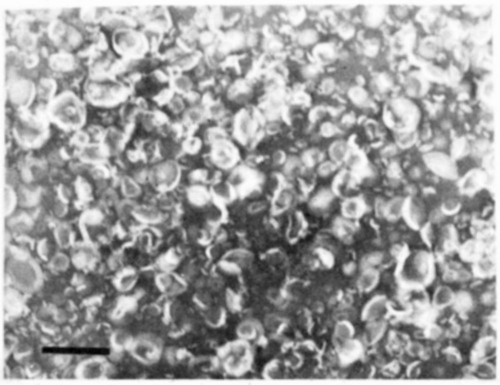

Figure 2. Transmission electron micrograph (2% ammonium molybdate stain) of polymerized vesicles of 1; bar represents 2000 Å.

distribution. Gel filtration of polymerized vesicles of **1**, using a Sephadex G-50 column, resulted in a quantitative recovery in the void volume (nitrogen analysis).[7] Similar to polymerized vesicles made from **2**,[3] and in contrast to linear disulfide-based phospholipid polymers,[8] freeze-dried polymerized vesicles of **1** were insoluble in chloroform and chloroform/methanol (1/1, v/v). We attribute this insolubility to extensive cross-linking within the bilayer.

The precise mechanism of initiation has not yet been established. Based on the pH dependence noted above, we hypothesize that polymerization proceeds via initial hydroxide displacement on the disulfide moiety, followed by ring opening via thiolate ion–disulfide interchange.[9] The greater sensitivity of this polymerization toward pH than that observed for vesicles of **2** is believed to be a consequence of the greater penetrability of the hydroxide ion across the ammonium surfactant bilayer.[10]

From a synthetic standpoint, surfactant **1** extends the applicability of polymerized vesicle chemistry to include substrates that are unstable under basic conditions, have limited stability under acidic pH, and decompose under standard thermal-induced or photoinduced polymerization conditions.[1] Efforts aimed at exploiting **1** for the synthesis of functional polymerized vesicles are now in progress.

Acknowledgment. We are grateful to James Stefely for valuable technical assistance.

Registry No. 1, 109088-38-2; **1** (homopolymer), 109088-39-3.

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(5) R_f 0.4 [silica, $CHCl_3/CH_3OH$ (9/1, v/v)]; IR ($CHCl_3$) $\nu_{C=O}$ 1720; ^1H NMR ($CDCl_3$) δ 1.30 (br s, 36 H, $(CH_2)_9$), 1.5–1.8 (m, 12 H, $(CH_2)_3$), 1.8–2.1 and 2.4–2.7 (m, 4 H, $SCHCH_2CH_2S$), 2.25–2.35 (t, 4 H, CH_2CO_2), 3.05–3.25 (t, 4 H, CH_2S), 3.4 (s, 6 H, CH_3N^+), 3.45–3.65 (m, 6 H, CH_2N^+ and CHS), 4.0–4.15 (t, 4 H, CH_2OCO); UV (EtOH) 330 nm. Anal. Calcd for $C_{40}H_{76}NO_4S_4Br$: C, 56.98; H, 9.08; N, 1.66; S, 15.21. Found: C, 56.68; H, 8.98; N, 1.64; S, 14.64. Surfactant 1 is best stored as a 0.01 M dichloromethane solution in the dark at 5 °C.

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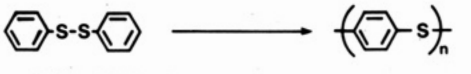
Poly(*p*-phenylene sulfide)-Yielding Polymerization of Diphenyl Disulfide by S–S Bond Cleavage with a Lewis Acid

Poly(*p*-phenylene sulfide) (PPS) has been commercially produced from *p*-dichlorobenzene and sodium sulfide.[1,2] Condensation of alkali-metal salts of *p*-halothiophenols has been also reported for the PPS preparation.[3-5] However, these polymerizations proceed at high pressure and temperature. PPS–like polymers have been prepared by oxidizing thiophenol with aluminum chloride and thionyl chloride[6,7] or concentrated sulfuric acid,[8] but these preparations result in highly branched and cross-linked polymers with primary chains of low molecular weight. We report in this paper that diphenyl disulfide reacts with a Lewis acid to cleave its S–S bond and is easily polymerized to a linear PPS at room temperature and atmospheric pressure (eq 1).



(1)

Diphenyl disulfide (0.1 mol) is allowed to react with $SbCl_5$ (0.1 mol) in nitrobenzene (100 mL) for 1 day at room temperature. The polymer was isolated in 88% yield as white powder having an empirical formula C_6H_4S[9] and was soluble in hot *N*-methylpyrrolidone. The structure including the 1,4-phenylene unit was confirmed by IR (Figure 1). The absorption attributed to 1,4-phenylene at 820 cm^{-1} indicates a linear or 1,4-conjugated phenylene sulfide structure. No typical absorption at ca. 850 cm^{-1}, which implies isolated ring hydrogen, excludes a branching and cross-linking structure. This spectrum agrees with that of commercially available PPS. The X-ray diffraction pattern was similar to that of commercial PPS Ryton. The DSC thermogram of the obtained PPS[10] suggested the molecular weight of more than 10^3 by using the relationship between the molecular weight and the melting point of PPS.[11]

The polymerization also proceeded with other Lewis acids such as $AlCl_3$, $TiCl_4$, and $MoCl_5$ although the polymer yield and molecular weight were influenced by the Lewis acid and solvent species. Similarly bis(2,6-diethylphenyl) disulfide with a Lewis acid yielded poly(2,6-diethyl-1,4-phenylene sulfide) of which structure was confirmed by IR, ^1H NMR, ^{13}C NMR, and elemental analysis.[12] The polymer was soluble in chloroform and its molecular weight was 4300–6000 (vapor pressure osmometry).

When thiophenol was used as a starting material, the polymerization in the presence of a Lewis acid and an oxidizing agent gave also PPS at room temperature. Thiophenol is considered to be first oxidized to diphenyl disulfide and then polymerized.

This polymerization did not proceed in basic solvents such as acetonitrile. Equimolar amounts of Lewis acid and

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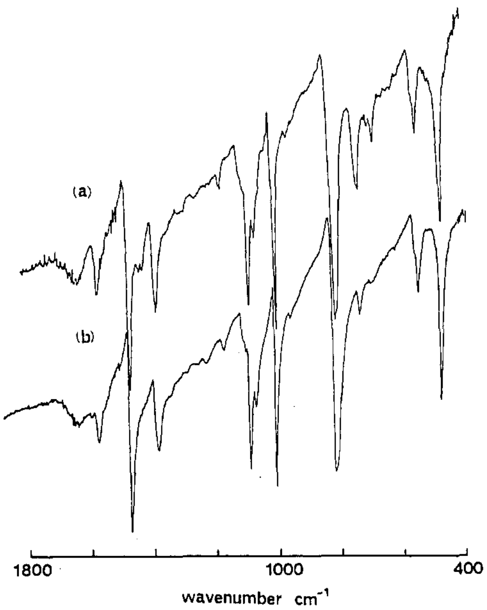

Figure 1. IR spectra of the obtained PPS (a) and commercially available PPS (noncuring type) (b).

diphenyl disulfide were necessary to give PPS quantitatively. Control experiments using diphenyl sulfide and thiophenol in the presence of $AlCl_3$ at room temperature did not give any polymer. These results suggest that the cation which is produced by cleavage of the S–S bond of diphenyl disulfide with the Lewis acid is an active species of this polymerization and substitutes electrophilically, on the phenyl ring as a Freidel–Crafts reaction.

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Registry No. PPS (homopolymer), 59371-97-0; PPS (SRU), 25212-74-2; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; $SbCl_5$, 7647-18-9; WCl_5, 13470-14-9; $C_6H_5SC_6H_5$, 139-66-2; thiophenol (homopolymer), 33411-63-1.

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Poly[1-(trimethylsilyl)-2-propen-1-one]: The First Example of a Poly(α,β-unsaturated acylsilane)

Electronic excitation involving n → π^* transitions in polymers containing pendant carbonyl chromophores results in photodegradation of the polymer via either the Norrish type I or type II mechanisms. In Norrish type I processes, a C–C bond adjacent to the carbonyl group is cleaved and CO is eliminated, resulting in the production of free-radical species. Norrish type II processes occur by a photoelimination reaction which involves hydrogen atoms at the carbon γ to the carbonyl group which leads directly to main-chain scission,[1] whereas the type I process only leads to scission when the radical formed by α-cleavage is a stable tertiary radical and there is little or no geminate recombination.[2]

Photodegradation, both in the solid state and solution, of poly(3-methyl-3-buten-2-one) (PMIPK), poly(2-methyl-1-phenyl-2-propen-1-one), and poly(methyl methacrylate) (PMMA), all of which have methyl substituents on the carbon γ to the carbonyl group, proceeds mainly via the type I process.[3] The same is true for the majority of polyketones containing hydrogen atoms at the γ carbon, provided they are irradiated below their glass transition temperature (T_g). Although one would expect the type II process to prevail, the reduced mobility of the polymer chain in the glassy solid state makes the cyclic transition state required for the Norrish type II mechanism more difficult to attain.[1b]

The main-chain scission which attends photodegradation of these polyketones is utilized in certain practical applications, most notably as resists in the lithographic fabrication of semiconductor devices[4a] and, to a lesser extent, as photodegradable packaging materials.[4b] In general, the molar absorptivity of the carbonyl chromophore in these polymers is very low, thus necessitating long exposure times in lithographic applications. Acylsilanes (α-silyl ketones),[5] on the other hand, exhibit molar absorptivity several times higher than that of the carbon analogues. In these compounds, the silicon atom is directly bonded to the carbonyl carbon which results in a large bathochromic shift in the electronic excitation spectrum of the carbonyl group.[5-11] The well-known n → π^* transition of aliphatic ketones at 280 nm ($\epsilon \approx 30$) is red-shifted in the case of the acylsilanes by 100–180 nm.[6] The transition also has greater intensity ($\epsilon \approx 130$) and the absorption spectrum exhibits a well-developed vibrational structure. There has been some controversy concerning the assignment of the long-wavelength absorption band of the acylsilanes. Most authors believe it is due to the n → π^* transition as in the case of the aliphatic ketones. Ramsey et al.,[10] on the other hand, have attributed it to the $\sigma \rightarrow \pi^*$ transition involving the σ electrons of the Si–C bond.

The magnitude of the red shift is determined by the electronic structure of the acylsilane.[6,9,11] An increased electron delocalization in the molecule caused by the introduction of conjugation into the π-electron system, can shift the transition to as high as 540 nm.[6,12,13] These observations suggest that poly(α,β-unsaturated acylsilanes) might exhibit higher photosensitivity to UV radiation than their carbon analogues. The former also possess a high silicon content which would be advantageous in microlithographic applications.[14]

Although there does not appear to be any prior literature reference to these polymers, the α,β-unsaturated acylsilanes themselves are known to be light and heat sensitive and can only be stored at low temperatures in the presence of free-radical scavengers.[12,15c] This instability suggested to us that polymerization of these compounds may indeed