Communications to the Editor

Protection and Polymerization of Functional Monomers. 7.[†] Anionic Living Polymerization of 2-(4-Vinylphenyl)-4,4-dimethyl-2-oxazoline

Poly(4-vinylbenzoic acid) and related polymers are attractive materials as ion-exchange resins and polymer chelates. The polymer has generally been prepared by free radical polymerization of 4-vinylbenzoic acid.[6,7] Radical-initiated copolymerizations of 4-vinylbenzoic acid with styrene and with acrylonitrile have also been investigated,[8-10] and the vinyl reactivity has been reported.[10,11] Kitano and co-workers[12] presented an interesting report concerning the radical polymerizations of *tert*-butyl and trimethylsilyl 4-vinylbenzoates. Linear poly(4-vinylbenzoic acids) could be obtained by hydrolysis of the resulting polymers. The narrow molecular weight distribution polymer is not easily obtained by means of radical polymerization since chain-transfer and termination reactions are inevitable during the polymerization. Kitano et al. also described briefly the possibility of anionic polymerization of *tert*-butyl 4-vinylbenzoate, but detailed results were not available.

We recently developed a new approach to the synthesis of tailor-made functional polymers involving anionic living polymerization of monomers with protected functional groups and removal of the protecting groups from the resulting polymers. Thus in our laboratory are obtained poly(4-vinylphenol),[1,2] poly[2-(4-vinylphenyl)ethanol],[3] poly(4-vinylaniline),[4] and poly(4-vinylbenzaldehyde)[13] of known molecular weight and narrow molecular weight distribution. These polymers have thus far been very difficult to prepare. As part of a series of studies, we report here the synthesis of linear poly(4-vinylbenzoic acid) with well-defined structure that is obtained by anionic living polymerization of 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline (1) followed by complete removal of the oxazolinyl group to regenerate the carboxyl group as shown in Scheme I.

Results and Discussion. Anionic polymerization of the new protected monomer, 1, with oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium (2) was investigated in THF at −78 °C. Upon mixing of 1 with initiator solution, the polymerization appeared to proceed instantly as evidenced by the observation of a viscosity increase of the solution. The characteristic red color of the system was not appreciably changed during the polymerization. The coloration remained unchanged at −78 °C for 1 h but disappeared immediately when the polymerization was quenched with a few drops of methanol. Addition to an excess of water precipitated a white solid, 3, yields of which were quantitative based on the form of poly[2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline]. ^{1}H NMR spectra of the resulting polymers showed signals of the expected poly[2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline], as shown in Figure 1a. The signals corresponding to the vinyl protons completely disappeared. Infrared spectra of 3 exhibited a characteristic oxazoline band at 1650 cm^{-1} as illustrated in Figure 2a. Thus, the spectroscopic data suggest that the polymerization of the vinyl group proceeds exclusively without side reactions.

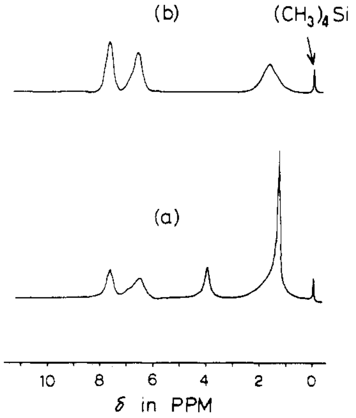

Figure 1. ^{1}H NMR spectra of 3 (a) and 4 (b).

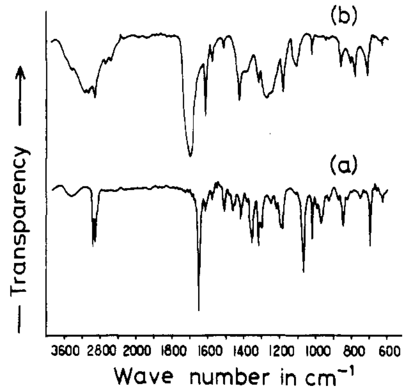

Figure 2. IR absorption spectra of 3 (a) and 4 (b).

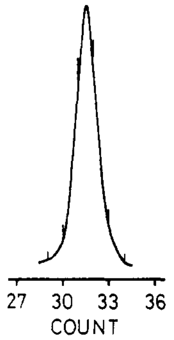

Figure 3. GPC profile of 3: $\bar{M}_n$(obsd) (VPO) = 13 000, $\bar{M}_w/\bar{M}_n$ = 1.13.

The results of the anionic polymerization of 1 are summarized in Table I. As can be seen, there is fair agreement between the measured values of molecular weight by vapor pressure osmometry (VPO) and the value which predicts the $\bar{M}_n$ of a "living" polymer obtained by a bifunctional initiator. All GPC curves of 3 show single peaks with narrow molecular weight distributions. A representative one is shown in Figure 3. The values of $\bar{M}_w/\bar{M}_n$,[14] calculated from the GPC curves and the standard polystyrene calibration, are around 1.1. These facts clearly indicate the rapidity of initiation and the lack of chain-transfer and termination reactions during the course of the anionic polymerization of 1. The poly[2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline] (3) thus obtained is soluble in THF, benzene, chloroform, acetone, diethyl ether, carbon tetrachloride, xylene, toluene, ethyl acetate, dichloromethane,

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[†] The main title of this series of studies[1-5] has been changed to this title. Part 6: ref 13.

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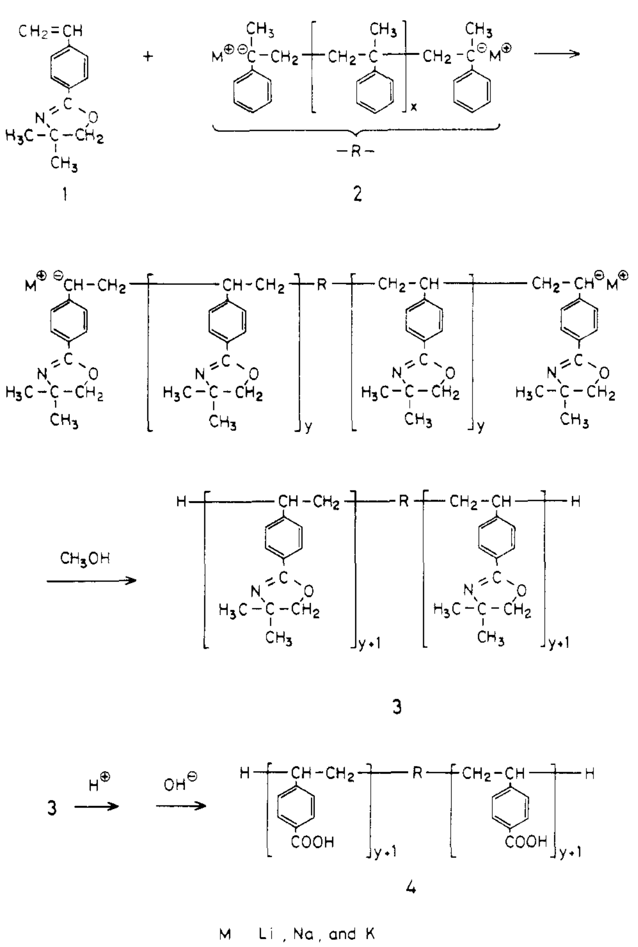
Table I
Anionic Polymerization of 1 with Various Initiators in THF at -78 °C for 10 min

(1), mmol	initiator (mmol)	α-methylstyrene, mmol	conversion, %	$\bar{M}_n$ (calcd)[a]	$\bar{M}_n$ (obsd)[b]	$\bar{M}_w/\bar{M}_n$
6.46	lithium naphthalide (0.190)	0.567	99	14000	13000	1.13
6.22	sodium naphthalide (0.172)	0.520	100	15000	16000	1.09
4.69	potassium naphthalide (0.204)	0.564	100	10000	9100	1.05

[a] $\bar{M}_n$(calcd): calculated from the monomer to initiator ratio. [b] $\bar{M}_n$(obsd): by vapor pressure osmometry in benzene.

Scheme I
Synthesis of Poly(4-vinylbenzoic acid)



pyridine, *N,N*-dimethylformamide, and 1,4-dioxane but is insoluble in hexane, ethanol, methanol, and water.

Acid hydrolysis and subsequent saponification of **3** gave pure poly(4-vinylbenzoic acid) (**4**), though the isolated yield was not quantitative, probably due to losses in handling. The resulting polymer was a white solid that was soluble in THF, methanol, ethanol, *N,N*-dimethylformamide, and dimethyl sulfoxide. The IR spectra of **4** showed the characteristic C=O and O—H stretching absorptions of the carboxyl group at 1700 and 2500–3300 cm^{-1}, respectively, whereas the absorptions corresponding to the oxazolinyl group (1650 cm^{-1}) disappeared as shown in Figure 2b. The ^{1}H NMR spectra of **4** showed signals of the expected poly(4-vinylbenzoic acid) but no trace of signals corresponding to the oxazolinyl protecting group (Figure 1b). Furthermore, the nitrogen was not detected by elemental analysis of **4**. The analytical values for carbon and hydrogen were in fair agreement with the calculated ones when the polymer was assumed to contain $^7/_{10}$ mol of H_2O per monomer unit in **4**: Anal. Calcd for $C_9H_8O_2 \cdot {}^7/_{10}H_2O$: C, 67.24; H, 5.89; N, 0.00. Found: C, 67.46; H, 5.51; N, 0.00. These results confirm that complete removal of the protecting group is achieved. Poly(4-vinylbenzoic acid) obtained by this method may have a predictable molecular weight with a narrow molecular weight distribution. A detailed study for the synthesis and characterization of poly(4-vinylbenzoic acid) and the block copolymers is currently under investigation.

Experimental Section. Materials. 4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co., Ltd. **1** was synthesized from 4-chlorostyrene via five reaction steps. The starting monomers, 4-vinylbenzoic acid and 4-vinylbenzoyl chloride, were prepared by procedures described by Ramsden et al.[15] and by Kojima et al.,[16] respectively. **1** was prepared by reaction of 4-vinylbenzoyl chloride and 2-amino-2-methyl-1-propanol in dichloromethane followed by treatment with thionyl chloride to cyclize to the corresponding oxazoline ring, according to the procedure of Meyers et al.[17] with some modification. The crude product was purified by fractional distillation: yield 41%; bp 83–85 °C (1 mbar); ^{1}H MNR (CCl_4, 60 MHz) δ 1.31 (s, 6 H, CH_3), 4.03 (s, 2 H, CH_2), 5.30–5.80 (2d, 2 H, J = 10, 18 Hz, CH_2=), 6.77 (2d, 1 H, CH=), 7.33–8.00 (m, 4 H, aryl H). **1** was distilled under vacuum and stored in ampules equipped with breakseals.

Solvent. THF was used as solvent in all polymerization experiments. It was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and then from sodium naphthalide solution. The oligomeric (α-methylstyryl)dilithium, -disodium, and -dipotassium (**2**) were freshly prepared just prior to polymerization from the corresponding metal naphthalides and a 2–4 molar quantity of α-methylstyrene at 30 °C for 1 min and then at -78 °C for 5 min. The concentration of metal naphthalide was previously determined by titration with standardized 1-octanol under vacuum.

Polymerizations. All operations were carried out under high vacuum (10^{-6} mbar) in an all-glass apparatus equipped with breakseals. All processes were carried out at -78 °C with shaking. The polymers were recovered, after adding methanol, by precipitation in excess water. They were filtered, redissolved in THF, and precipitated into hexane two additional times. Then they were freeze-dried from benzene solution.

Isolation of **4**. A 0.8-g quantity of **3** was refluxed in 3 N hydrochloric acid (25 mL) containing THF (5 mL) for 10 h. The mixture was neutralized with 3 N sodium hydroxide solution and concentrated to a small quantitiy. It was refluxed in 30 mL of 1:1 methanol–water containing 20% sodium hydroxide for 6–10 h. The methanol was removed under reduced pressure and the residue was poured into 3 N hydrochloric acid (300 mL). The polymer precipitated was filtered, washed with water, redissolved in methanol, and precipitated into diethyl ether, and then freeze-dried from dioxane containing a small amount of methanol. A 0.44-g quantity (75% of the theoretical values) of pure **4** was obtained.

Measurements. IR spectra were run on a JASCO FT/IR-3 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL JNM-PMX 60 instrument. Gel permeation chromatograms were obtained with a Toyo Soda HLC-802 instrument with a UV detector, THF being the elution solvent. Styrene–divinylbenzene cross-linked gel was used in the column. VPO measurements were made with a Corona 117 instrument in benzene solution.

Registry No. **3**, 102920-04-7; **2**·2Li, 57486-16-5; **2**·2Na, 37244-89-6; **2**·2K, 52219-57-5.

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Characterization of Polysilanes by Carbon-13, Silicon-29, and Proton NMR

The recent discovery of soluble polysilanes[1–5] $-(RR'Si)_n-$ (R and R′ = alkyl or phenyl) has stimulated interest in the properties and applications of these materials. Of particular note is their intense UV absorption at 300–380 nm, both in solution[6] and in the solid state.[7] It has been shown[6a] that λ_{max} of the absorption band and the absorptivity per Si–Si bond increase with the length of the silicon backbone, reaching a maximum when the chain is very long. In addition, it is reported that certain polysilanes exhibit abrupt transitions in the UV spectrum at low temperature for dilute solutions[6b] and at the melting point in the case of poly(di-*n*-hexylsilane).[7] These are bathochromic shifts with decreasing temperature and have been attributed to the onset of highly ordered conformations.[6b,c,7]

To better our understanding of the solution and solid-state properties of the polysilanes we have conducted solution-state NMR studies to characterize in detail the microstructure of a number of dialkylsilane homopolymers and copolymers. Previously,[2,4] proton and ^{13}C peak positions have been given for certain polysilanes, but without spectra and mostly without assignments. We report here for the first time ^1H, ^{13}C, and ^{29}Si spectra of four dialkylsilane polymers: poly(methyl-*n*-propylsilane), poly(methyl-*n*-hexylsilane), poly(methyl-*n*-dodecylsilane), and poly(di-*n*-hexylsilane). Peak assignments have been made, in part, with the aid of 2D experiments. Results of studies on the solid state and on copolymers will be reported later.

All polymers were prepared by the sodium metal dechlorination of the corresponding dialkylchlorosilanes and were of relatively low polydispersity (<1.5) and high molecular weight ($M > 10^6$).[8] NMR spectra were obtained with a Varian XL-200 or JEOL GX-500 spectrometer and 1.0–18.5% solutions in benzene-d_6, toluene-d_8, 1,2,4-trichlorobenzene/dioxane-d_8, or methylene-d_2 chloride at 0 to +100 °C. Ten scans were accumulated for ^1H spectra and $(10–20) \times 10^3$ scans for ^{13}C and ^{29}Si spectra. The recorded proton-decoupled ^{29}Si spectra of these polymers contain negative resonances resulting from the nuclear Overhauser enhancement. Because the magnetic moment and the spin of ^{29}Si are antiparallel, the gyromagnetic ratio, γ, is negative. Therefore the maximum enhancement which can result from irradiation of the protons is -1.5. In cases of partial Overhauser enhancement a weak positive or negative signal will be produced. The ^1H COSY and ^{13}C–^1H heterocorrelated spectra were obtained by using data matrices of 256 spectra in 1024 points, with zero filling to 512 by 1024 points. The two-dimensional data were multiplied by a combination of trapezoidal and exponential functions. The COSY spectrum was recorded with 2000 Hz in each frequency dimension, while the heterocorrelated spectrum provided a sweep width of 2000 and 7000 Hz for the proton and carbon frequency dimensions, respectively. (See figure captions for further details.) The sharp resonances labeled with an "×" in Figures 1 and 3 represent as yet unidentified sample impurities. Since the impurities do not produce resonances in the silicon-29 NMR spectra we attribute them to nonpolymeric species unrelated to our polysilane materials.

In Figure 1 the 500-MHz ^1H spectra of these polymers are shown. As expected, the C-1′ protons, being bonded to carbons directly attached to silicon, are strongly shielded; the C-1 protons are less so. Both move downfield as the side chain is lengthened. With the exception of poly(di-*n*-hexylsilane), these polymers contain pseudoasymmetric silicon atoms and must be viewed in terms of triad (or higher "odd-ad") configurational sequences. These sequences are reflected in the C-1′ proton resonances, which show splittings even though there can be no observable J coupling. The broadening of the C-1 and C-2 proton resonances in spectra a and b also arises mainly from this cause. The C-4, C-5, and C-6 proton resonances in hexyl side chains show increasingly resolved multiplet structure as they experience decreasing stereochemical influences. However, the proton resonances of poly(methyl-*n*-dodecylsilane) (spectrum c) show no resolved multiplet structure with the exception of the terminal methyl, C-12. It is probable that in this case homogeneous broadening from short spin–spin relaxation times is beginning to play a dominant role, all motions being impeded by the very long side chains.

The assignments of the methylene resonances in the *n*-hexyl and *n*-dodecyl groups are not self-evident from the one-dimensional spectra. In order to establish these assignments, a two-dimensional J-correlated (2D COSY) experiment was performed on the poly(methyl-*n*-hexylsilane). The results are shown in Figure 2. Protons on neighboring carbons, which are coupled through three