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Studies of the Anionic Polymerization of Phenyl Vinyl Sulfoxide and Its Copolymer with Styrene

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ABSTRACT: Phenyl vinyl sulfoxide (PVS) was polymerized in THF at −78 °C with various anionic initiators. Delocalized carbanion initiators such as (triphenylmethyl)lithium are effective initiators as are methyllithium and the dipole-stabilized 1-lithio-1-(phenylsulfinyl)ethane. There was excellent correlation between the measured molecular weight and the calculated molecular weight. The molecular weight distribution was found to be narrow. Initiation at ambient temperatures resulted in a bimodal distribution. A side reaction at higher temperatures was observed, leading to broadening of the molecular weight distribution. Both A–B and A–B–A block copolymerizations with styrene were carried out. The molecular weight distributions of the block copolymers were, in general, narrower than those of the homopolymers.

Introduction

In the course of previous investigations on the stereochemistry and mechanism of anionic oligomerization and polymerization of phenyl vinyl sulfoxide (PVS),[1,2] it was discovered that within 24 h at room temperature the polymer poly(phenyl vinyl sulfoxide) (PPVS) changed color from white to yellow. It subsequently became red and finally black. The color change is indicative of decomposition and occurred in air, under vacuum, or under an argon atmosphere. It was suppressed to some extent by storage at −20 °C and was essentially immediate upon heating the polymer to 100–150 °C.

The color changes were consistent with the formation of polyacetylene (PA) through a concerted, cyclic, sigmatropic thermal elimination of phenylsulfenic acid from PPVS as illustrated in Figure 1. The sulfoxide elimination was first proposed by Kingsbury and Cram,[3] and phenyl vinyl sulfoxide (PVS) was subsequently used as an acetylene synthon in Michael addition–elimination[4-9] and a Diels–Alder cycloaddition–elimination reaction.[10] Thus PPVS could be regarded as a soluble polyacetylene precursor. Interestingly, thermal elimination was not observed upon oxidation of PPVS to poly(phenyl vinyl sulfone).

Precursor routes for PA syntheses have been extensively studied by Feast in Durham, U.K.[11-14] The precursor polymers are synthesized by a metathesis ring-opening polymerization of monomers such as 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene, which yields soluble precursors to PA. Recently, Grubbs[15] found that ring-opening metathesis polymerization (ROMP) of benzvalene affords poly(benzvalene), which is another polyacetylene precursor.

The synthesis of PA from PPVS has potential advantages. First the polymerization of PVS proceeds through a stable carbanion so that the molecular weight distribution is expected to be narrow. Moreover, the control of molecular weight through the ratio of monomer to initiator is quite good, and formation of high molecular weight PPVS is possible. Thus, in principle, the synthesis of a series of monodisperse PAs of known molecular weights and narrow molecular weight distribution is possible.

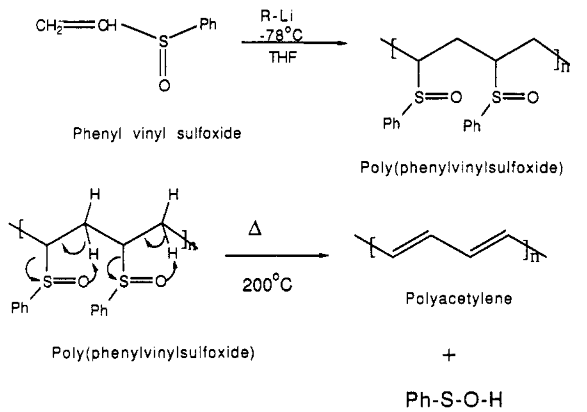

Figure 1. Scheme for the elimination of phenylsulfenic acid from PPVS.

Another advantage of the sulfoxide precursor route to PA is the formation of monodisperse A–B and A–B–A type block copolymers with monomers such as styrene, butadiene, and isoprene. These could then be subjected to elimination to form block copolymers of styrene (or other monomers) and PA.

In this paper we report the polymerization of PVS using various anionic initiators and the copolymerization with styrene. A side reaction was observed during the polymerization, especially at ambient temperature. Studies on the elimination of the PPVS homo- and copolymers will be reported separately.[2]

Experimental Section

All the polymerization reactions were carried out under high vacuum using conventional breakseal techniques.[16-18] THF was purified by refluxing over a Na/K alloy for 24 h, followed by distillation onto fresh alloy containing benzophenone as an indicator. Phenyl vinyl sulfoxide (PVS) was purchased from Aldrich and purified by repeated (threefold) vacuum distillation from calcium hydride. The clear distillate from the final distillation was collected in ampules equipped with breakseals.

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Styrene was purchased from Fisher Scientific Co. and purified by distilling once over calcium hydride and once over a potassium mirror. The distillate from the latter was then collected in ampules equipped with breakseals. The purification of 1,1-diphenylethylene (DPE) was carried out in a similar way.

Initiators. Carbanion initiators such as (triphenylmethyl)lithium and (1,1-diphenylhexyl)lithium were prepared by an in situ reaction of the parent hydrocarbon with alkyllithium. The details of the synthesis and purification are described elsewhere.[19] The concentration of the carbanion initiators was determined by titration with fluorene and by UV–vis spectroscopy.[19] Methyllithium and *tert*-butyllithium were purchased from Aldrich. Methyllithium was used as received but *tert*-butyllithium was further purified by sublimation under high vacuum (10^{-6} Torr).[19] Lithium naphthalide was synthesized by mixing an excess of naphthalene (Aldrich, Gold Label) with lithium wire in THF at room temperature for 12 h.[19] The dark green solution was then filtered through a coarse frit into an ampule and further subdivided as needed.

Polymerization of Phenyl Vinyl Sulfoxide. Polymerization of PVS was carried out by mixing a solution of the initiator and monomer in THF at −78 °C. The polymerization reaction was carried out at −78 °C for 30 min and terminated using degassed methanol. The polymer was purified by precipitation into diethyl ether and was dried under vacuum at room temperature. Most of the polymer characterization (SEC, NMR, IR, etc.) was carried out immediately after the synthesis since the polymer tended to degrade upon storage. The polymer was stored in the freezer (−20 °C). Oxidation of the sulfoxide polymers was accomplished by stirring a solution of the polymer in glacial acetic acid with 30 molar excess of 30% hydrogen peroxide for 24 h.[1] The polymer precipitates out as a flaky white precipitate at the end of the reaction.

Block Copolymerization. The preparation of an A–B diblock copolymer of styrene and PVS was carried out by vapor phase addition of styrene to a solution of *tert*-butyllithium in THF at −78 °C. The cherry red solution turned dark red upon capping with 1,1-DPE and was then divided into various ampules equipped with breakseals. One of the ampules was used for the determination of the concentration of the carbanion. The molecular weight and MWD of the methanol-terminated polystyrene was characterized by SEC. The capped, living polystyryllithium was then used as the initiator of PVS. There was an instantaneous change in the color of the solution from dark red to yellowish green as PVS was added. After termination by methanol the copolymer was precipitated in an excess of methanol/diethyl ether (70/30 (v/v)) and characterized by SEC. The A–B–A triblock copolymer was synthesized in a similar way using lithium naphthalide as the bifunctional initiator for the polymerization of styrene.

Characterization. The apparent MWs of the homo- and copolymers were determined by SEC using a Waters 6000-A liquid chromatograph and a Perkin-Elmer LC-75 spectrophotometric UV detector. Phenomenex TSK Gel G-3000 and G-5000 (10^3 and 10^5 Å, respectively) columns (75 mm × 30 cm) were used in series. The eluting solvent was THF at 1 mL/min. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. UV–vis spectra were recorded on a Perkin-Elmer Lambda-9 UV–vis–near-IR spectrophotometer.

Results

Homopolymerization. Various initiators were investigated for the homopolymerization of PVS, and the results are summarized in Table I. It is seen from Table I that the delocalized carbanions, viz., (triphenylmethyl)lithium (TPML), (triphenylmethyl)potassium (TPMK), and (diphenylhexyl)lithium (DPHL), are excellent initiators. TPML was the initiator of choice and most of the studies of the polymerization of PVS (kinetics, temperature effects, etc.) were carried out with this carbanion. TPML is easy to synthesize, is extremely stable at room temperature in THF, and has an intense absorption in the visible region (ϵ at 500 nm = 31 000) so that its concentration can be accurately measured by UV–vis spectrometry. The intense color also helps in visually monitoring the initiation process since a dramatic change in color is seen in going from the TPML carbanion to the α-lithio sulfinyl carbanion (dark red to yellowish green). Also TPML is not sufficiently nucleophilic at −78 °C to attack the sulfur atom in the monomer.

Table I
Homopolymerization of PVS Using Various Anionic Initiators in THF at −78 °C

initiator	app mol wt (exptl)[a] M_w	app mol wt (exptl)[a] M_n	M_n(calcd)[b]	M_w/M_n	yield, %
TPML	2680	2070	1980	1.33	95
	2750	2470	3200	1.11	60
	5940	4220	5330	1.41	92
	33100	24600		1.34	90
TPML[c]	4500	3310	3970	1.36	90
TPMK	8060	6060	12500	1.33	95
DPHL	1240	1170	6090	1.1	>70
methyllithium	3020	2600	6240	1.16	94
	10300	7400	7540	1.39	95
	11300	7700	6730	1.46	90
	17800	12300	12180	1.44	84
	18400	15500	19980	1.18	75
EPSL	9750	7500	11870	1.3	70
	14400	12000	11720	1.2	86
LiNph	19000	14600	15220[d]	1.3	90

[a] From SEC using polystyrene standards. [b] M_n(calcd) = [monomer] converted/[initiator] × M_{monomer}. [c] Solvent system = 1:1 THF–toluene. [d] M_n(calcd) = [monomer]/[initiator] × 2 × M_{monomer}.

Methyllithium was the only alkyllithium successfully employed as the initiator.[1,2] Interestingly, *n*-butyllithium and *tert*-butyllithium attack the sulfur atom, causing an S_N2 displacement of the aryl group.[20-24] Electron-transfer initiators such as lithium naphthalide were also employed. A two-ended living polymer of PVS was thus generated similar to conventional monomers such as styrene.[16] Thus the initiation of polymerization of PVS appears to be similar to the conventional anionic polymerization of styrene. The dipole-stabilized initiator 1-lithio-1-(phenylsulfinyl)ethane (EPSL), which is a carbanion analogous to that of the growing chain,[11] was also found to be an effective initiator. EPSL afforded polymers of controlled molecular weight and narrow molecular weight distribution (Table I).

Effect of Temperature. A series of experiments were performed to explore the effect of temperature on the initiation and polymerization of PVS. The results of these experiments are summarized in Table II. After initiation at 25 °C, the reaction mixture was immediately divided into two portions, one of which was cooled to −78 °C while the other was kept at 25 °C and polymerization allowed to proceed at that temperature. Runs 6 and 7 were similarly initiated at −78 °C and polymerized at −78 and 25 °C. The effects of temperature on initiation and polymerization were quite distinct. Thus raising the temperature to 25 °C during initiation gives rise to a bimodal distribution, and a higher temperature during polymerization appears to broaden the molecular weight distribution (Table II).

Copolymerization. Both A–B and A–B–A type block copolymers of styrene and PVS were synthesized. Styrene was polymerized by a slow vapor phase addition of the monomer onto a rapidly stirred THF solution of initiator at −78 °C in vacuo. Purified *tert*-butyllithium was found to be the most efficient initiator, giving polymers with reproducible molecular weights and narrow molecular weight distributions (Table III).[19] The DPE-capped polystyryllithium (DPPL) was seen to be an excellent initiator for PVS. Table III summarizes the SEC data of various

Table II
Effect of Temperature on Polymerization of PVS^a

run	T_i,^{b} °C	T_p,^{c} °C	M_w	M_n	M_n(calcd)^d	M_w/M_n	distribution
1	-85	-85	10800	7600	19000	1.42	unimodal
2	-25	-25	11000	7130	19000	1.55	unimodal
3	-78	-78	5950	4220	5330	1.41	unimodal
4	25	25	8500	3750	4890	2.26	bimodal
5	25	-78	9180	3670	4030	2.5	bimodal
	25	25	8810	3110	4030	2.83	bimodal
6	-78	-78	6950	4530	4650	1.53	unimodal
	-78	25	6830	3950	4650	1.73	unimodal
7	-78	-78	4800	3140	4570	1.53	unimodal
	-78	25	4910	2390	4570	2.05	unimodal

^{a} Initiated by TMPL in THF. ^{b} Temperature of initiation. ^{c} Temperature of polymerization. ^{d} M_n(calcd) = [monomer]/[initiator] × M_{monomer}.

Table III
A–B Diblock Copolymerization of Styrene and PVS in THF at –78 °C

sample	mol of styrene × 10^3	polystyrene block			mol of DPPL^b × 10^3	mol of PVS added × 10^3	AB diblock			% yield^e	% PPVS	
		M_n(calcd)^a	M_p(SEC)	M_w/M_n			M_n(calcd)^c	M_p(SEC)^d	M_w/M_n		exptl^f	calcd^g
AB21	8.76	3430	2700	1.10	0.360	2.25	3660	3980	1.16	98.6	21.3	20.6
AB53	6.13	3430	2700	1.10	0.250	6.75	6790	7950	1.22	97.0	47.1	52.4
AB66	7.00	3430	2700	1.10	0.288	14.30	10300	11200	1.27	96.9	66.8	66.6
AB85	6.13	3430	2700	1.10	0.252	35.00	16900	17100	1.24	68.1	74.9	85.0
AB90	1.93	3430	2700	1.10	0.079	15.80	19100	19200	1.41	54.3	78.4	89.1
PSPVS	28.40	8690	9120	1.04	0.250	23.00	16600	13100	1.09	56.2	47.4	44.7

^{a} M_n(calcd) = [(mol of styrene)/(mol of *tert*-butyllithium)] × 104. ^{b} DDPL = polystyryllithium capped with DPE. Measured by UV–vis spectroscopy. ^{c} M_n(calcd) = [(mol of PVS converted)/(mol of DPPL)] × 152.22 + M_n(polystyrene block). ^{d} M_p(SEC) with reference to polystyrene standards. ^{e} % yield = [(weight of copolymer)/(weight of styrene + weight of PVS)] × 100. ^{f} % PPVS calculated from the ratio of aromatic absorptions of sulfoxide phenyl (δ 7.4) and polystyrene phenyl δ 7.0 (meta and para protons) and δ 6.5 (ortho protons)]. ^{g} [(Mol of PVS (in feed))/(mol of PVS + mol of styrene)] × 100.

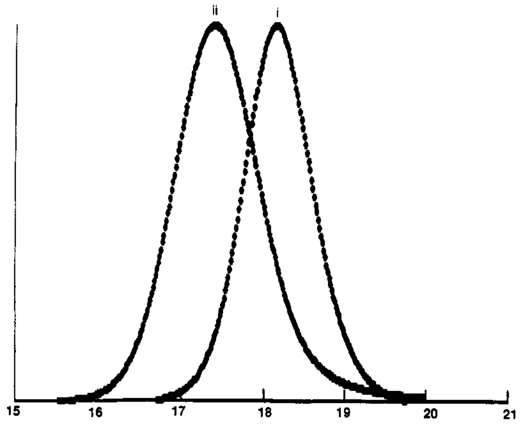


Figure 2. SEC chromatograms of (i) polystyrene homopolymer (M_p = 8200, M_w/M_n = 1.09) and (ii) A–B copolymer of styrene and PVS (M_p = 13 100 M_w/M_n = 1.09). Eluting solvent: THF at 1 mL/min.

A–B copolymerizations. The molecular weight distributions of the copolymers were narrower than those for homopolymers of PVS, which is expected since the polymeric initiators have a narrow molecular weight distribution. Figure 2 shows a typical SEC chromatogram of the polystyrene homopolymer (i) and styrene–PVS copolymer (ii). At high PVS concentrations, considerable termination during polymerization was observed as seen from a broadening of the molecular weight distribution and decreased yield (entries 4 and 5 in Table III). In five of the samples (AB21 to AB90; Table III) the polystyrene block was kept constant (M_p(SEC) = 2700) whereas the sulfoxide content was varied. There was a good correlation between the calculated sulfoxide content (from the ratio of moles of styrene to moles of PVS) (21, 53, and 66%) and that observed from ^{1}H NMR (21, 47, and 67%, respectively) for the first three samples. However, a large variation was seen for samples AB85 and AB90 (85 and 90% calculated and 75 and 78% observed). This again indicates substantial termination when the concentration of PVS in the feed is high.

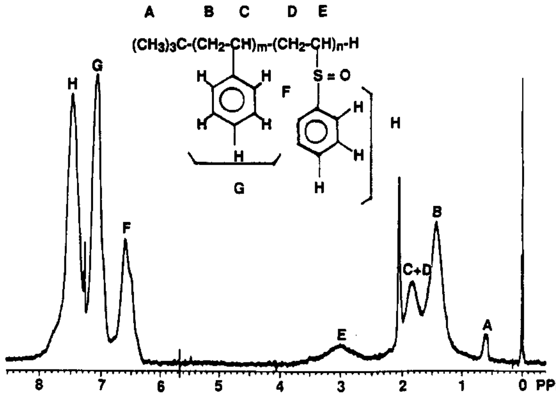


Figure 3. 200-MHz ^{1}H NMR of poly(styrene-*b*-PVS) copolymer in $CDCl_3$ at room temperature.

The PPVS content in the copolymer was calculated from the ^{1}H aromatic absorptions of the polystyrene phenyls (δ 7.0 (meta and para) and δ 6.5 (ortho)) and the sulfoxide phenyls (δ 7.5) (Figure 3). The shielded ortho protons in polystyrene are seen to be shifted upfield relative to those in the meta and para position.[25]

Lithium naphthalide was employed as the initiator of styrene for the A–B–A triblock copolymerization. Table IV summarizes the SEC data. As is well-known, lithium naphthalide initiates the polymerization of styrene by electron transfer to form the radical anion of the monomer, which then immediately couples and forms the dimer dianion.[16,17] This dianion then propagates to give two-ended polystyryllithium. Table IV once again shows that the dianion of polystyryllithium is an excellent initiator for PVS. Again the polydispersity of the copolymer increases with increasing content of sulfoxide. The bi-

Table IV
A–B–A Triblock Copolymerization of Styrene and PVS in THF at −78 °C

sample	mol of styrene × 10³	polystyrene block			mol of DDPPL[b] × 10³	mol of PVS added × 10³	A–B–A triblock			% yield[e]	% PPVS	
		M_n(calcd)[a]	M_p(SEC)	M_w/M_n			M_n(calcd)[c]	M_p(SEC)[d]	M_w/M_n		exptl[f]	calcd[g]
ABA30	6.35	11 960	11 400	1.07	0.132	2.7	14 510	18 100	1.14	97.9	41.8	29.8
ABA50	6.10	11 960	11 400	1.07	0.127	6.1	18 670	21 200	1.23	96.6	49.8	50.0
ABA78	5.55	11 960	11 400	1.07	0.116	19.7	29 970	30 600	1.33	74.3	65.5	78.0
ABA90	2.96	11 960	11 400	1.07	0.062	26.0	33 360	28 100	1.51	35.4	69.8	89.7
ABAS0	19.0	55 000	59 500	1.08	0.079	15.0	79 230	79 100	1.12	90.5	29.5	44.1
ABAS1	25.0	26 670	29 700	1.04	0.169	15.0	43 670	48 100	1.10	98.2	35.5	37.5

[a] M_n(calcd) = [(mol of styrene)/(mol of lithium naphthalide)] × 2 × 104. [b] DDPPL = dianion of DPE-capped polystyryllithium. Concentration measured by UV–vis spectroscopy. [c] M_n(calcd) = [(mol of PVS converted)/(mol of DDPPL)] × 152.22 + M_n(polystyrene block). [d] M_p(SEC) with reference to polystyrene standards. [e] % yield = [(weight of polymer)/(weight of styrene + PVS)] × 100. [f] % PPVS calculated from the ratio of aromatic absorptions of sulfoxide phenyl (δ 7.4) and polystyrene phenyl [δ 7.0 (meta and para protons) and δ 6.5 (ortho protons)]. [g] [(Mol of PVS (in feed)/(mol of PVS + mol of styrene (in feed)] × 100.

functionality of the DPE-capped living polystyryllithium initiated by lithium naphthalide was independently shown by determination of the molar ratio of the living carbanion solution (titration with fluorene and determination by UV–vis spectroscopy) and the terminated polystyrene homopolymer (by SEC). The ratio was found to be 2.05 (±0.1), indicating a perfectly two-ended living polystyryllithium carbanion.

Discussion

The initiation of PVS at −78 °C in THF is instantaneous as seen from an immediate change in color from dark red (for delocalized carbanions such as TPML and DPE-capped living polystyryllithium) to yellowish-green (the color of the growing α-lithio sulfoxide carbanion). It is seen from Table I that there is excellent agreement between the calculated and experimental M_n in most runs. This is consistent with the "living" character of the polymerization.[16] The molecular weight distributions are similar to that observed for other polar monomers such as methyl methacrylate.[16,17]

Nature of the Propagating Carbanion. The living α-sulfinyl carbanion has been shown to be a dipole-stabilized ion pair in THF.[2] For instance, the UV spectra of ethyl phenyl sulfoxide (EPS) and the carbanion derived from it show almost no difference in absorption maxima.[2] The ^{13}C NMR signals for the carbanion are almost the same as those of the parent hydrocarbon. Since delocalization of the negative charge into the aromatic ring would generally result in an upfield shift of the para carbon due to shielding,[26–28] there appears to be little or no delocalization of the negative charge into the aromatic ring. Also the IR spectra of the carbanion of EPS and the parent hydrocarbon exhibit the same absorption wavelength for the S=O stretch.[2] These observations indicate the absence of delocalization of the negative charge into the S=O bond. From bond moments and bond lengths,[28] the S–O bond can be best described as a bond with substantial ionic character. Elegant ^{13}C NMR studies by Marquet[26–28] reveal that the Δ^1J_{C-H} in the α-lithio sulfoxide shows a large increase (+16.5 Hz) in the ^{13}C NMR upon metalation of the α-carbon of methyl phenyl sulfoxide. Thus, the carbon bearing the negative charge was shown to have a high sp² character similar to that found in Ph_2CHLi. In methyl phenyl sulfoxide it was found that the $^{13}C-^1H$ coupling constant decreases in the cryptated potassium salt as compared to the uncryptated complex. Thus the carbanion appears to become more pyramidal (sp³ character increases) upon cryptation. This suggests that the planar sp² configuration is stabilized by interaction with the cation. It is therefore reasonable to assume that a chelated structure of the growing α-lithio sulfoxide (Figure 4) is possible because of the high charge density present on the oxygen in the S–O bond. This structure is possible even for potassium, which is expected to have a looser interaction with the anion. The α-potassio sulfoxide would be expected to have a reactivity similar to that of the α-lithio sulfoxide, and this is indeed found upon using TPMK as initiator (Table I). The resulting molecular weight distribution, which is a good indicator of the efficiency of the initiation, is similar to that for TPML.

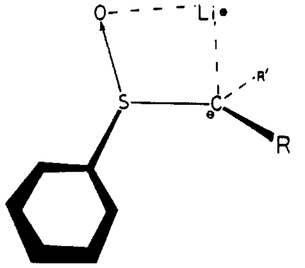


Figure 4. Chelated ion pair structure of α-sulfinyl carbanions with lithium as counterion.

Temperature. The effect of temperature in both the initiation and the propagation was found to be dramatic (Table II). It was seen that during initiation of PVS at 25 °C the color changed from dark red (TPML) to yellowish-green, characteristic of the α-sulfinyl carbanion, and then once again to red within minutes. The color progressively became darker with time and did not discharge when the solution was terminated with methanol. An attempt made to monitor the formation of the colored side products using UV–vis spectroscopy failed. Only a tail was seen in the visible region which gave no useful information as to the identity of the colored products. It was seen that initiation at low temperatures (<−25 °C) led to a unimodal distribution in the SEC chromatogram. However, initiation at 25 °C gave rise to a bimodal distribution (Table II, runs 4 and 5), which did not change even when the solution was cooled to −78 °C immediately after initiation followed by addition of new monomer (Figure 5). This leads us to believe that at low temperatures, the initiation process forms only one propagating species. However, in the case of initiation at higher temperatures, two distinct, propagating or initiating species may be present: a major one giving rise to the high molecular weight peak in SEC, and a minor species giving rise to low molecular weights (Figure 5). Obviously, the high molecular weight (major) initiating species propagates or initiates faster than the low molecular weight (minor) one.

Reactions of alkyllithium with sulfoxides having an α-proton have been well studied.[21–23,29] Methyllithium and LDA mainly abstract the α-proton. n-Butyllithium and

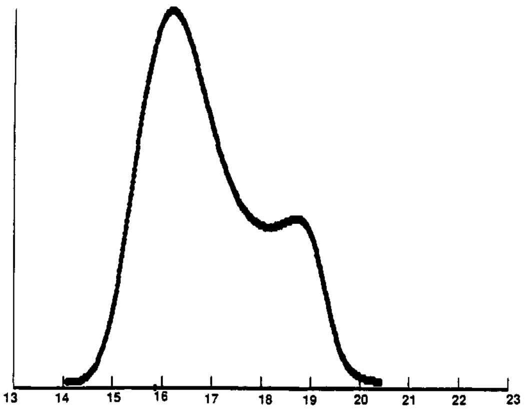


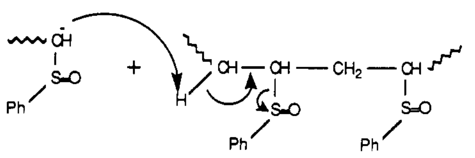
Figure 5. SEC chromatogram of PPVS initiated by TPML at 25 °C and polymerized at -78 °C in THF. Eluting solvent: THF. Flow rate: 1 mL/min.

tert-butyllithium, on the other hand, attack the sulfur, causing a ligand exchange on the sulfoxide. Durst et al.[23] found two competing reactions when various sulfoxides were reacted with alkyllithiums: (a) abstraction of an α-hydrogen to give α-lithio sulfoxide and (b) carbon-sulfur bond cleavage via an S_N2 displacement at sulfur. In our system displacement of the phenyl group by TPML at -78 °C is unlikely because TPML is less basic and more sterically hindered compared with alkyllithium. The red color associated with the side reaction observed at 25 °C may be due to a base-promoted elimination of PPVS by the growing carbanion leading to polyene structures (see below).

We found the polymerization of PVS to be extremely rapid even at -78 °C (half-life of ca. 4 s). Thus at 25 °C the polymerization is expected to be even more rapid. The two initiating or propagating species (slow and rapid) that are seen would be expected to form and propagate in the first few seconds of the polymerization. Thus cooling the reaction mixture after initiation at 25 °C does not have much effect on the distribution and we still see the bimodal nature of the molecular weight distribution (run 5 in Table II).

The total absence of bimodal distributions for the samples initiated at -78 °C suggests that at -78 °C we form only one initiating species which propagates further. Warming the solution to 25 °C after initiating at -78 °C does not give rise to a bimodal distribution (runs 6 and 7 in Table II). However, the molecular weight distribution of the sample was considerably broadened when it was warmed to 25 °C. This was an indication that polymerization side reactions played an important role at ambient temperatures. This also indicates a different effect of temperature on the polymerization as compared to the initiation.

It was also noticed that the side reactions were more prominent in polymerizations with long reaction times so that the growing polymer chain is somehow deactivated during the polymerization. Several explanations are possible since we have a number of sites in the polymer chain that could be attacked by the growing carbanion leading to various side products. Apparently, these side reactions are strongly temperature dependent and lead to broad molecular weight distribution (Table II) and formation of colored side products. As mentioned before, efforts to determine the colored side products by UV-vis spectrometry failed due to the strong UV absorption of the sulfoxide group (λ_{max} 253 nm). A plausible deactivation reaction could be an E2 elimination of phenylsulfenic acid in the polymer chain by the growing carbanion[30,31] to form polyene linkages in the chain:



Conclusion

In conclusion, it is seen that homo- and copolymerization of PVS can be carried out by conventional anionic polymerization techniques. A variety of initiators could be employed but it was seen that delocalized carbanions such as TPML are very effective. Electron-transfer initiators could also be employed to achieve two-ended polymerization of PVS. In both of these cases there was a good correlation between the calculated M_n and the experimental M_n determined by SEC and ^{1}H NMR. The molecular weight distribution in most homopolymers was found to be relatively narrow ($M_w/M_n \leq 1.4$). The effect of temperature on initiation and propagation was seen to be dramatic. In general, lower temperatures resulted in well-defined and narrow molecular weight distribution polymers. Initiation at -78 °C led to a unimodal distribution, indicating one initiating species, whereas initiation at 25 °C led to a bimodal distribution due to the possible presence of two initiating or propagating species. Also, polymerizations at ambient temperatures resulted in colored side products and polymers with broader MWDs. Both A-B diblock and A-B-A triblock copolymers of styrene and PVS were synthesized by reaction of mono- and bifunctional living polystyrene with PVS at low temperatures. The molecular weight distributions of the block copolymers were, in general, narrower than those of the homopolymers.

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References and Notes

(1) Buese, M.; Hogen-Esch, T. E. *Macromolecules* **1987**, *20*, 1509.
(2) Kanga, R. S.; Hogen-Esch, T. E.; Randrianalimanana, E.; Soum, A.; Fontanille, M. *Macromolecules*, **1990**, *23*, 4241.
(3) Kingsbury, C. A.; Cram, D. J. *J. Am. Chem. Soc.* **1960**, *82*, 1810.
(4) Takinaga, R.; Sugihara, H.; Tanaka, K.; Kaji, A. *Synthesis* **1975**, 299.
(5) Walling, C.; Bollyky, L. *J. Org. Chem.* **1964**, *29*, 2699.
(6) Koppel, G. A.; Kinnick, M. D. *J. Chem. Soc., Chem. Commun.* **1975**, 473.
(7) Kice, J. L.; Campbell, J. D. *J. Org. Chem.* **1967**, *32*, 1631.
(8) Tsuchihashi, G.; Mitamura, S.; Ogura, K. *Tetrahedron Lett.* **1973**, *27*, 2469.
(9) Tsuchihashi, G.; Mitamura, S.; Ogura, K. *Tetrahedron Lett.* **1976**, *11*, 855.
(10) Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597.
(11) Feast, W. J.; Taylor, M. J.; Winter, J. N. *Polymer* **1987**, *28*, 593.
(12) Feast, W. J.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1985**, 202.
(13) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395.
(14) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595.
(15) Swager, T.; Dougherty, D.; Grubbs, R. *J. Am. Chem. Soc.* **1988**, *110*, 2973.
(16) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Wiley-Interscience: New York, 1968.
(17) Morton, M. *Anionic Polymerization, Principles and Practice*; Academic Press: New York, 1983.
(18) Morton, M.; Milkovich, R.; McIntyre, D. B.; Bradley, L. J. *J. Polym. Sci., Part A* **1963**, *1*, 443.
(19) Kanga, R. Ph.D. Dissertation, University of Florida, 1988.
(20) Jacobus, J.; Mislow, K. *J. Am. Chem. Soc.* **1967**, *89*, 5228.

(21) Andersen, K.; Yeager, S.; Peynircioglu, N. B. *Tetrahedron Lett.* **1970**, *28*, 2485.
(22) Lockard, J. P.; Schroek, C. W.; Johnson, C. R. *Synthesis* **1973**, 485.
(23) Durst, T.; LeBelle, M.; Van den Elzen, R.; Tin, K. *Can. J. Chem.* **1974**, *52*, 761.
(24) Solladie, G. *Synthesis* **1981**, 185.
(25) Bovey, F. A.; Hood, F. P., III; Anderson, E. W.; Snyder, L. C. *J. Am. Chem. Soc.* **1965**, *42*, 3900.
(26) Lett, R.; Marquet, A. *Tetrahedron Lett.* **1975**, *19*, 1579.
(27) Lett, R.; Chassaing, G.; Marquet, A. *J. Organomet. Chem.* **1976**, *111*, C17.
(28) Chassaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399.
(29) Kunieda, N.; Wada, H.; Kinoshita, M. *Makromol. Chem.* **1973**, *172*, 237.
(30) Wallace, T.; Hofmann, J.; Schriesheim, A. *J. Am. Chem. Soc.* **1963**, *85*, 2739.
(31) Russell, G. A.; Becker, H. D. *J. Am. Chem. Soc.* **1963**, *85*, 3406.

Registry No. PVS, 20451-53-0; St, 100-42-5; TPML, 733-90-4; TPMK, 1528-27-4; DPHL, 128631-46-9; EPSL, 111736-41-5; (St)(PVS) (block copolymer), 110783-14-7; PVS (homopolymer), 87500-51-4; *t*-butyllithium, 594-19-4; methyllithium, 917-54-4; lithium naphthalide, 7308-67-0.