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Homopolymerization and copolymerization of 1-phenylsulfonylbicyclobutane

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Summary

1-Phenylsulfonylbicyclobutane (SBB) undergoes free radical homopolymerization to give soluble homopolymers, but attempted anionic homopolymerizations did not succeed. With free radical initiators, SBB copolymerizes with p-methoxystyrene, p-methylstyrene, methyl methacrylate, acrylonitrile and 1-cyanobicyclobutane to yield novel copolymers. The reactivity of SBB toward vinyl monomers is lower than that of 1-cyanobicyclobutane.

INTRODUCTION

Bicyclobutanes with an electron-attracting substituent at the bridgehead are known to polymerize in the presence of radical or anionic initiators due to the large ring strain (1-3). The polymers formed contain cyclobutane rings in the backbone, which can lead to interesting physical properties compared to their vinyl analogs.

Bicyclobutanes substituted at the bridgehead with an electron-attracting group, such as a cyano or an ester group, are known to be excellent monomers for free radical polymerization. Our attention was drawn to another bicyclobutane of this type,(4) namely 1-phenylsulfonylbicyclobutane (SBB), because the electron-attracting ability of the phenylsulfonyl group is between that of the cyano and the ester group. The polymerization behavior of SBB will be described in this paper.

RESULTS

Synthesis

The synthesis of 1-phenylsulfonylbicyclobutane (SBB) has been described in the literature by Gaoni.(4) Phenyl methyl sulfone is treated with ethyl magnesium bromide and allyl bromide to obtain phenyl 3-butenyl sulfone, which is oxidized to the epoxide. In one flask the epoxide is treated consecutively with base, methanesulfonyl chloride and another equivalent of base to yield SBB in 35% overall yield.

The preparation of γ,δ-unsaturated sulfone was improved by adding the phenylsulfonylmethyl Grignard reagent to the allyl bromide solution. In this manner the formation of dialkylated sulfone side product was almost completely excluded and the product could be purified by recrystallization instead of chromatography. Secondly, the more selective lithium N,N-diisopropylamide was used instead of n-BuLi for the ring closures, resulting in higher yields than the literature procedure.

SBB is a white crystalline solid, m.p. 80°C. No significant decomposition or oligomerization of SBB is observed at room temperature for one day. Thus, SBB is more stable than the corresponding 1-cyanobicyclobutane.

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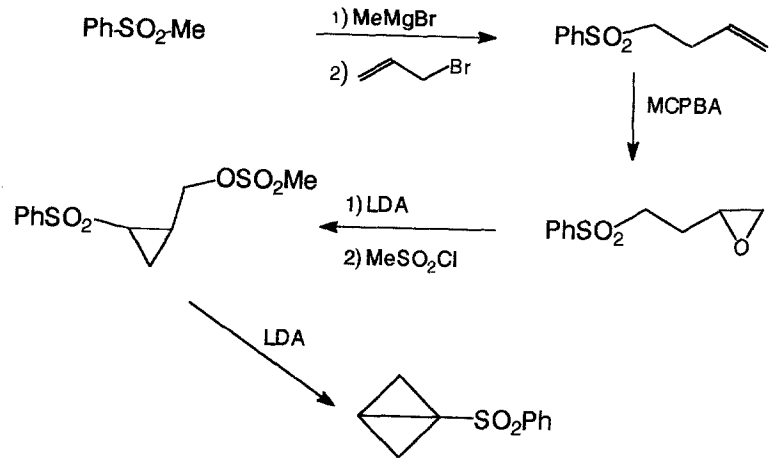

SBB

Homopolymerization

SBB was subjected to conventional solution radical polymerization using DMSO as the solvent and AIBN as the initiator at 65°C. Homopolymer was obtained in good yield, as shown in Table 1. The polymer was readily soluble in acetone or DMSO.

For comparison, data on the polymerization of other 1-substituted bicyclobutanes are also included in Table 1. 1-Cyanobicyclobutane (CBB) and methyl 1-bicyclobutanecarboxylate with free radical initiators lead to extremely high molecular weight polymers and gelation. Transfer agent has to be added to the polymerization to obtain soluble polymers.(2,3,7) The more bulky isopropyl 1-bicyclobutanecarboxylate leads to soluble high molecular weight polymer without chain transfer agent.(6)

As to attempted anionic homopolymerization of SBB, CH_3MgBr, nBuLi and potassium t-butoxide were used as initiators, but no polymers were obtained. Both CBB and methyl 1-bicyclobutanecarboxylate can be polymerized using anionic initiators, the latter rather sluggishly.

Free Radical Copolymerization

Bulk free radical-initiated copolymerization of SBB with p-methoxystyrene, p-methylstyrene, methyl methacrylate and acrylonitrile led to copolymers with rather low incorporation of SBB, 12% or less, as shown in Table 2. Insoluble copolymers were obtained from SBB with CBB, but addition of 1 mole % of butyraldehyde led to a soluble copolymer containing about 15% SBB units. With the more bulky methyl bicyclobutanecarboxylate, only 7% SBB is incorporated. The molecular weights of all these copolymers were rather high and the molecular weight distributions narrow, but the yields were low.

Table 1. Homopolymerization of SBB and Comparison with other 1-Substituted Bicyclobutanes.[a]

Monomer	Transfer agent[b]	Yield (%)	η_{inh}[c] dL/g	Tg (°C)	Soluble in
1-Phenylsulfonyl-Bicyclobutane (SBB)	no	51	0.19	118	DMSO, Acetone
1-Cyanobicyclo-butane (CBB)	no	>95	Rigid gel		
	yes	70	3.0	205	DMSO, hexa-fluoro-2-propanol
Methyl 1-Bicyclobutane-carboxylate[d]	no	66	2.9		
	yes	78	1.2	95	DMSO, Acetone, $CHCl_3$, Toluene
Isopropyl 1-Bicyclobutane-carboxylate[e]	no	66	2.9		
	yes	78	1.2	85	DMSO, Acetone, $CHCl_3$, Toluene

a. All polymerizations run in solution (DMSO) at 65°C using 3 mole % of AIBN for 16 hours.
b. Transfer agent: 1 mole % butyraldehyde.
c. Inherent viscosity measured in DMF (0.5g/dL).
d. Ref. 7
e. Ref. 6

In Table 3, the reactivity of SBB in copolymerizations with acrylonitrile or methyl methacrylate is compared to the reactivity of CBB. CBB is incorporated to a much greater extent than SBB.

DISCUSSION

The synthesis of SBB extends the alkylation route used earlier by Wiberg (5) and by Drujon (6) for ester monomers. Thus the alkylation route complements our cycloaddition route for the synthesis of polymerizable bicyclobutanes.

The polymerization behavior of 1-phenylsulfonylbicyclobutane was investigated. In free radical conditions, homopolymers with high molecular weights are obtained. In contrast to CBB and the ester-substituted bicyclobutanes, SBB does not gel. The cross-linking of the former is due to tertiary hydrogen abstraction of cyclobutane units of adjacent chains leading to highly branched polymers. Mild transfer agents are usually added to circumvent this problem. However if the ester group is bulky enough, as in isopropyl 1-bicyclobutanecarboxylate polymer, the hydrogen

Table 2. Copolymerizations of SBB[a]

Comonomer	Yield	η_{inh}[b]	Tg (°C)	Mole % SBB in copolymer[c]	M_n	M_w	MWD
p-Methoxy-styrene	30	0.18	105	6.7	47,900	62,400	1.3
p-Methyl-styrene	35	0.40	95	10.8	124,900	212,700	1.7
Methyl Methacry-late	41	1.34	72	3.8	63,900	99,800	1.5
Acrylo-nitrile	53	0.95	90	12.0			
CBB[d]	40	0.56	85	15.3			
Methyl 1-bicyclo-butane carboxy-late	62	1.20		7.0			

a. Reactions in bulk using 3 mole % of AIBN at 65°C for 16 hours, feed ratio[SBB]/[vinyl monomer] = 1/2.
b. Inherent viscosity measured in acetone at 30°C, C=0.5 g/dL.
c. Determined by chemical analysis.
d. 1 mole % butyraldehyde added to prevent gel formation, feed ratio [SBB]/[CBB] = 1/1.

Table 3. Comparison of Copolymerizations of 1-Cyanobicyclobutane (CBB) and 1-Phenylsulfonylbicyclobutane (SBB)[a]

Comonomer	Monomer	Mole % of BB in copolymer
Acrylonitrile	CBB	58
	SBB	12
Methyl Methacrylate	CBB	75
	SBB	3.8

a. Feed ratio [bicyclobutane]/[comonomer] = 1/2.

abstraction does not occur.(6) The bulky phenylsulfonyl group also prohibits attack of a growing center at the highly crowded bridgehead positions in the polymer.

Unlike 1-cyanobicyclobutane, methyl 1-bicyclobutanecarboxylate or phenyl vinyl sulfone (8), 1-phenylsulfonylbicyclobutane does not undergo anionic polymerization. The role of steric hindrance could be dominant during the anionic polymerization.

The copolymerizations of SBB with both electron-rich and electron-poor olefins did not proceed very well and the incorporation of SBB was always below 12%. The lowest value (3.8%) was obtained with methyl methacrylate, which is due to steric hindrance. The low incorporation values are in agreement with the behavior of phenyl vinyl sulfone as reported in the literature. The Q-value of phenyl vinyl sulfone (9) is only 0.1, which indicates the very poor stabilization of a free radical by an adjacent sulfone group. This low Q value along with the steric hindrance of the phenyl sulfonyl substituent explain the poor copolymerization behavior of the title monomer.

EXPERIMENTAL

All reaction solvents were reagent grade and were distilled prior to use. ^{1}H NMR spectra were obtained using a Bruker WM 250 NMR spectrometer at 250 MHz. Infrared spectra were recorded on a Perkin Elmer 983 spectrometer. Microanalyses were performed by Desert Analytics, Tucson, AZ.

Materials

p-Methoxystyrene, p-methylstyrene, methyl methacrylate and acrylonitrile were purchased from Aldrich and distilled from calcium hydride.

SBB was prepared by modifying a literature procedure.(4)

Preparation of Phenyl 3-Butenyl Sulfone

At room temperature methyl magnesium bromide (34 ml, 3M in ethyl ether) was added to a solution of phenyl methyl sulfone (0.10 mol) in benzene (100ml). After 6 hours, this metallated sulfone solution was added slowly to a solution of allyl bromide (0.09 mol) dissolved into an equal volume of benzene. The reaction was stirred for 1 day at room temperature and then warmed for 2 hours at 65°C, cooled and poured on ice mixed with 5% hydrochloric acid. Extraction with ether yielded crude product, which was recrystallized twice from chloroform-n-hexane at -40°C. The product is an oil at room temperature. Yield 75%. NMR ($CDCl_3$): δ 2.3-2.6 (m,2H), 3.05-3.31 (m,2H), 4.87-5.23 (m,2H), 5.51-6.02 (m,1H), 7.51-8.02 (m,5H). IR: 1309, 1142, 1082, 996, 924 cm^{-1}.

Preparation of the Epoxide of Phenyl 3-Butenyl Sulfone

MCPBA (1.1 molar equiv. of active peracid) was added in portions to a solution of phenyl 3-butenyl sulfone (0.05 mol) in 200 ml dichloroethane. After 20 hours, the reaction mixture was cooled and filtered. The filtrate was washed with sodium sulfite and sodium carbonate solution. The crude product was purified by recrystallization. m.p. 48.5-50°C. Yield 85%. NMR ($CDCl_3$): δ 1.65-3.37 (m,7H), 7.51-8.03 (m,5H). IR: 1312, 1142, 1089 cm^{-1}.

Preparation of Bicyclobutane (SBB)

A stirred solution of the epoxide in THF (5-7ml/mmol, 1-20 mmol of epoxide) was cooled with dry ice-acetone and 1 molar equivalent of lithium N,N-diisopropylamide was added. After 1 hour the temperature was raised to 0°C and the mixture was stirred for 1 additional hour. Methanesulfonyl

chloride (1 molar equivalent, 2N in THF) was added and stirring was continued for 1 hour. Lithium N,N-diisopropylamide (1 molar equivalent) was added to the solution which was precooled to ~-50°C and stirring was continued for 0.5 hour. The temperature was raised to ~-10°C and the mixture was poured into ammonium chloride solution, followed by usual workup. Chromatography on silica gel using hexane/chloroform as eluent yielded SBB in 50% yield. M.p. 80-81.5°C. NMR ($CDCl_3$) δ 1.39 (s,2H), 2.56 (s,3H), 7.52-8.03 (m,5H); IR. 1302, 1142, 1012, 815, 750 cm^{-1}.

General Procedure for the Polymerization

Free radical polymerization reactions were carried out under argon atmosphere in Pyrex polymerization tubes with high vacuum valves, 3 mole% of AIBN was used as initiator, polymerizations were run at 65°C for 16 hrs. The polymers were precipitated twice into methanol.

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