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The polymerization of 3-methyl-*N*-(phenylsulfonyl)-1-aza-1,3-butadiene

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Summary

A study of the polymerizability of the first crystalline 1-azabutadiene carrying an electron-withdrawing group on nitrogen is described. A convenient one-step synthesis of 3-methyl-N-(phenylsulfonyl)-1-aza-1,3-butadiene (MPAB) from methacrolein and benzenesulfonamide using titanium tetrachloride and triethylamine led to a crystalline azabutadiene monomer in good yield. With anionic initiators the monomer readily oligomerized to materials in which MPAB has reacted in a 4,1-fashion. Under radical conditions the monomer did not homopolymerize, but did copolymerize with styrene monomers to polymers with molecular weights up to 10,000. These radical copolymerizations involved exclusive 4,3-propagation (vinyl) for the azadiene monomer.

Introduction

The synthesis and polymerization of imines and azadienes has been of continued interest in our laboratories (1). Based on our studies of different azadiene structures, the 1-azabutadienes appear to have the best potential for polymerization. 1-Azabutadienes carrying aryl substituents on nitrogen were synthesized via several steps including the cracking of a norbornene precursor (2). Radical polymerizations of these compounds did not give satisfactory results. With either anionic or cationic initiators, polymers with a mixture of 4,1- and 4,3- (vinyl polymerization) structures were obtained, with anionic polymerizations giving the best results. A 1-azabutadiene monomer carrying an electron-withdrawing carboethoxy group on nitrogen was similarly synthesized (3). This monomer also did not yield polymer under high temperature free radical conditions (a result of competing dimerization), but did give polymers anionically with enhanced 4,1-propagation. The monomers described above were all high boiling oils which were difficult to purify to monomer purity and this could account for the low molecular weights of the polymers.

Recently many manuscripts have appeared describing the synthesis of substituted azabutadienes for hetero Diels-Alder reactions (4). Boger and coworkers have shown that 1-azabutadienes carrying a sulfonyl group on nitrogen are a useful class of inverse-electron-demand dienes (5). Simultaneously with our discovery of a one-step synthesis of N-substituted azadienes, Boger published the direct condensation of α β -unsaturated aldehydes with sulfonamides (5). Based on our previous experience, unsubstituted N-sulfonyl-1-aza-1,3-butadienes with their simple synthesis appeared to have potential as good monomers or comonomers.

In this paper we outline the investigation of 3-methyl-N-(phenylsulfonyl)-1-aza-1,3-butadiene as a potential monomer.

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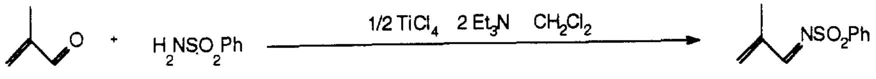
Results and Discussion

Monomer Synthesis

MPAB was synthesized via the direct condensation of methacrolein and benzenesulfonamide using $TiCl_4$ and triethylamine as the dehydrating system.



The synthesis of MPAB was simultaneously reported by Boger et al., who describe a rapid purification on silica to obtain the pure compound in 56% yield (5). We found MPAB to be solid and chose to purify MPAB via recrystallization. The only significant impurity present in MPAB was its own Diels-Alder dimer. Pure monomer could be obtained by recrystallizing from diethyl ether, since the dimer was not soluble in this solvent. MPAB had a melting point of 80.5 - 82.5 ° C. Our synthesis gave 86% crude yield and after recrystallization a 74% yield of the pure monomer was obtained. The ^1H and ^{13}C NMR spectra of the monomer are shown in Figures 1 and 2.

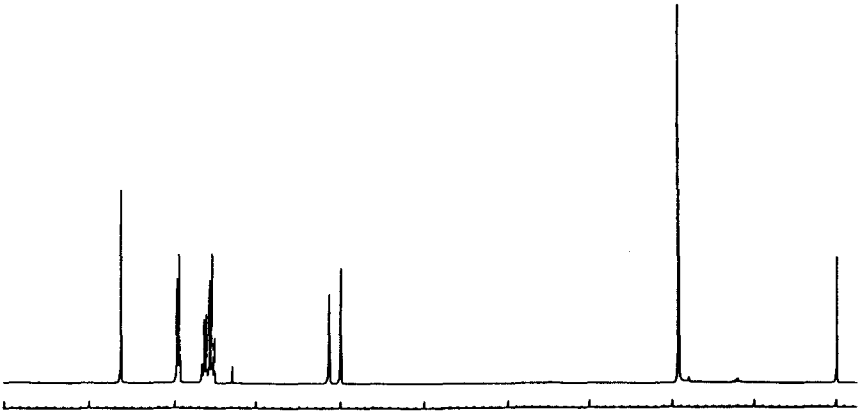


Figure 1: ^1H NMR of MPAB

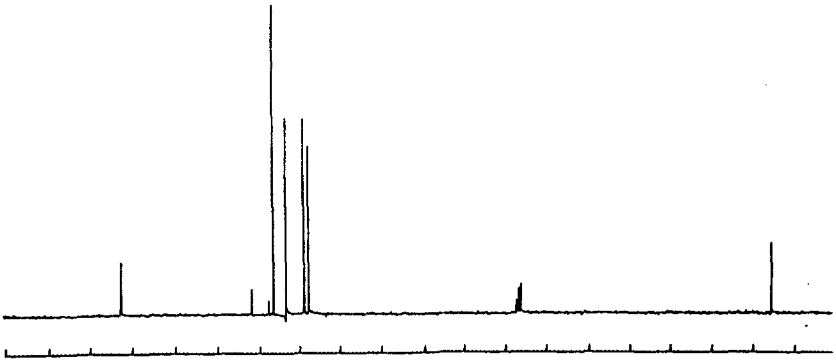
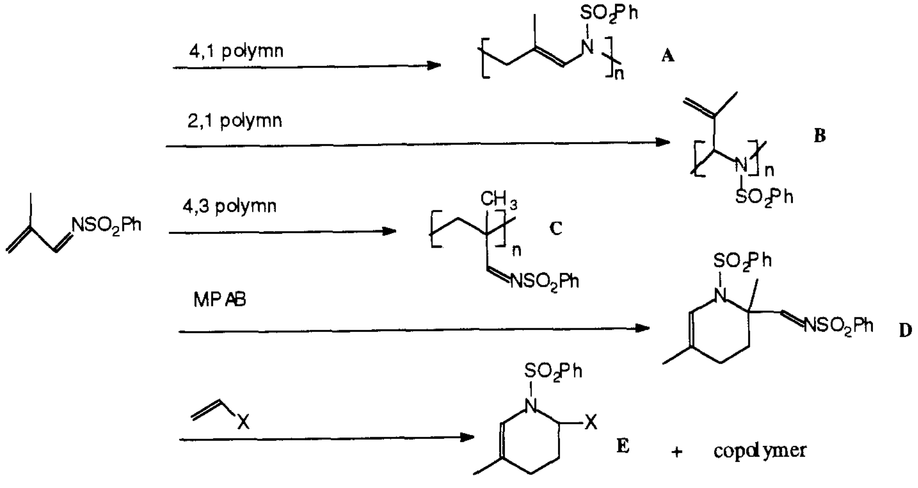


Figure 2: ^{13}C NMR of MPAB

This direct synthesis appears to be general for N-sulfonyl, N-carboethoxy [which was previously synthesized via the protected norbornene route (3)], N-phenylcarbonyl (which is not stable) and N-aryl derivatives starting from methacrolein. However this synthesis does not succeed for acrolein.

Reaction Modes of MPAB

We have previously shown (2,3) that the polymerizations of 1-azadienes can follow three possible routes: 4,1-propagation which would lead to an enamine in the backbone (structure A); 2,1-addition which would leave the terminal vinyl as a pendant group from the polymethanimine backbone (structure B); or 4,3-addition which would leave the imine group as a pendant group on the all-carbon backbone (structure C). MPAB can also undergo Diels-Alder reactions both in a dimerization with itself (structure D) or with another dienophile (structure E). The possible reaction modes of MPAB are shown in Scheme 1.



Scheme 1: Reaction Modes for MPAB

Radical Homopolymerizations

At 65° C in bulk with no initiator, MPAB forms dimer nearly quantitatively in 24 hours. In benzene solutions with AIBN or benzoyl peroxide at 65° C for 24 hours, MPAB gave only a trace of polymeric material upon precipitation. When homopolymerizations were attempted in dichloroethane at 0° C for 24 hours with the photoactive initiators benzoyl peroxide or benzoin methyl ether, precipitation resulted in only a trace of polymeric material. The materials obtained were of very low molecular weight.

Anionic Polymerizations

MPAB underwent oligomerization with both the nucleophile KCN and the strong base BuLi as shown in Table 1. The conversions were in the range of 30 to 70%. The low reaction temperatures minimized the self-dimerization of MPAB. Both initiators gave oligomeric materials obtained as white powders with molecular weights near 1,000 by SEC.

NMR analysis of the polymer structure showed that MPAB reacted mainly (90%) in a 4,1-fashion (structure A), but a mixture of structures was evident. A broad peak at δ 1.6 - 2.0 is indicative of the vinylic methyl and the vinyl proton is evident as a broad peak at δ 4.8 - 5.4. The other clearly evident structure (but in low proportion) resulted from a 4,3 opening (structure C), and is characterized by a small peak for the pendant imino proton at δ 8.5 and a small signal for the methyl at δ <1.

Table 1: Anionic Oligomerization at MPAB[a]

Run	Initiator	Temp. (° C)	% Conv.	M_W	Structure
1	KCN 3%	0	31.9	936	mainly 4,1 with a small percent of other structures present
2	KCN 8%	0	53.4	961	
3	BuLi 15%	0	63.7	648	
4	BuLi 15%	-50	trace	703	
5	BuLi 15%	-78	67.6	578	

[a] Reaction Conditions: 0.3 g MPAB in 1 mL THF for 24 hrs.

Table 2: Free Radical Copolymerizations of MPAB[a]

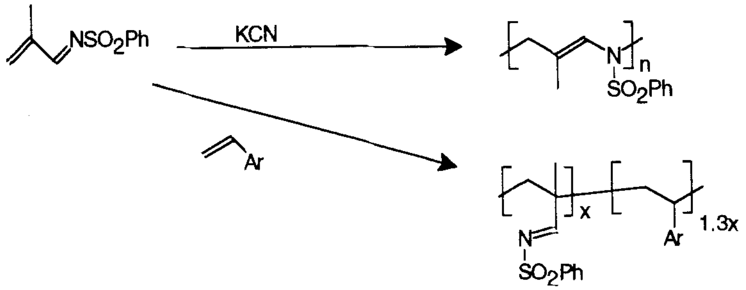
Run	MPAB	Comonomer	Solvent	Init (10 mg)	Yield	M_W
6	0.3 g	MMA[b]	THF	MeOB[c]	5.0%	752
7	0.3 g	CNF[b]	THF	MeOB[c]	8.9%	478
8	0.3 g	iBuVE[b]	THF	MeOB[c]	2.8%	724
9	0.3 g	NVCz[b]	benzene	AIBN	6.4%	723
10	0.3 g	pMeOSt[b]	benzene	AIBN	80.0%	1,951
11	0.2 g	pMeOSt[b]	---	---	0.30 g	5,275
12	0.2 g	St[b]	---	AIBN	0.25 g	10,085

[a] Reaction Conditions: 1 mL solvent at 0° C irradiated at 254nm for 24 hrs.
[b] Equimolar amounts with MPAB except runs 11 and 12 (1 mL comonomer): MMA = methyl methacrylate, CNF = dimethyl cyanofumarate, iBuVE = isobutylvinyl ether, NVCz = N-vinylcarbazole, pMeOSt = p-methoxystyrene, St = Styrene
[c] benzoin methyl ether

Copolymerizations

The results obtained from copolymerizations of MPAB with a variety of comonomers at 0° C are shown in Table 2. Using electron-deficient comonomers, only low conversions to low molecular weight materials were obtained. Copolymerization with styrene and p-methoxystyrene gave material with molecular weights in range of 2,000 to 10,000. Spontaneous copolymerizations do occur with p-methoxystyrene.

The NMR spectra of pMeOSt copolymers show that MPAB is incorporated in these copolymers in 4,3-fashion with from the imine portion of the molecule acting only as a stabilizing group for the vinyl polymerization. The ^1H NMR contains a peak between δ 0 and δ 1 which corresponds to the methyl of MPAB which is now β to the pendant imine group. The imino proton is buried under the aromatic protons. Integration shows the pMeOSt:MPAB ratio to be 1.3:1. The ^{13}C NMR contains a peak at δ 182 which is indicative of the imine carbon. The styrene copolymer gives similar results upon analysis.



Scheme 2: Polymerization Modes of MPAB

Conclusion

The polymerization of the first crystalline 1-azabutadiene monomer, 3-methyl-N-(phenylsulfonyl)-1-aza-1,3-butadiene has been accomplished. The monomer was made in one step from readily available starting materials in good yield and it was purified by recrystallization to monomer purity. Anionic and radical homopolymerizations gave only oligomeric materials in high and low percent conversions, respectively. Copolymerizations with styrene and p-methoxystyrene led to high molecular weight materials with propagation occurring exclusively in a 4,3-fashion for the new monomer. Our work in the systematic study of the polymerization of imines and azabutadienes is continuing.

Experimental

Chemicals

Dichloromethane, dichloroethane and benzene were distilled over CaH_2. Triethylamine was distilled over KOH. Tetrahydrofuran was distilled over Na with benzophenone as an indicator. Titanium tetrachloride, benzenesulfonamide, and n-butyllithium were used as received from Aldrich. Methacrolein was dried over $MgSO_4$ and distilled. Styrene and p-methoxystyrene were distilled over CaH_2 under vacuum.

Methods

^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer at 250 and 62.9 MHz, respectively. IR spectra were obtained from a Perkin-Elmer 938 spectrometer. Average molecular weights were measured using 10^5, 10^4, and 10^3Å Phenomonex SEC columns in series calibrated with polystyrene standards using chloroform as the eluent. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

3-Methyl-N-(phenylsulfonyl)-1-aza-1,3-butadiene (MPAB):
A solution of methacrolein (5.02 g, 71.7 mmoles), benzenesulfonamide (11.27 g, 71.7 mmoles) and triethylamine (15.96 g, 157.7 mmoles) in 200 mL of dichloromethane was stirred in a 3-neck flask with a mechanical stirrer under Ar. A solution of titanium tetrachloride (7.55 g, 39.8 mmoles) in 50 mL of dichloromethane was added dropwise over 30 minutes. The heterogeneous reaction mixture turned orange and warmed slightly during the addition. This mixture was stirred for 2 hours at room temperature. The solution was filtered over celite and washed with excess dichloromethane. This filtrate was concentrated to near dryness and the solid residue was treated with anhydrous ethyl ether. The ether mixture was filtered through celite to remove any remaining triethylammonium chloride. The filtrate was concentrated under reduced pressure to yield crude MPAB (12.89 g, 86%) as a yellow solid, which was recrystallized from anhydrous ethyl ether using activated charcoal to give MPAB (11.1 g, 74%) as white crystals, mp 80.5-82.5° C. ^{1}H NMR ($CDCl_3$, 250 MHz, ppm) 8.64 (1H, s), 7.96 (2H, dd, J = 9 Hz, 1 Hz), 7.51-7.67 (3H, m), 6.14 (1H, s), 6.00 (1H, s), 1.93 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm) 172.7, 142.0, 137.9, 136.7, 133.5, 129.0, 127.9, 16.0; IR (KBr pellet, cm^{-1}) 3068, 2917, 1621, 1571, 1447, 1324, 1309, 1160, 1092, 1027, 962, 816, 754, 725, 687, 605. Anal. Calc'd for $C_{10}H_{11}NO_2S$: C, 57.40; H, 5.30; N, 6.69. Found: C, 57.53; H, 5.28; N, 6.67.

MPAB Dimer:
MPAB was heated in bulk at 65° C under vacuum in a sealed tube for 24 hours. ^{1}H NMR showed the conversion of MPAB to dimer to be greater than 95%. ^{1}H NMR ($CDCl_3$, 250 MHz, ppm) 8.75 (1H, s); 8.02 (2H, dd, J = 8 Hz, 1 Hz); 7.70-7.27 (8H, m); 6.38 (1H, s); 1.96-1.83 (3H, m); 1.69 (3H, s); 1.56-1.48 (1H, m); 1.23 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm) 179.4, 132.6, 129.1, 128.9, 128.8, 128.3, 127.0, 126.9, 126.8, 118.4, 113.6, 61.0, 32.5, 22.9, 20.5, 18.4.

Anionic Polymerization
The anionic polymerizations were conducted in pyrex tubes with a vacuum line teflon valve. MPAB (0.3 g) was dissolved in 1 mL of THF and the solutions were placed at -78° C and the initiator was added. When KCN was used as the initiator, the solution was heterogeneous. The solution was mixed well and brought to the reaction temperature. After 24 hours the solution was precipitated in 40 mL of ethyl ether. The solid was collected by filtration and dried under vacuum. Representative data for run 2 (KCN initiated) are given. ^{1}H NMR ($CDCl_3$, 250 MHz, ppm) broad peaks with approximate integration at 7.3-7.8 (5H); 4.8-5.4 (1H); 3.1-4.1 (2H); 1.3-2.0 (3H) with other small peaks present; IR (KBr pellet, cm^{-1}) 3062, 2917, 1624, 1445, 1345, 1163, 1090, 1071, 1024, 750, 721, 689. Anal. Calc'd for $C_{10}H_{11}NO_2S$; C, 57.40; H, 5.30; N, 6.69; S, 15.29. Found: C, 55.72; H, 5.01; N, 6.64; S, 15.15.

Radical Homopolymerization
For thermally initiated radical polymerizations, MPAB (0.3 g) was dissolved in 1 mL of solvent in pyrex tubes with vacuum line teflon valve. Several freeze pump thaw cycles were performed and the initiator was added. After stirring for 24 hours at the reaction temperature, the solution was precipitated in ethyl ether, the solid was collected by filtration and dried under vacuum.

Photoinitiated polymerizations were run in jacketed quartz tubes. MPAB (0.3 g) was dissolved in 1 mL of solvent and argon was bubbled through the solution for several minutes. The initiator was added and the tube was sealed. The stirred solution was kept at 0° C and irradiated at 254 nm. After 24 hours the solution was precipitated in ethyl ether. The solid was collected and dried under vacuum.

Copolymerization

All copolymerizations were run in jacketed quartz tubes. In cases where solvents were used, MPAB (0.3 g) and an equimolar amount of the comonomer were dissolved in 1 mL of solvent and argon was bubbled through the solution. When no solvent was used, MPAB (0.2 g) was dissolved in 1 mL of the comonomer and argon was bubbled through the solution. The initiator (when used) was added and the solution was stirred at 0° C for 24 hours and irradiated at 254 nm. The solutions were precipitated in ethyl ether, the solid was collected and dried under vacuum. Spectroscopic data for run 11 (copolymerization with pMeOSt) are given. ^{1}H NMR ($CDCl_3$, 250 MHz, ppm) broad peaks with approximate integration at 7.4-7.8 (8H); 6.5-6.7 (2H); 3.7-3.9 (3H); 2.2-2.4 (1H); 1.2-1.9 (4H); 0.4-0.8 (3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm) broad peaks at 182.5, 158.5, 138.1, 137.6, 133.3, 133.1, 129.3, 128.8, 128.5, 128.1, 127.6, 127.2, 114.6, 114.1, 55.0, 98.7, 44.7, 36.3, 20.8. IR (KBr pellet, cm^{-1}) 2929, 1611, 1511, 1445, 1322, 1250, 1161, 1089, 1034, 831, 803, 753, 721, 688, 669. Anal. Found: C, 67.55; H, 6.19; N, 3.71; S, 9.27. The elemental analysis corresponds to a 1.2:1 ratio of pMeOSt:MPAB in the copolymer.

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