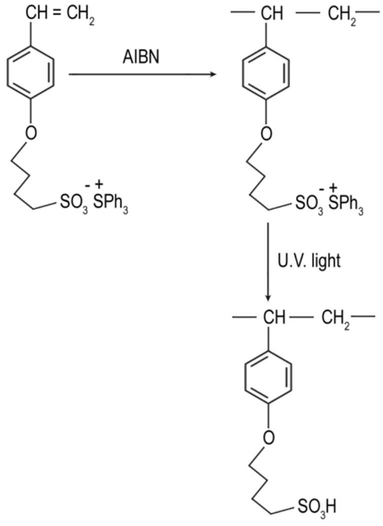
IR, UV and NMR spectra revealed the successful preparation of the polymer. 4–(4’– sulfonato butoxy ) styrene sodium was synthesized by the treatment of 4 – hydroxy styrene with 1 , 4 – butane sultone in presence of 50 wt % aqueous solution of sodium hydroxide and tetrabutyl ammonium bromide in the solvent medium of DMSO . The reaction mixture was heated at $125^0$c for 6h. The reaction mixture was cooled and precipitated into 500 ml of acetone. The resulting product was collected by filtration and recrystallized from acetone. Triphenyl sulfonium salt of 4–(4’– sulfonato butoxy) styrene sodium was prepared with 50 % aqueous solution of triphenyl sulfonium chloride in water at room temperature overnight. The product was refined with dichloromethane and hexane. The synthetic route of monomer was described in scheme - I.

Scheme - I



The polymer was synthesized by free radical polymerization in sealed pressure vessel. Triphenyl sulfonium salt and azobisisobutyro nitrile (5 mol % to the monomer) were dissolved in freshly distilled anhydrous THF and acetonitrile. Polymerization was performed at $65^0$c for 24h. The polymer solution were precipitated into a large amount of diethylether and dried in vacuum, The product was then redissolved in THF and precipitated with petroleum ether and then dried in vacuum. The synthetic route of the polymer was described in scheme -II.

Scheme – II



After irradation of U.V. light the lipophilic polymer is converted to hydrophilic sulfonic acid polymer by reaction with a photochemically generated acid. This change of polarity from nonpolar to a polar state allows the polymer to be alkali soluble. The use of polar solvent such as aqueous base results in the generation of positive-tone images. Although this polarity change concept has become the basis for the design of aqueous-base-developable positive resist systems.

## IV. Conclusion:

The chemical amplification concept was invented by IBM and quickly applied to the manufacture of DRAM s by deep–UV lithography. After more than twenty years since its invention, the entire litho graphy community is moving toward deep–UV lithography, a technology made possible by chemical amplification. In addition to enhanced sensitivity, high contrast and high resolution are the major reasons for the industry-wide acceptance of chemical amplification. Materials and processes of chemical amplification resists will continue to be refined to support highly demanding future lithographic technologies.

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