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The Synthesis and Evaluation of Cyclic Olefin Sulfone Copolymers and Terpolymers as Electron Beam Resists

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Synopsis

Poly(cyclopentene sulfone) (PCPS) and poly(bicycloheptene sulfone) (PBCHS) copolymers have been evaluated as potential positive electron beam resists which have good thermal properties and which show high sensitivity to ionizing radiation. It was found that thin copolymer films could be processed as resists but that films greater than 3000 Å thick cracked in the solvents used to dissolve the radiation-exposed regions. Incorporation of plasticizing additives did not improve the film properties. Films from low molecular weight polymer fractions cracked less in solvents, but higher radiation doses were required to offset the reduced sensitivity. This resulted in the formation of intractable residues in the exposed regions which appear to be crosslinked polymer. Bicycloheptene monomers with specific functional groups did not improve the properties of the copolymer films. Terpolymerization with α-olefins such as butene-1 and *cis*-2-butene plasticized these films and reduced their tendency to crack in solvents. Poly(cyclopentene sulfone–co–butene-1 sulfone) films were found to have the best properties, and 1.25-μ resist images could be etched in SiO_2 layers at an exposure dose of 4×10^{-6} C/cm^2 at 25 KV. However, one important limitation of this terpolymer was the low dissolution rate ratio between the exposed and unexposed regions. Since straight-walled relief images are essential to the formation of high-resolution patterns, the usefulness of this terpolymer as an electron beam resist appears to be hindered by the limited choice of good solvents to maximize the dissolution rate ratio. PBCHS block terpolymers containing methyl methacrylate (MMA) or methacrylic acid (MAA) were synthesized to improve the solubility in solvents and to incorporate the properties of methacrylates. PBCHS–MMA films cracked in solvents after irradiation; PBCHS–MAA polymers were too insoluble to form resist films.

INTRODUCTION

The high radiation sensitivity of poly(olefin sulfones) has been well-established.[1,2,3] These polymers when irradiated with doses as low as 1 to 2×10^{-6} C/cm^2 undergo rapid chain scission, resulting in a significant lowering of the molecular weight. Compared to other degrading polymers, such as poly(methyl methacrylate),[4] the $G_{(\text{scission})}$ value of 10 to 12 for poly(olefin sulfones) is one of the highest reported. These high sensitivities have made this class of polymers excellent candidates for use as positive electron beam resists.[3] (Polymeric films are used as resists in electron lithographic processes. Patterns are delineated in these films by a finely focused beam of electrons. The irradiated regions degrade and are removed by fractional dissolution in a solvent, i.e., development, to leave a positive image in the film.)

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TABLE I
Thermal Properties of Cyclic Poly(olefin Sulfones)

Polysulfone	Temperature, °C				Wt. loss, %
	T_g	T_c	T_m	T_d	
Bicycloheptene	117	>150	240–290[a]	200[b]	8[c]
Cyclopentene	82	103	200[a]	130[b]	8[c]

[a] Melting with decomposition.
[b] Onset of decomposition.
[c] Weight loss after 1 hr.

The selection and use of a particular poly(olefin sulfone) as a resist will depend on polymer properties such as film quality, adhesion, resistance to acid and alkaline etchants, and thermal stability. These properties were investigated extensively by Bowden and Thompson[3,5] and by Himics and co-workers[6,7] during studies in which aliphatic, cycloaliphatic, and functionally substituted poly(olefin sulfone) films, 3000 Å thick, were evaluated as potential positive electron beam resist materials. Poly(butene-1 sulfone) and poly(1-methyl cyclopentene sulfone) were reported to have the best resist properties.

Many of the poly(olefin sulfones) evaluated by these investigators have also been investigated in our laboratories. Our objective was to obtain a resist material of high radiation sensitivity and possessing those thermal properties which would permit films of about 1 μ (10,000 Å) thick to be processed without degradation. Those poly(olefin sulfones) having ceiling temperatures T_c below 60°C gave visible images after electron beam exposure but were thermally unstable and degraded during processing. Two cyclic poly(olefin sulfones), poly(cyclopentene sulfone), (PCPS) and poly(bicycloheptene sulfone) (PBCHS), having ceiling temperatures above 100°C and melt temperatures above 200°C,[8,9] were the most stable thermally. In addition, the glass transition temperatures of PCPS and PBCHS were below their respective T_c's (cf. Table I). Thus, spun films could be annealed without decomposition. A more extensive evaluation of these cyclic poly(olefin sulfones) as potential electron beam resist materials has been carried out, and the results of this study are reported.

EXPERIMENTAL

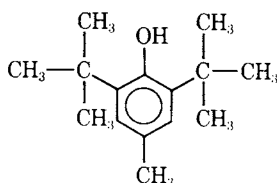
Synthesis of Polysulfones

Solution polymerizations were carried out at −30° to 10°C initiated with *t*-butyl hydroperoxide in a 1-l. four-necked jacketed resin flask equipped with stirrer, thermometer, jacketed addition funnel, and helium gas inlet. Polymerizations were also carried out in a 2-l. glass-lined Parr stainless steel stirring-type pressure reactor. A circulating refrigerated liquid was used to control the polymerization temperature. High-purity (>99%) commercial-grade olefins and anhydrous sulfur dioxide were used without further purification. Spectrograde cyclohexanone (MCB CX 2334, 99+ mole-%) and spectrophotometric-grade hexane ("Baker analyzed" reagent) solvents were used as received. Polymers of different molecular weight were prepared by varying the initiator concentration and the amount of chain transfer agent (dodecyl mercaptan) in

the mixture. The polymers were recovered by precipitation into methyl alcohol, a nonsolvent, and purified by repeated dissolution in chloroform and precipitation in methyl alcohol which was followed by vacuum drying at 50–60°C for 24 to 48 hr.

Gel Permeation Chromatography[10]

Molecular weight averages $\bar{M}_w$ and $\bar{M}_n$ (relative to polystyrene standards) of the synthesized polymers were determined with a modified Waters Associates gel permeation chromatograph (GPC) Model 200 with five 4-ft fractionating columns having permeability limits from 5×10^6 to 5×10^3 Å. The mobile phase used in this work was chloroform distilled in glass (Burdick and Johnson) which was stabilized with 1% ethyl alcohol by volume. In preparing the samples, a free-radical scavenger-type stabilizer, Ionol (Shell Chemical Co. trademark)



di-*t*-butyl cresol, Antioxidant No. 29, a product of the Shell Chemical Co.

was added to prevent degradation or gelation of the polysulfone during the analysis.

Intrinsic Viscosities

A Bausch and Lomb Fica Viscomatic automatic viscometer was used to measure the intrinsic viscosity (dl/g) of some of the polymers.

Pyrolysis Gas Chromatography and Mass Spectrometry

Pyrolysis studies of some of the experimental polymers were carried out in a Perkin–Elmer 990 gas chromatograph connected in series to a Hitachi RMS4 mass spectrometer. The pyrolysis products were separated in the gas chromatograph and each fraction passed into the mass spectrometer for confirmation of the products and their respective ratios. From these data, the sequence distribution and the structure of the polymer could be determined.[11]

NMR and IR Spectroscopy

NMR spectra were obtained with a Varian HA-100 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were obtained with a Perkin–Elmer 521 grating spectrophotometer.

Thermal Measurements

Thermogravimetric analyses were carried out under nitrogen at a 5°C/min heating rate with a du Pont 950 TGA instrument. Glass transition temperatures

were measured by dilatometry and by differential thermal analysis with a du Pont 901 DTA instrument.

Radiation Sensitivity

Gamma radiolysis studies of the solid polymers and some dilute polymer solutions (2 to 5 wt %) in chloroform, nitromethane, and cyclohexanone were carried out at the facilities of the Texaco Research Center, Beacon, New York, and those of International Nutronics Inc., Palo Alto, California. The polymers were exposed at 0.5, 1.0, 1.8, and 3.5 Mrad doses of ^{60}Co gamma radiation. The changes in molecular weight versus irradiation dose were measured by GPC and by solution viscometry in chloroform or cyclohexanone at 25°C.

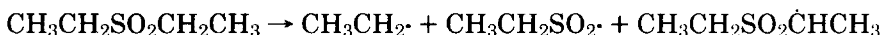
Electron Beam Exposure

SiO_2 substrates were spin coated with the polymers from filtered solutions using a Headway Research Model EC-101 spinner. These films were baked to remove solvent and then exposed to 15 and 25 kV at doses from 3 to 18 $\mu C/cm^2$. The thickness of the exposed and unexposed film areas was measured on a Rank Talystep instrument after development in an appropriate solvent. The resist films were etched in buffered HF at 25°C, and the image fidelity was examined at 400X on a Bausch and Lomb Dynoptic metallurgical microscope.

RESULTS AND DISCUSSION

GPC measurements of PCPS and PBCHS, irradiated *in vacuo* at 25°C, showed rapid degradation for doses up to about 2 Mrad and decreased degradation rates at higher doses. Plots of $1/\bar{M}_n$ versus dose (cf. Fig. 1) were linear up to 1.5 Mrad and gave $G_{(\text{scission})} = 6.4$ for PCPS and 6.2 for PBCHS. These G values are lower than those reported[1,2] for aliphatic poly(olefin sulfones) such as poly(butene-1 sulfone), $G = 11.2$, and poly(hexene-1 sulfone), $G = 9.8$.

The sensitized decomposition of poly(olefin sulfones) has not been reported, and the singlet and triplet levels of these polymers are not known. Electron spin resonance studies[12] of irradiated poly(olefin sulfones) suggest successive main-chain C—S scission and SO_2 elimination. In the radiolysis of a model compound, diethyl sulfone, three radical species were identified, i.e.,



$$CH_3CH_2SO_2CH_2CH_3 \rightarrow CH_3CH_2\cdot + CH_3CH_2SO_2\cdot + CH_3CH_2SO_2\dot{C}HCH_3$$

Therefore, the decomposition of primary olefin sulfones involves scission of C—S and C—H bonds. In tertiary olefin sulfones, higher yields of radicals are obtained:

$$[(CH_3)_3C]_2SO_2 \rightarrow (CH_3)_3C\cdot + (CH_3)_3CSO_2\cdot$$

In this case, only the weaker C—S bonds (55 kcal/mole) undergo scission.

The photoexposure and electron beam exposure of PCPS was examined by adding triplet sensitizers such as fluorene or halocarbon additives such as CBr_4 (cf. Table II). Both types of additives (5 w/v%) enhanced the formation of positive images. In the photoexposure, the radiation (>3000 Å) was selectively absorbed by the triplet sensitizers. If the reaction proceeds via the triplet state

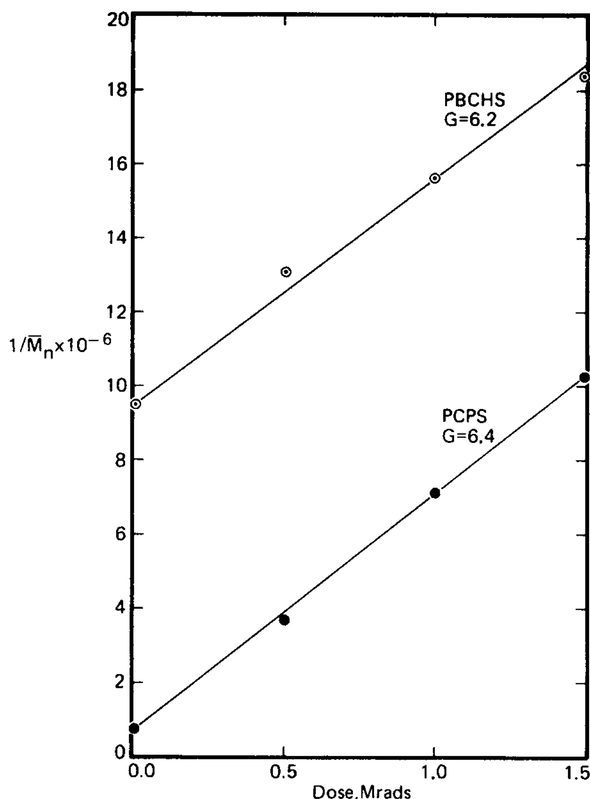


Fig. 1. $1/\bar{M}_n$ vs. dose plots for poly (cyclopentene sulfone) (PCPS) and poly(bicycloheptene sulfone) (PBCHS) irradiated in vacuo at 25°C.

of the polymer, the triplet state of the additive would have to be higher than that of the polymer. From the known triplet energy levels of the additives, the triplet state of PCPS is estimated to be about 65 to 70 kcal/mole. Halocarbon additives have been reported to sensitize the decomposition of polymers in solution.[4] CBr_4 enhanced the solid-state decomposition of PCPS about 5 times and produced excellent images (cf. Fig. 2).

For the processing studies, films of PCPS and PBCHS, 1500 to 9000 Å thick, were spin coated from 7 w/v% solutions of 1,3-dichloropropane and 1,5-dichloropentane, respectively. An important requirement of the spinning solvent was that its boiling point be below the decomposition temperature of the polysulfone. This is to ensure removal of the solvent during the prebake step without decomposition of the resist. Intrinsic viscosity measurements of PCPS films baked at 90° and 135°C for 1 hr indicated that no change had occurred at 90°; but at 135°C, the molecular weight had been reduced by a factor of 4. Thermal gravimetric analysis indicated that the initial weight loss of PCPS began at 130°C and that of PBCHS began at 200°C (cf. Figs. 3 and 4). Therefore, PCPS and PBCHS films were prebaked below the T_c, but above the T_g at 90° and 135°C, respectively, for 1 hr. These films were exposed and then placed in solvents to dissolve the irradiated regions. Some cracks were observed in the thin films, but those films greater than 3000 Å thick cracked severely. The thicker films

TABLE II
Sensitizers for Radiation of Poly(cyclopentene Sulfone)

Additive	Type	Quality of image
CBr_4[a]	radical	excellent
Azulene	triplet	good
Fluorene[b]	triplet	good
p-Nitroaniline	triplet	good
Azobenzene	triplet	good

[a]Photodecomposition to yield Br free radicals, A. P. Zeelonberg, *Nature*, 181, 42 (1958); T. Tagawa, E. Tsuchida, I. Shinohara, M. Hagierara and T. Kagiya, *Polym. Lett.*, 13, 287 (1975).

[b]Triplet energy level is 68 kcal/mole in J. Turro, *Molecular Photochemistry*, W. A. Benjamin, New York, p. 132.

appear to be highly stressed. Annealing near or at the melt temperatures resulted in extensive decomposition of the polymers.

In order to gain a better understanding of the cracking phenomenon in cyclic poly(olefin sulfone) films, the solution behavior of PBCHS has been investigated in $CHCl_3$ and cyclohexanone solvents.[10] Light-scattering studies have also been carried out on PCPS and PBCHS hot-pressed and solvent-cast films to determine the effect of polymer crystallinity on cracking and whether crystallization can be induced by the solvents used to dissolve the irradiated areas of the film.[13] This study indicated that cracking depended on the glass temperature as well as the crystallinity of the polymer. Further studies are continuing.

The following measures were taken to improve the film properties: (1) plas-

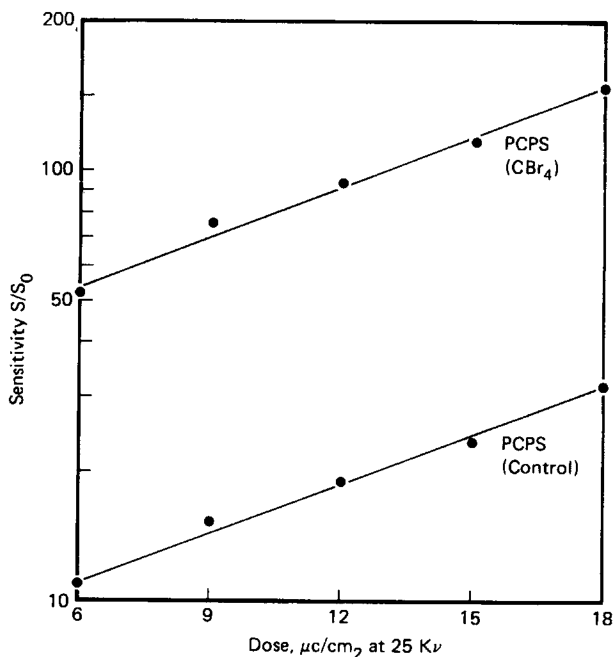


Fig. 2. Sensitivity of poly(cyclopentene sulfone) (PCPS) with and without CBr_4; 2000–3000 Å films developed in 1,6-dichlorohexane.

TABLE III
Molecular Weights Determined by GPC After Gamma Radiation of Poly(cyclopentene Sulfone)

Solvent	Molecular Weight				
	0 MRads	0.5 MRads	1.0 MRads	1.5 MRads	3.5 MRads
Neat	1330 K[a]	269 K	140 K	87 K	157 K
$CHCl_3$	1330 K	83 K	51 K	45 K	80 K
CH_3NO_2	1330 K	181 K	129 K	84 K	118 K

[a] Original number-average molecular weight of the polymer.

ticizers were added to lower the softening point of the polymers; (2) the use of low molecular weight (50,000 K) polymer fractions was investigated; (3) bicycloheptene derivatives with specific functional groups were synthesized to improve the spin-coating characteristics and to improve the adhesion and acid resistance; and (4) terpolymers were synthesized to internally plasticize the polymer. Terpolymerization increases the temperature range between softening and decomposition;[14] i.e., the glass transition temperature T_g is lowered as a result of internal plasticization and a diminution in the concentration of sulfone groups.

Phthalates, chlorinated biphenyls, and small-molecule sulfone compounds such as dibutyl sulfone, diphenyl sulfone, and tetramethylene sulfone were added as plasticizers in 1 to 10 wt % concentrations to PBCHS and PCPS solutions. The plasticized films became opaque and mottled after baking, indicating that the plasticizers and polymers were noncompatible.

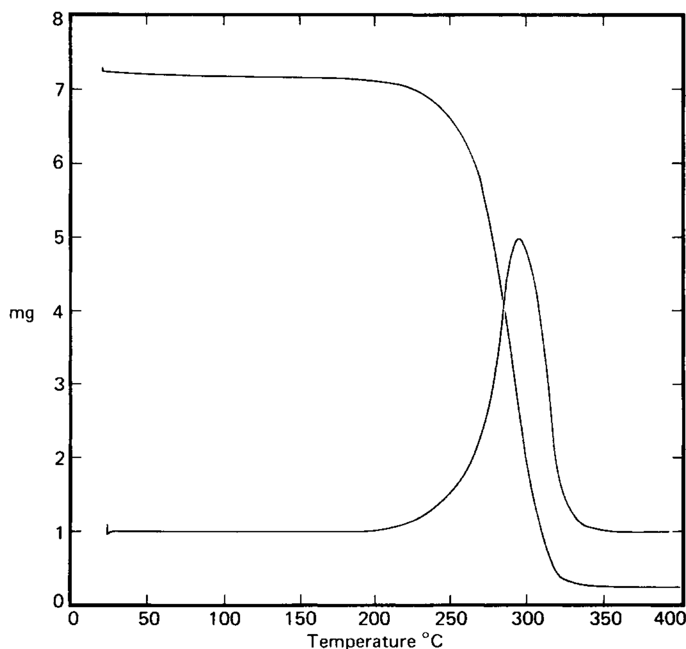


Fig. 3. TGA of poly(bicycloheptene sulfone) showing first derivative; heating rate, 5°C/min; N_2 atmosphere.

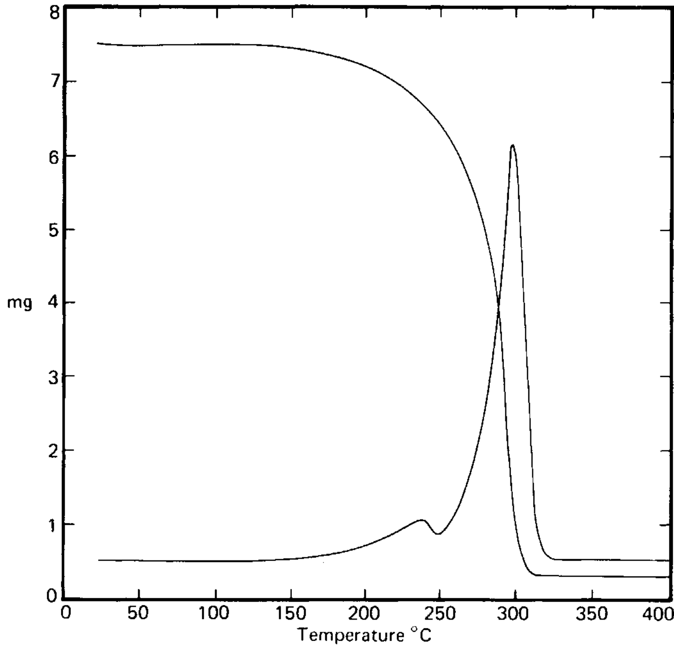


Fig. 4. TGA of poly(cyclopentene sulfone) showing first derivative; heating rate, 5°C/min; N_2 atmosphere.

Films from the low molecular weight fractions of PBCHS and PCPS cracked less in the developing solvents but required high exposure doses, i.e., 10 to 20 × 10^{-6} C/cm^2, to offset the reduced sensitivity. The exposed regions could not be fully dissolved in solvents (cf. Fig. 5) because intractable residues were produced. These residues appear to be crosslinked polymer networks which probably originate from side-chain irradiation to form free-radical sites. Presumably, the electron beam exposure of poly(olefin sulfones) at high doses results in both chain scissioning and crosslinking.

The formation of insoluble residues had also been reported by Bowden and Thompson[3,15] during their studies of the vapor development of low T_c poly(olefin sulfones). They found that the amount of residue produced in the irradiated regions depended on the exposure dose, the molecular weight of the polymer,

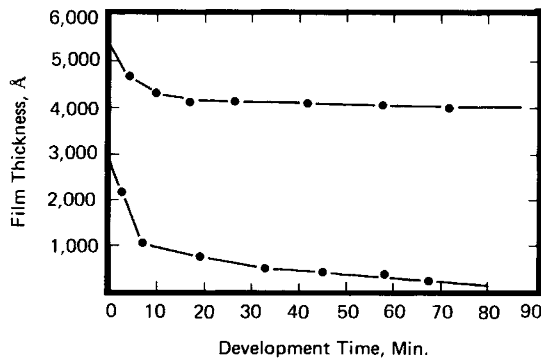


Fig. 5. Rates of development of low molecular weight PBCHS in 1,5-dichloropentane.

TABLE IV
Poly(bicycloheptene Sulfone) Derivatives

Derivative	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$[\eta]$,[a] dl/g	T_g, °C
Acetate ($OCOCH_3$)	416 K	175 K	2.40	—	100
Methyl ester ($COOCH_3$)	1786 K	468 K	5.6	0.75	133
Carboxylic acid (COOH)	soluble in poor solvents such as DMF, DMAC, DMSO				—
Alcohol (OH)	soluble in poor solvents such as DMF, DMAC, DMSO				—

[a] Measured in $CHCl_3$ at 25°C.

TABLE V
Poly(cyclopentene Sulfone) Terpolymers

Olefin	Conversion, %	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	T_g, °C
Hexene-1	99	339,200	171,650	1.98	64
Butene-1	92	3,161,222	243,481	12.9	57[a] 74[b]
cis-2-Butene	97	408,800	109,600	3.72	70
trans-2-Butene	99	653,146	103,667	5.98	85
cis-trans-2-Butene	90	217,000	83,000	3.03	78

[a] 50/50 PCPS/B-1-S Composition.
[b] 70/30 PCPS/B-1-S Composition.

TABLE VI
Poly(bicycloheptene Sulfone) Terpolymers

Olefin	Conversion, %	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	T_g, °C
Hexene-1	78	91,000	32,000	2.77	68
Octadecene-1[a]	38	680,100	52,000	13.1	80
cis-2-Butene	79	444,270	174,540	2.55	65
Butene-1	81	194,416	59,912	3.23	75

[a] Composition by pyrolysis GC: 80 mole-% bicycloheptene sulfone:20 mole-% octadecene-1 sulfone.

TABLE VII
Maximum Coating Thickness of PCPS and PBCHS Terpolymer Films Without Cracking

	Film thickness, Å	
Olefin	PCPS	PBCHS
Hexene-1	6400	4300
Octadecene-1	—	3000
cis-2-Butene	5800	5300
trans-2-Butene	5300	5000
Butene-1	9400	4700

TABLE VIII
Process Conditions for Poly(cyclopentene Sulfone–co–Butene-1 Sulfone)[a]

Adhesion promoter	bis(trimethylsilylacetamide) (BSA)
Coating solvent	nitromethane, 8% solution
Film thickness	4000 to 9400 Å
Prebake	80 to 100°C, vacuum, 30 min
Postbake	120 to 160°C, 30 min
Developer	cycloheptanone/cyclohexanone (80/20)
S/S_0	1.6 to 2.3
Etch	HF, 5 min

[a] Exposed at 4×10^{-6} C/cm^2 at 25 kV.

the film thickness, and the temperature at which the polymer was heated during exposure.

The effect of increasing doses of γ radiation on the formation of insoluble residues was demonstrated with PCPS, neat and in solution. These experiments demonstrated that the molecular weight of PCPS decreased at low doses and then increased at higher doses (cf. Table III). The insoluble residues formed in the irradiated areas would appear to originate primarily from the higher doses of electron irradiation. Therefore, a process using poly(olefin sulfones) as resists would require materials having a very high sensitivity to low doses of radiation.

The acetate, methyl ester, carboxylic acid, and hydroxyl derivatives of PBCHS were synthesized and evaluated (cf. Table IV). The acetate and methyl ester films had excellent adhesive properties but cracked in solvents. The acid and hydroxyl derivatives were too insoluble to form films.

Terpolymerization of PCPS and PBCHS improved the film properties and reduced the cracking. Elemental, pyrolysis GC, and NMR analyses indicated that these terpolymers were of approximate 1:1:2 (olefin:olefin:SO_2) molar

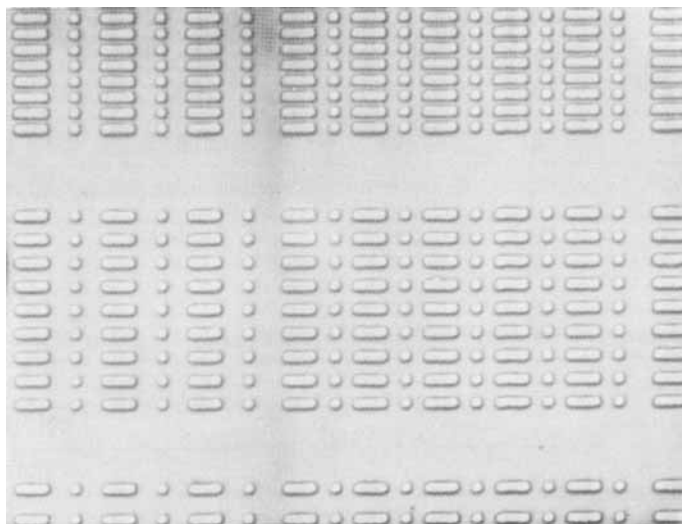


Fig. 6. Poly(cyclopentene sulfone-co-butene-1-sulfone) (6000 Å) 1.25 μ resist images etched in SiO_2 with HF at 25°C.

TABLE IX
Methacrylate–Olefin–SO_2 Block Terpolymers

Monomers[a]		Catalyst, g	Conversion, %	Structure, mole %	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
BCH,	9.5 g	AIBN, 0.07	65	BCH, 29	229K	40K	5.63
MMA,	10.0 g			MMA, 42			
SO_2,	45 psig			SO_2, 29			
BCH,	18.8 g	AIBN, 0.07	34	BCH, 32			
MAA,	6.4 g			MAA, 46			b
SO_2,	45 psig			SO_2, 32			

[a] MMA = Methyl methacrylate; MAA = methacrylic acid.
[b] Insoluble in common organic solvents.

composition (cf. Tables V and VI). Films could be spun to thicknesses about twice those of the respective copolymers before cracking (cf. Table VII) in solvents. Only the film properties of the octadecene-1-modified PBCHS terpolymer were not improved, and this is attributed to side-chain crystallization by the large alkyl group.[16] PCPS–butene-1 sulfone terpolymer films had the best properties. Films from 4000 to about 10,000 Å thick were exposed at 4×10^{-6} C/cm^2 at 25 kV and processed without cracking or loss of adhesion (cf. Table VIII). Patterned films were used as resist masks to etch 1.25-μ linewidth images in SiO_2 layers (cf. Fig. 6). The adhesion to SiO_2 layers was improved by the use of an adhesion promotor, bis(trimethylsilyl acetamide) (BSA). However, the differential dissolution rate ratio (S/S_0), the ratio of the dissolution rate of the exposed (S) regions to the dissolution rate of the unexposed (S_0) regions, in cyclic ketone solvents was less than 4, the minimum ratio required to obtain satisfactory high-resolution images. To maximize the differential dissolution rate ratio, narrow dispersivity, high molecular weight terpolymer fractions, and different solvent developers were evaluated.

Polymer fractions with molecular weights from 500,000 to 1,000,000 and dispersivities from 1.8 to 2.5 were evaluated. Dissolution rate ratios from 2.5 to 2.8 were obtained.

Cyclohexanone and cycloheptanone were the only solvents in which a moderate dissolution rate ratio could be obtained for the terpolymer film. Dissolution rate ratios could not be obtained in nitromethane or in nitroethane because of the very high dissolution rates of both the exposed and unexposed regions. In nitropropane or in nitrobutane, the dissolution rate was very slow; and after 24 hr, these areas had not dissolved completely.

Bicycloheptene–methacrylate–SO_2 terpolymers were also synthesized[17–19] to improve the solubility in solvents and to incorporate the properties of methacrylates. Methacrylates do not copolymerize readily with sulfur dioxide,[20,21] and the formation of PBCHS terpolymers can be regarded as the copolymerization of a complex of bicycloheptene and SO_2 with the free methacrylate monomer. The block sequences of methacrylate and methacrylic acid in these polymers (cf. Table IX) was confirmed by pyrolysis gas chromatography and mass spectrometry.[11]

The properties of PBCHS–methyl methacrylate polymers were not improved, and these films cracked in solvents. PBCHS–methacrylic acid polymers were too insoluble to form films.

CONCLUSIONS

PBCHS and PCPS copolymer films greater than 3000 Å thick could not be formulated into useful electron beam resists because these films cracked in solvents. Terpolymerization of PBCHS and PCPS with α-olefins improved the film properties. PCPS–co–butene-1 sulfone films had the best properties except for a low dissolution rate ratio between irradiated and nonirradiated regions. Poor solubility and a limited choice of solvents to optimize the dissolution rate ratio limits the usefulness of the terpolymer as an electron beam resist. Other applications for these cyclic copolymers and terpolymers, i.e., x-ray resists or as ion milling masks,[15] are being investigated.

References

1. J. Brown and J. O'Donnel, *Macromolecules,* **3,** 265 (1970).
2. J. Brown and J. O'Donnel, *Macromolecules,* **5,** 109 (1972).
3. M. Bowden and L. Thompson, *J. Appl. Polym. Sci.,* **17,** 3211 (1973).
4. A. Chapiro, in *Radiation Chemistry of Polymeric Systems,* Interscience, New York and London, 1962, pp. 509–545.
5. L. Thompson and M. Bowden, *J. Electrochem. Soc.,* **120,** 1722 (1973).
6. R. Himics, M. Kaplan, N. Desai, and E. Poliniak, *ACS Coating Plastics Prepr.,* **35**(2), 266, 273 (1975).
7. R. Himics and E. Poliniak, (to RCA Corp.), U.S. Pat. 3,935,332 (Jan. 27, 1976).
8. E. Hill and J. Caldwell, *J. Polym. Sci.,* **2,** 1251 (1964).
9. N. Zutty, C. Wilson, G. Potter, D. Priest, and C. Whitworth, *J. Polym. Sci.,* **3,** 2781 (1965).
10. A. Ouano, E. Gipstein, W. Kaye, and B. Dawson, *Macromolecules,* **8,** 558 (1975).
11. M. Seeger and E. Barrall II, *J. Polym. Sci.,* **13,** 1515 (1975).
12. P. Ayscough, K. Ivin, and J. O'Donnel, *Trans. Faraday Soc.,* **61,** 1601 (1965).
13. W. Chu, E. Gipstein, and A. Ouano, paper presented at First Chemical Congress of the North American Continent, Mexico City, Nov. 29–Dec. 8, 1975.
14. K. Ivin and J. Rose, *Advan. Macromolec. Chem.,* **1,** 355 (1968).
15. M. Bowden and L. Thompson, *Polym. Eng. Sci.,* **14,** 525 (1974).
16. J. Crawford and D. Gray, *J. Appl. Polym. Sci.,* **15,** 1881 (1971).
17. N. Zutty (to Union Carbide Corp.), U.S. Pat. 3,313,785 (Apr. 11, 1967).
18. M. Iino, K. Seki, and M. Matsuda, *J. Polym. Sci.,* **10,** 2993 (1972).
19. M. Matsuda, M. Hno, and S. Numata, *J. Polym. Sci. A-1,* **10,** 829 (1972).
20. N. Tokura, in *Encyclopedia of Polymer Technology,* Vol. 9, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley, New York, 1969, pp. 460–485.
21. S. Iwatsuki, T. Okada, and Y. Yamashita, *J. Polym. Sci. A-1,* **6,** 2451 (1968).

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