Design and Synthesis of Thermally Labile Polymers for Microelectronics. Poly(vinyl *tert*-butyl carbonate–sulfone)

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ABSTRACT: Poly(vinyl *tert*-butyl carbonate–sulfone) has been synthesized by using *tert*-butyl hydroperoxide as initiator at low temperatures. In order to optimize the reaction conditions, a series of model reactions was conducted by using vinyl acetate and sulfur dioxide. The reaction conditions for the model study were successfully applied to the copolymerization of vinyl *tert*-butyl carbonate and sulfur dioxide. Best results for the copolymerization were obtained by using excess liquid sulfur dioxide serving as both the solvent and the monomer. A study of the effect of temperature on the reaction showed a ceiling temperature near −20 °C under the conditions of typical experiments. Elemental and spectroscopic analyses of the poly(vinyl *tert*-butyl carbonate–sulfone) indicated that it had incorporated the two monomers in a 1:1 ratio and that it possessed an alternating structure. Thermal decomposition of the polymer resulted in a clean "unzipping" of both the polymer main chain and the pendant BOC groups with exclusive formation of volatile molecules carbon dioxide, acetaldehyde, isobutylene, and sulfur dioxide as confirmed both by thermogravimetric analysis (TGA) and GC mass spectroscopy.

Introduction

Polysulfones have attracted much attention due to their potential application in high-resolution microlithography.[1,4] One of the most attractive features of polysulfones is their well-known high sensitivity to radiation. For instance, poly(butene-1-sulfone)[2] has a sensitivity that is more than 1 order of magnitude greater than that of the standard electron-beam resist, poly(methyl methacrylate). However, poly(butene-1-sulfone) is primarily used as a wet-etch mask in the fabrication of chrome photomasks and has found little use as a dry-etch mask because of its lack of etch resistance in plasma environments.[5] Besides poly(butene-1-sulfone), a variety of poly(alkene–sulfones),[4,6-7] poly(cyclic alkene–sulfones),[8] and aromatic polysulfones[9] have been synthesized and tested as positive resist materials in several laboratories. Only some of them, however, have found limited applications as imaging materials. The search for new polysulfones that satisfy all the requirements for electron-beam lithographic fabrication is still extensive, while new materials also containing sulfur dioxide[4] are receiving attention for their potential use as deep-UV photoresists.

In this study, we report the first example of the synthesis of poly(vinyl *tert*-butyl carbonate–sulfone) and its thermal properties. Our original objective was to explore the thermolysis of poly(vinyl *tert*-butyl carbonate–sulfone) and its potential application as a self-developing electron-beam resist.

We have previously described the synthesis and thermolysis of two interesting polymers with *tert*-butyl carbonate pendant groups: poly[*p*-[[(*tert*-butyloxy)carbonyl]oxy]styrene][10] and poly(vinyl *tert*-butyl carbonate).[11] The former, used in the fabrication of high-density microcircuits by deep-UV microlithography,[12] is the best known example of a chemically amplified dual-tone resist.[13] The latter has been shown to be easily transformed into the water-soluble poly(vinyl alcohol) by thermal deprotection of the pendant BOC groups.[11]

However, in contrast to the successful use of poly[*p*-[[(*tert*-butyloxy)carbonyl]oxy]styrene],[12] attempts to use poly(vinyl *tert*-butyl carbonate) as a chemically amplified deep-UV resist material were not very successful. Exposure of a polymer film containing a few percent of a photoacid generator, followed by treatment with water, failed to produce a good image, as the system appears to have a very low sensitivity. This lack of sensitivity may be related to the relatively high basicity of the deprotected polymer, poly(vinyl alcohol). A strong interaction of the photogenerated protons with alcohol oxygens of the poly(vinyl alcohol) may result in their immobilization within the polymer film and restrict their ability to participate in multiple deprotection reactions; in the absence of a high degree of chemical amplification, the sensitivity of the system is low.

Our design for the use of poly(vinyl *tert*-butyl carbonate–sulfone) is to obtain a decomposition along the polymer main chain in an "unzipping" process that might be triggered by external radiation, for example, from an electron beam. The lability of the C–S bonds of polysulfones on exposure to certain types of radiation has been established previously by others.[2-9] Therefore, with the possible concomitant decomposition of the pendant BOC groups, the polysulfone could be cleaved completely to give all volatile small molecules. This approach is shown schematically in Scheme I. In theory, not only does this system have the advantage of chemical amplification but it is also expected to give images with "self-developing" character.[13]

Results and Discussion

The first attempt to prepare the copolymer of vinyl *tert*-butyl carbonate and sulfur dioxide was carried out under a standard condition for polysulfone synthesis using *tert*-butyl hydroperoxide as the initiator at low temperatures. It was found that the reaction was difficult to control. Although oligomers with irregular structure were obtained in several cases, all initial attempts to make high molecular weight polymers using standard conditions previously described for poly(alkene–sulfones)[2,3] failed.

Model Study: Copolymerization of Vinyl Acetate and Sulfur Dioxide. In order to optimize the reaction conditions for the copolymerization of vinyl *tert*-butyl carbonate and sulfur dioxide, a series of model reactions was carried out by using vinyl acetate as the vinyl monomer as shown in Scheme II.

Vinyl acetate was chosen as the monomer as it possesses some structural analogies with vinyl *tert*-butyl carbonate.

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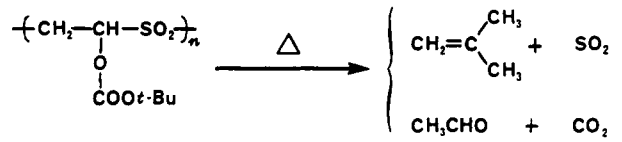
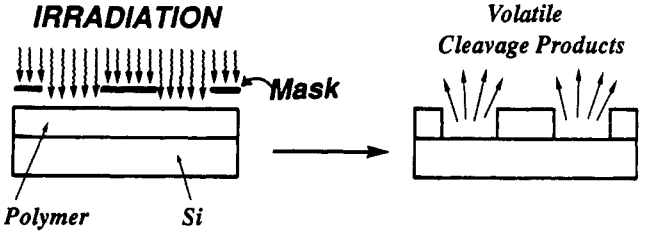
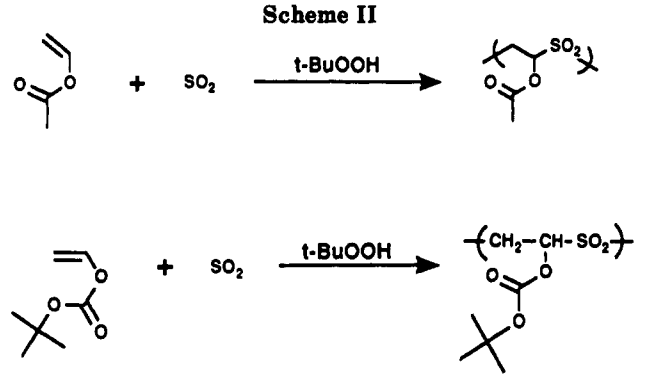
Scheme I





Scheme II



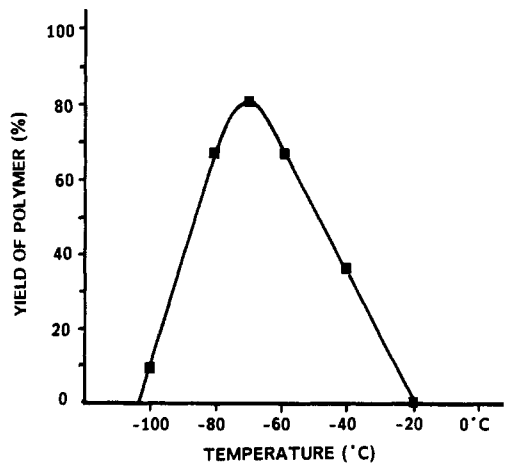


Figure 1. Relationship between polymerization yield and reaction temperature for the copolymerization of vinyl acetate and sulfur dioxide.

In addition, poly(vinyl acetate–sulfone) itself may be interesting as a resist material as claimed in several patents[14] that unfortunately contain little experimental evidence, even only of its preparation. The copolymer of vinyl acetate and sulfur dioxide was first synthesized by ionizing radiation[15] in the early 1960s, but it has remained poorly characterized.

The copolymerization of vinyl acetate and sulfur dioxide was performed at temperatures ranging from −100 to 0 °C. Figure 1 shows the yield of polymer as a function of temperature for reactions lasting 1 h under otherwise identical reaction conditions. Under these conditions, a ceiling temperature of −20 °C is observed and the optimum reaction temperature to maximize polymer yield appears to be near −70 °C. Below this temperature, the polymerization yield decreases with decreasing temperature. This is due to the partial lack of miscibility of vinyl acetate and sulfur dioxide at low temperatures. When the temperature reaches approximately −110 °C, the two monomers do not mix at all and two separate phases are formed; therefore, the copolymerization does not occur below this temperature.

Table I
Effect of Temperature on Copolymerization[a] of Vinyl Acetate with SO_2

		copolymer composition			
temp,[b] °C	yield, %	wt % S	wt % VA[c]	VA:SO_2[d]	M_n[e]
−20	0				
−40	38.4	17.59	68.82	1.42	43 900
−60	63.7	20.76	58.48	1.02	26 900
−70	79.0	20.10	58.80	1.08	31 400
−80	64.2	19.30	61.40	1.15	29 700
−100	9.2	18.86	62.28	1.19	32 500

[a] Conditions: 1.00 g of vinyl acetate, 10 mL of SO_2, 0.15 mL of *tert*-butyl hydroperoxide; reaction for 1 h. [b] Refers to bath temperatures. [c] VA = vinyl acetate. [d] Molar ratio within the copolymer. [e] M_n, measured by osmometry.

The infrared spectrum of poly(vinyl acetate–sulfone) shows two characteristic absorption peaks located at 1138 and 1342 cm^{-1}, which are associated with the stretching modes of the sulfones, $-SO_2-$, and a C–S–C stretching at 775 cm^{-1}. The absorption of the acetate carbonyl groups is seen at 1776 cm^{-1}. The ^1H NMR spectrum of the copolymer shows clear signals with methyl groups located at about 2.3 ppm, and signals for the polyvinyl backbone are found near 6.5 ppm, lower than would be expected for a normal vinyl homopolymer, due to the strong electron-withdrawing effect of the neighboring $-SO_2-$ groups. In addition, the NMR spectrum shows no signal for the connection of two vinyl acetate monomers in the polymer backbone, suggesting a regularly alternating structure for the poly(vinyl acetate–sulfone).

As may be seen in Table I, the reaction temperature is also important for its effect on the polymer composition. Reaction temperatures ranging from −70 to −60 °C seem ideally suited for the copolymerization since the polymers prepared in this temperature range have the required alternating structure as confirmed by their spectroscopic and elemental analyses. Reactions performed outside this temperature range afforded copolymers that are sulfur deficient and that contain some structural irregularities such as vinyl acetate to vinyl acetate linkages in the polymer main chain.

The nature of the solvent also appears to have an effect on the incorporation of sulfur dioxide into the copolymer chain. Table II lists a number of solvents used in combination with an equal volume of sulfur dioxide at the optimum polymerization temperature of −70 °C. As expected, very poor results are obtained in the presence of polar solvents such as methanol, DMF, or DMSO. Best yields of polymer are obtained in dichloromethane or toluene, though the polymers that are obtained do not contain the ideal 1:1 ratio of comonomers. Overall, it was found that the use of sulfur dioxide as both the solvent and the comonomer gave the most satisfactory results. This choice also results in a simplified experimental procedure. However, the monomer feed ratio, vinyl acetate/sulfur dioxide, is another important factor. Table III shows the effect of the feed ratio on copolymerization yields, copolymer composition, and copolymer molecular weight. As can be seen from Table III, the larger the amount of vinyl acetate used, the higher the reaction yield. With a vinyl acetate/sulfur dioxide ratio of 0.1,

Table II
Effect of Solvent on the Copolymerization[a] of Vinyl Acetate with SO_2

solvent	yield, %	copolymer composition			
		wt % S	wt % VA[b]	VA:SO_2[c]	M_n[d]
NeOH	0				
DMF	0				
DMSO	0				
toluene	84	19.11	61.78	1.17	12 800
cyclohexane	58	19.20	61.60	1.16	10 600
CCl_4	80	19.97	60.06	1.09	14 300
CH_2Cl_2	88	18.65	62.70	1.22	60 500
SO_2	63	21.10	57.80	1.02	25 900

[a] Conditions: 1.00 g of vinyl acetate, 10 mL of SO_2, 0.15 mL of *tert*-butyl hydroperoxide, 10 mL of solvent; 1-h reaction time at −70 °C. [b] VA = vinyl acetate. [c] Molar ratio within the copolymer. [d] M_n, measured by osmometry.

Table III
Effect of Feed Ratio on Copolymerization[a] of Vinyl Acetate with SO_2

feed ratio[b] VA:SO_2 molar ratio	yield %	copolymer composition			
		wt % S	wt % VA	VA:SO_2[c]	M_n[d]
0.026	63.0	21.1	57.8	1.02	25 900
0.035	75.1	21.2	57.6	1.01	12 100
0.052	79.1	20.1	59.8	1.08	31 400
0.069	84.9	17.9	64.2	1.33	32 400
0.104	90.0	18.0	64.0	1.32	15 700

[a] Conditions: 1.00 g of vinyl acetate, 0.15 mL of *tert*-butyl hydroperoxide; reaction for 1 h at −70 °C. [b] VA = vinyl acetate. [c] Molar ratio within the copolymer. [d] M_n, measured by osmometry.

the reaction yield can reach up to 90%. However, such reactions that produce higher yields do not give satisfactory polymer structures. Copolymers with the required alternating structures are only obtained by using a 20–40-fold excess of sulfur dioxide, while the yields obtained under such conditions are somewhat lower (60–80%).

The thermogravimetric analysis of poly(vinyl acetate–sulfone) shows that the copolymer is stable to ca. 140 °C and then undergoes decomposition with approximately 40% mass loss when the temperature reaches 160 °C. This mass loss is in a good agreement with the decomposition of the pendant acetate groups by elimination of acetic acid and concurrent formation of a polysulfone structure that has double bonds conjugated with $-SO_2-$ in its backbone. Differential scanning calorimetry on poly(vinyl acetate–sulfone) shows a small endotherm near 70 °C, which is attributed to T_g and the occurrence of a large endothermic event centered at 157 °C corresponding to the 40% weight loss of the copolymer.

Copolymerization of Vinyl *tert*-Butyl Carbonate and Sulfur Dioxide. The reaction conditions for the model study were successfully applied to the copolymerization of vinyl *tert*-butyl carbonate and sulfur dioxide. Figure 2 shows the relationship between copolymerization yield and reaction temperature for reactions carried out over a 2-h period. Here again sulfur dioxide was used as the solvent as well as comonomer and *tert*-butyl hydroperoxide was used as the initiator (Scheme II).

Interestingly, the copolymerization of vinyl *tert*-butyl carbonate and sulfur dioxide has the same ceiling temperature (−20 °C) as was observed in the model study with poly(vinyl acetate–sulfone) under similar experimental conditions. No polymer is obtained above this ceiling temperature, while the yield of copolymer increases up to 85% as the reaction temperature is lowered to −80 °C. Unlike the vinyl acetate–SO_2 system, vinyl *tert*-butyl carbonate and sulfur dioxide mix well at low temperatures and do not show any tendency to form separate phases even at a temperature as low as −80 °C.

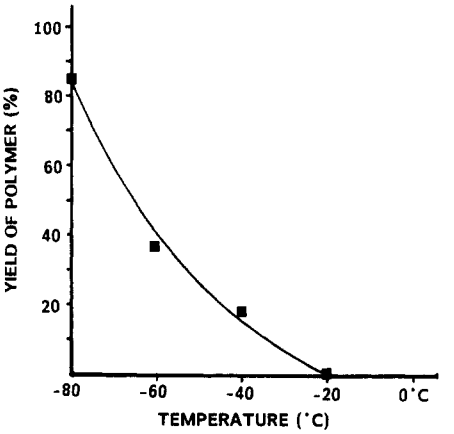


Figure 2. Relationship between polymerization yield and reaction temperature for the copolymerization of vinyl *tert*-butyl carbonate and sulfur dioxide.

Table IV
Effect of Temperature on Copolymerization[a] of Vinyl *tert*-Butyl Carbonate with SO_2

temp,[b] °C	yield, %	copolymer composition			
		wt % S	wt % VBC[c]	VBC:SO_2[d]	M_n[e]
−20	0				
−40	15.0	14.51	70.98	1.09	8 400
−60	34.0	14.80	70.40	1.06	10 500
−80	85.2	15.35	69.30	1.00	11 800

[a] Conditions: 1.00 g of vinyl *tert*-butyl carbonate, 10 mL of SO_2, 0.15 mL of *tert*-butyl hydroperoxide; reaction for 2 h. [b] Refers to bath temperature. [c] VBC = vinyl *tert*-butyl carbonate. [d] Molar ratio within the copolymer. [e] M_n, measured by osmometry.

The experimental data in Table IV summarizes the results of the copolymerization of vinyl *tert*-butyl carbonate and sulfur dioxide at different temperatures. The incorporation of SO_2 into the copolymer is only very slightly affected by the reaction temperature. The results from sulfur microanalyses of the copolymers indicate that all the copolymers obtained at different temperatures have essentially 1:1 alternating structure. This is likely a result of the excellent miscibility of the comonomers. However, the reaction temperature does affect the molecular weights of the copolymers, higher molecular weights being obtained at the lower temperatures.

The copolymer, isolated by precipitation in methanol, is a white solid that is soluble in a variety of organic solvents. The FT-IR spectrum of the copolymer (Figure 3) shows two large bands at 1350 and 1141 cm^{-1} corresponding to the sulfonyl groups in the copolymer main chain and an absorption at 1765 cm^{-1}, which is attributed to the carbonyl groups of the carbonate. The ^1H NMR spectrum of poly(vinyl *tert*-butyl carbonate–sulfone) resembles that of poly(vinyl acetate–sulfone), the *tert*-butyl group being at 1.53 ppm and backbone methylene and methine being located near 3.76–3.84 and 6.08–6.14 ppm, respectively.

Thermal Properties of Poly(vinyl *tert*-butyl carbonate–sulfone). The thermogravimetric analysis of poly(vinyl *tert*-butyl carbonate–sulfone) afforded results comparable to those of our previous study with BOC-containing polymers[10] and polysulfones.[16] The copolymer is stable to 85 °C and then undergoes rapid and quantitative decomposition, with evolution of four volatile molecules: carbon dioxide, acetaldehyde, isobutylene, and sulfur dioxide. Figure 4 shows the TGA trace for the copolymer. The nature of the thermal decomposition

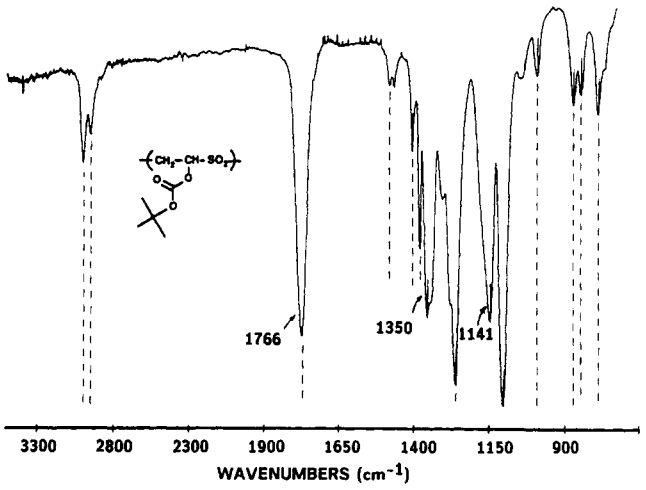


Figure 3. Infrared spectrum of poly(vinyl *tert*-butyl carbonate–sulfone).

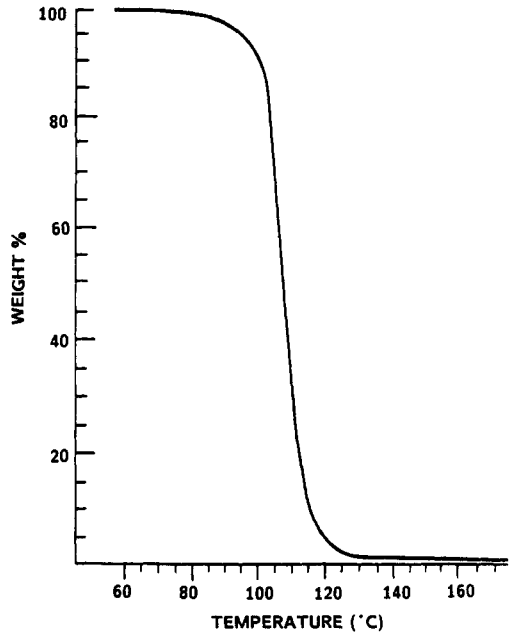


Figure 4. Thermogravimetric analysis of poly(vinyl *tert*-butyl carbonate–sulfone).

products is further confirmed by GC mass spectrometry. As expected, the decomposition occurs quantitatively as a copolymer sample is injected into the heated injection port of the gas chromatograph; the thermolysis products are then easily identified by the mass spectrometer as follows: CO_2 [m/e = 44 (M^+)]; isobutylene [m/e = 56 (M^+)], 41 (loss of CH_3)]; SO_2 [m/e = 64 (M^+)]; CH_3CHO [m/e = 44 (M^+), 43 (loss of H), 29 (loss of CH_3)].

The results of this thermal decomposition study are in accordance with our proposed decomposition mechanism shown in Scheme I. It is interesting to note that poly(vinyl *tert*-butyl carbonate–sulfone) has a much lower decomposition temperature than poly(vinyl *tert*-butyl carbonate)], 85 vs 170 °C.[11] This low thermal stability of the copolymer is obviously due to the incorporation of sulfone groups in the polymer backbone and may also be related to the inherently low ceiling temperature of polysulfones. It has been found that poly(alkene–sulfones) having lower ceiling temperatures usually also have lower thermal stabilities.

While our original design suggests that poly(vinyl *tert*-butyl carbonate–sulfone) ought to function as a "self-developing" imaging material, and indeed we have observed great lability to X-ray radiation, the usefulness of the material for direct use as an imaging material appears to be limited by its low thermal stability. Data currently available suggest that self-development is readily achievable, but this is not readily applied to practical imaging processes as the polymer's resistance to pre- and post-baking steps, as well as other processing steps, is not sufficient in most cases. It may, however, be possible to use the poly(vinyl *tert*-butyl carbonate–sulfone) as a fugitive radiation-sensitive dissolution inhibitor for matrix resins such as novolac or poly(*p*-hydroxystyrene). This application may be of particular importance in X-ray imaging where ultrahigh-sensitivity materials are required.

Experimental Section

NMR spectra were recorded on IBM-Bruker WM300 or Varian XL300 spectrometers in $CDCl_3$ or acetone-d_6 solution using tetramethylsilane as the internal standard. Infrared spectra were recorded on Nicolet 10DX or IR-44 FT-IR instruments using KBr pellets or film cast on NaCl disks. GC–MS analyses were performed on VG-7070E double-focusing mass spectrometer using the normal thermal probe and 3-m capillary gas chromatographic columns. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on Mettler DSC and TGA modules. Molecular weight determination and molecular weight distribution were done by using a Wescan Model 231 recording membrane osmometer with 1,2-dichloroethane or benzene as the solvents. Sulfur content in polymers was measured by Volhard titration of 200–300-mg samples ignited in a Parr peroxide bomb. Some of sulfur analysis and other quantitative analyses were performed by MHW Laboratory (Phoenix, AZ).

Sulfur dioxide obtained from Air Products was passed through a drying tube packed with calcium chloride and condensed into a graduated funnel using dry ice/acetone as a coolant. As a general rule, all reactions were carried out in oven-dried glassware under nitrogen atmosphere. The synthesis of the monomer, vinyl *tert*-butyl carbonate, has been reported previously.[11]

Copolymerization of Vinyl Acetate and Sulfur Dioxide. A typical procedure is as follows. Distilled vinyl acetate (1.00 g) was mixed with 10 mL of condensed sulfur dioxide with vigorous stirring at −78 °C and under nitrogen atmosphere. The mixture was treated with 0.15 mL of *tert*-butyl hydroperoxide, which resulted in a vigorous reaction. The reaction mixture was brought to a cooling bath at the required temperature and kept stirring for 1 h. The reaction was stopped by pouring the mixture into 300 mL of methanol. The white solid that was obtained was then dissolved in acetone and reprecipitated into methanol. The polymer was dried in vacuo for 24 h. In this way, 1.12 g (64.2%) of the desired polymer was isolated. Alternately, the reaction was carried out in a series of organic solvents to investigate the effect of solvent on the copolymerization (Table II).

^1H NMR (acetone-d_6): 2.26 (s, 3 H, $-CH_3$, acetate); 4.10–4.18 (br m, 2 H, CH_2, polyvinyl backbone); 6.43–6.49 (br m, 1 H, –CH, polyvinyl backbone). FT-IR (cm^{-1}): 1776 (C=O str, acetate); 1343 and 1139 ($-SO_2-$ str, sulfone). Elem anal. Calcd: C, 32.0; H, 4.0; S, 21.0. Found: C, 33.5; H, 4.53; S, 20.8. M_n (osmometry): 29 700.

Copolymerization of Vinyl *tert*-Butyl Carbonate and Sulfur Dioxide. a total of 1.00 g of vinyl *tert*-butyl carbonate was placed in a dry 50-mL three-necked flask at −78 °C under nitrogen. After 10 mL of condensed sulfur dioxide was introduced, the flask was moved to another cooling bath at the required temperature as stated in Table IV. This mixture was stirred for 10 min and then slowly treated with 0.15 mL of *tert*-butyl hydroperoxide. The copolymerization started immediately, and the solution increased in viscosity. After 2 h of reaction, the mixture was poured into 300 mL of methanol and a white solid precipitated. The precipitate was left standing at room temperature for 1 h (until sulfur dioxide evolution ceased). The polymer was dissolved in chloroform and precipitated into methanol. After filtration, the recovered polymer was dried in vacuo at room temperature. In this way, 1.23 g (85.2%) of the desired polysulfone was isolated.

^{1}H NMR (chloroform-d_3): 1.52 (s, 9 H, $-CH_3$, *tert*-butyl); 3.76–3.84 (br m, 2 H, $-CH_2$, polyvinyl backbone); 6.08–6.14 (br m, 1 H, –CH–, polyvinyl backbone). FT-IR (cm^{-1}): 1765 (C=O, str, carbonate); 1349 and 1141 ($-SO_2-$ str, sulfone).

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Registry No. (Vinyl acetate)(sulfur dioxide) (copolymer), 88882-83-1; (vinyl *tert*-butyl carbonate)(sulfur dioxide) (alternating copolymer), 133648-97-2.