

Photoreactive Polymers. IV. The Synthesis and Characterization of Photocrosslinkable Polysulfonates

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Synopsis

A series of new light-sensitive polysulfonate copolymers have been prepared by the interfacial polycondensation of mixed bisphenols and aromatic disulfonyl chlorides. The light-sensitive bisphenols contain the styryl ketone group. These polymers exhibit good light sensitivity, and upon exposure to light they crosslink and harden to give alkali- and acid-resistant materials which are useful in photoresist applications.

INTRODUCTION

Following the advent of the first synthetic photocrosslinkable polymer, Minsk's^{1,2} poly(vinyl cinnamate), efforts have been directed toward polymers with higher rates of photocrosslinking. These rate increases have been attained by modification of the light-absorbing chromophore as well as of the spectral sensitizers.³ The utility of photocrosslinked polymers as photoresists resides in their resistance to chemical decomposition by various acidic or basic etchants. It has been, therefore, important to seek a series of polymers which exhibit high resistance to hot etchants. Hill indicated that polymers such as poly(ethylene terephthalate) show such resistance, a property growing out of the regularity of structure imparted by the terephthalate.⁴ Thus, the terephthalate polyesters show marked increases in resistance to hydrolysis over aliphatic polyesters, as well as much higher melting points and values of modulus.⁴

In our present investigation, we prepared some aromatic polysulfonate copolymers which were found to be remarkably resistant to both acid and base hydrolysis. The high hydrolytic stability is attributed to the regularity of structure as well as to steric factors of the polymer chain.

EXPERIMENTAL

The light-sensitive polysulfonate copolymers were prepared by the interfacial polycondensation method. A typical preparation (of copolymer II, Table I) is as follows:

TABLE I
 Light-Sensitive Polysulfonate Copolymers^a

Polymer number	Bisphenol, nonlight-sensitive, mole-%	Bisphenol, light-sensitive, mole-%	Aromatic disulfonyl chloride, mole-%	η_{inh}	$T_g, ^\circ C$	Elemental analysis calcd (found)		
						C	H	S
I	BPA,25	DVA,25	$\alpha_0,50$	0.68	130	57.5 (56.9)	4.0 (3.8)	13.4 (13.0)
II ^b	BPA,25	DVA,25	$\alpha_1,50$	1.0	141	58.4 (57.9)	4.2 (4.3)	13.0 (13.4)
III	BPA,25	DVA,25	$\alpha_2,50$	0.59	—	59.2 (58.8)	4.5 (4.8)	13.0 (12.6)
IV	BPA,25	DVCP,25	$\alpha_0,50$	0.72	135	58.6 (58.6)	4.1 (4.1)	13.0 (13.0)
V	BPA,25	DVCP,25	$\alpha_1,50$	0.88	147	59.1 (59.4)	4.3 (4.3)	12.6 (12.2)
VI	BPA,25	DVCP,25	$\alpha_2,50$	0.96	—	60.0 (60.2)	4.6 (4.7)	12.6 (12.2)

^a BPA = bisphenol A; DVA = divanillalacetone ($\lambda_{max} = 343$ nm); DVCP = divanillalicyclopentanone ($\lambda_{max} = 358$ nm); $\alpha_0 = m$ -benzenedisulfonyl chloride; $\alpha_1 = 1$ -methyl-2,4-benzenedisulfonyl chloride; $\alpha_2 = 4,6$ -dimethyl-1,3-benzenedisulfonyl chloride; η_{inh} = inherent viscosity in phenol-chlorobenzene (1:1) (0.25 g./100C at 25°C).

^b Number-average molecular weight = 54,000 (Dohrman membrane osmometer at 35°C).

In a 2000-ml, three-necked flask equipped with a condenser, a dropping funnel, and an air stirrer were placed 22.8 g (0.10 mole) bisphenol-A, 32.6 g (0.10 mole) divanillalacetone, and 415 ml 1*N* NaOH (0.415 mole) (a 4% excess of caustic). The solution was stirred for 10 min, and 1.13 g benzyltriethylammonium chloride was added (1% by weight based on the weight of the reactants). The solution was stirred an additional 5 min. To this stirred solution was added rapidly (1–2 min) 57.8 g (0.2 mole) 1-methyl-2,4-benzenedisulfonyl chloride dissolved in 415 ml methylene chloride. After 1½ hr, the wine-red color characteristic of the disodium salt of the divanillalacetone disappeared and the reaction mixture turned yellow. The yellow solution was stirred an additional 2½ hr (total reaction time, 4 hr). To isolate the polymer, the reaction mixture was dripped into hot water with vigorous stirring. The resulting mixture was filtered, and the polymer was washed on the filter with water, then with methanol, and then dried in a vacuum oven at 50°C for 24 hr. The yellow polymer was isolated in better than 90% yield. The inherent viscosity in phenol-chlorobenzene (1:1) (0.25 g/100 ml at 25°C) was 1.0.

Anal. Calcd for C, 58.4%; H, 4.0%; S, 13.4%. Found: C, 57.9%; H, 4.3%; S, 13.0%.

RESULTS AND DISCUSSION

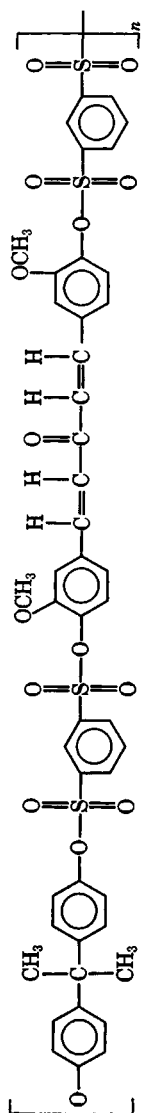
The initial light-sensitive polysulfonate copolymers were prepared by the interfacial polycondensation of bisphenol-A (BPA), divanillalacetone (DVA), and *m*-benzenedisulfonyl chloride (α_0) (copolymer I, Table I); and BPA, divanillalicyclopentanone (DVCP), and α_0 (copolymer IV, Table I).

Polymers I and IV exhibited excellent stability in hot 20% sodium hydroxide and in ferric chloride; however, the polymers were soluble (10% solids) only in a mixture of cyclohexanone and 4-butyrolactone. As a result of this limited solubility, a program was initiated to improve the solubility of the light-sensitive polysulfonate copolymers to make them more desirable for photoresist applications.

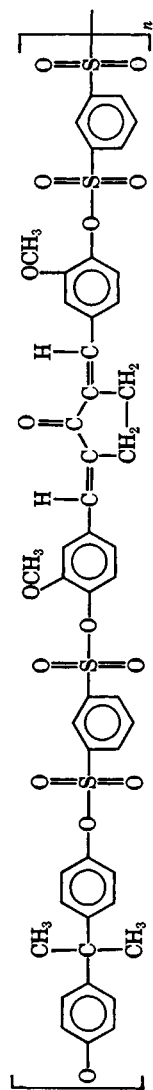
In this program, a series of light-sensitive polysulfonate copolymers were prepared based on structure I.

The bisphenol-A moiety in structure I was replaced by other nonlight-sensitive bisphenols such as bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl) ether, 2,2-bis(4-hydroxyphenyl)hexane, or 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane. Modification did not improve the solubility (10% solids) of the resulting polymers in chlorinated solvents such as 1,2-dichloroethane, 1,1,2-trichloroethane, and chlorobenzene.

The next modification was the replacement of the 1,3-benzenedisulfonyl chloride with two additional aromatic disulfonyl chlorides (1-methyl-2,4-benzenedisulfonyl chloride and 4,6-dimethyl-1,3-benzenedisulfonyl chloride) (α_1 and α_2 in Table I). This modification led to the preparation of high-molecular-weight, light-sensitive polysulfonate copolymers possessing



copolymer I



copolymer IV

TABLE II
Relative Photographic Speeds of Photoresist Formulations

Plate	Coating thickness, mils	Speed (last visible step)
A	0.22	1.10
B	0.12	1.25
C	0.20	1.40
D	0.13	1.40

the desired solubility (10% solids) in chlorinated solvents such as 1,2-dichloroethane, 1,1,2-trichloroethane, and chlorobenzene. The composition and properties of the polymers prepared in this phase of the program are summarized in Table I.

For a comparison of the polysulfonates with known light-sensitive polymers, four 1/8-in. aluminum supports were pumiced, cleaned in alkaline solution, and treated for 3 min at room temperature with a chromate conversion solution. Formulation A, a 10% dope of a copolycarbonate of 1.98 moles tetrachlorobisphenol-A, 2.557 moles divanillalicyclopentanone, and 1,3-dichloroformyloxy-2,2-dimethylpropane prepared by the method of Borden and co-workers⁵ was whirl coated on one of the supports at 80 rpm for 1 hr at room temperature. A second formulation, B, a resist composition based on poly(vinyl cinnamate),⁶ was coated on another of the supports in a similar manner. A third formulation, C, based on a cyclized natural rubber,⁷ was similarly coated on a third support. The fourth formulation, D, consisting of a 10% dope of polymer II, was coated in a similar manner on the fourth support. These four plates were prebaked for 10 min at 80°C and exposed imagewise for 5 min at a distance of 4 ft to a 95-amp carbon arc (6500 ft candle min) through a 0.15 log *E* density step table. The relative photographic speed is measured by the last visible step obtained after development. Plates A and D were tray developed with dichloroethane for 1.5 min. Plate B was developed in a trichloroethylene vapor degreaser for 15 sec at 2 lb spray pressure. After development, each plate was postbaked for 10 min at 160°C. The relative speeds of the samples in relation to each other and the coating thickness of each sample are shown in Table II.

The plates shown in Table II were etched simultaneously with 20% NaOH solution at 150°F until breakdown. Sample D held up in the presence of hot alkali better than A and B, but not so well as C, which was twice as thick a coating.

CONCLUSIONS

The preparation of some new light-sensitive polysulfonate copolymers is described. These polymers have excellent chemical resistance to both acid and base etchants. The excellent hydrolytic stability of these polymers renders them useful for photofabrication and printed-circuit applications.

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