Novel Polyaddition Catalyzed by Transition Metals. 1. Synthesis of Polysulfones by Addition Reactions of Arenesulfonyl Chlorides to Vinylic Compounds

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ABSTRACT: A novel polyaddition of arenedisulfonyl chlorides to divinylbenzenes was performed in the presence of a copper or ruthenium catalyst. The product polymer was polysulfones (PS) (Scheme I) consisting of a sulfonyl group between an arenylene and a chloroethylene group. Treating them with a base easily induced dehydrochlorination to give polysulfones of the PVS series (Scheme I). The same polysulfones were also prepared directly from arenedisulfonyl chloride and divinylbenzene with $RuCl_2(PPh_3)_3$ as a catalyst in the presence of a tertiary amine. The activity of the catalyst for this polymerization decreased in the following order: $CuCl/2Et_3N{\cdot}HCl > CuCl_2/2Et_3N{\cdot}HCl > RuCl_2(PPh_3)_3 \gg CuCl$. The thermal degradation of the polymers of the PS series was examined, which was shown to proceed via at least three steps. The first and the second steps correspond to loss of hydrogen chloride and sulfur dioxide, respectively.

Introduction

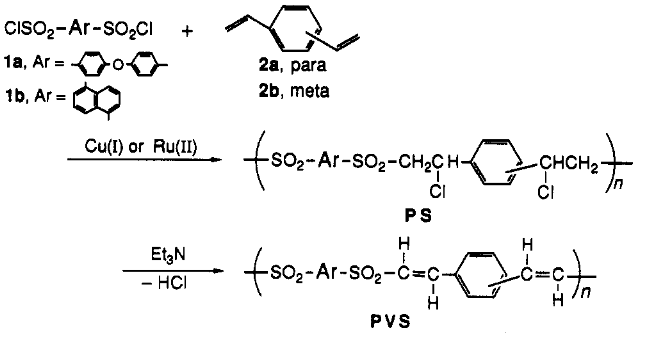
Exploration of new methods for polymer synthesis utilizing useful organic reactions has been important throughout the history of polymer science. We have directed our attention to the transition-metal-catalyzed reactions and recently reported two novel polycondensations by using the Heck reaction[1] and palladium-catalyzed amination.[2] This article deals with the synthesis and characterization of a new class of polysulfones that was prepared via a novel polyaddition of arenedisulfonyl chlorides (1) to divinylbenzenes (2) catalyzed by complexes of transition metals such as Cu(I) and Ru(II) (Scheme I). The product polysulfones have sulfonyl groups between arenylene groups and chloroethylene or trans vinylene ones. Thus, they are comparable with aromatic and aliphatic polysulfones, which have been extensively studied.[3,4]

Experimental Section

Materials. Monomers of bis(*p*-(chlorosulfonyl)phenyl) ether (**1a**),[5] 1,5-naphthalenedisulfonyl chloride (**1b**),[6] *p*- and *m*-divinylbenzenes (**2a** and **2b**),[7] and *p*-styrenesulfonyl chloride (**3**)[8] were prepared according to the reported methods. Further purification of **1a** was carried out by recrystallization from acetone: mp 131–132 °C (lit.[5] 128–129 °C). Cuprous chloride was purified by the following procedure: water was added to a saturated solution of CuCl in concentrated aqueous HCl to precipitate CuCl, which was washed with ethanol and dried in vacuo. Triethylamine hydrochloride was dried at 100 °C in vacuo. Dichlorotris(triphenylphosphine)ruthenium(II) [$RuCl_2(PPh_3)_3$] was prepared by the method described in the literature.[9] Solvents for polymerization were conventionally dried and distilled.

A Model Reaction of *p*-Toluenesulfonyl Chloride (1c) with *p*-Divinylbenzene (2a) Catalyzed by Cuprous Chloride. To a solution of **1c** (400 mg, 2.1 mmol), CuCl (2.0 mg, 0.02 mmol), and $Et_3N{\cdot}HCl$ (5.5 mg, 0.04 mmol) in CH_2Cl_2 (1 mL) was added **2a** (130 mg, 1 mmol) under argon. The mixture was degassed and then sealed under argon. After 10 h at 100 °C with stirring, the reaction mixture was poured into methanol (50 mL) to give a white solid, 1,4-bis(2-tosyl-1-chloroethyl)benzene (**4**) (484 mg, 95%): ^1H NMR (60 MHz, $CDCl_3$) δ 2.36 (s, 6 H, CH_3), 3.84 (d, $J = 6.9$ Hz, 4 H, CH_2), 5.28 (t, $J = 6.9$ Hz, 2 H, CHCl), 7.14 (s, 4 H, C_6H_4CHCl), 7.19 (d, $J = 8.4$ Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.58 (d, $J = 8.4$ Hz, 4 H, protons on the ortho positions to the sulfonyl groups); IR (KBr, cm^{-1}) 3063, 2995, 2978, 2940, 1596, 1438, 1310, 1293, 1210, 1145, 1084, 1058, 1037, 1020, 918, 817, 808, 796, 775, 629, 551, 526.

Scheme I



Polyadditions of 1 to 2 Catalyzed by Copper(I or II) Chloride. The polyadditions were carried out according to a procedure similar to that of the model reaction described above; typically, a solution of **1a** (367 mg, 1 mmol), **2a** (130 mg, 1 mmol), CuCl (2.0 mg, 0.02 mmol), and $Et_3N{\cdot}HCl$ (5.5 mg, 0.04 mmol) in CH_2Cl_2 (2.5 mL) was heated in a sealed tube at 100 °C for 10 h. The reaction mixture was diluted with DMF (2 mL) and was poured into methanol (50 mL) to precipitate a white polysulfone, PS1, which was collected by filtration and dried in vacuo (482 mg, 97%): ^1H NMR (400 MHz, DMSO-d_6) δ 4.35 (br, 4 H, CH_2), 5.42 (t, $J = 6.95$ Hz, 2 H, CHCl), 7.15 (d, $J = 8.73$ Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.38 (s, 4 H, C_6H_4CHCl), 7.80 (d, $J = 8.73$ Hz, 4 H, protons on the ortho positions to the sulfonyl groups); IR (KBr, cm^{-1}) 3096, 3069, 2982, 2929, 1579, 1487, 1321, 1300, 1248, 1163, 1085, 912, 899, 837, 554, 526. Anal. Calcd for $(C_{22}H_{18}Cl_2O_5S_2)_n$: C, 53.12; H, 3.65; Cl, 14.26; S, 12.87. Found: C, 52.60; H, 3.62; Cl, 13.51; S, 12.82.

Spectroscopic and analytical data of other polymers are as follows.

PS7: ^1H NMR (400 MHz, DMSO-d_6) δ 4.38 (br, 4 H, CH_2), 5.40 (t, $J = 6.90$ Hz, 2 H, CHCl), 7.12 (d, $J = 8.73$ Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.20 (br, 2 H, protons on C-4 and C-6 of the 1,3-phenylene group), 7.37 (br, 1 H, a proton on C-5 of the 1,3-phenylene group), 7.62 (br, 1 H, a proton on C-2 of the 1,3-phenylene groups), 7.82 (d, $J = 8.73$ Hz, 4 H, protons on the ortho positions to the sulfonyl groups); IR (KBr, cm^{-1}) 3097, 3071, 2982, 2973, 1579, 1486, 1405, 1321, 1301, 1248, 1137, 1087, 874, 838, 775, 698, 525. Anal. Calcd for $(C_{22}H_{18}Cl_2O_5S_2)_n$: C, 53.12; H, 3.65; Cl, 14.26; S, 12.87. Found: C, 53.22; H, 3.65; Cl, 13.57; S, 12.84.

PS9: ^1H NMR (400 MHz, DMSO-d_6) δ 4.45 (br, 4 H, CH_2), 5.48 (br, 4 H, CHCl), 6.88 (br, 1 H, a proton on C-5 of the 1,3-phenylene group), 7.13 (br, 2 H, protons on C-4 and C-6 of the 1,3-phenylene group), 7.53 (br, 1 H, a proton on C-2 of the 1,3-

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phenylene group), 7.83 (br, 2 H, protons on C-3 and C-7 of the 1,5-naphthalene group), 8.21 (br, 2 H, protons on C-4 and C-8 of the 1,5-naphthalene group), 8.93 (br, 2 H, protons on C-2 and C-6 of the 1,5-naphthalene group); IR (KBr, cm^{-1}) 3097, 3062, 2988, 2934, 1502, 1317, 1200, 1230, 1167, 1123, 892, 799, 699, 649, 530. Anal. Calcd for $(C_{20}H_{16}Cl_2O_4S_2)_n$: C, 52.72; H, 3.54; Cl, 15.57; S, 14.08. Found: C, 52.33; H, 3.68; Cl, 14.47; S, 13.51.

PS10: IR (KBr, cm^{-1}) 3090, 3061, 2993, 2921, 1597, 1416, 1313, 1158, 1141, 1087, 904, 848, 829, 796, 779, 572, 537. Anal. Calcd for $(C_8H_7ClO_2S)_n$: C, 47.71; H, 3.40; Cl, 17.49; S, 15.82. Found: C, 47.11; H, 3.48; Cl, 17.29; S, 15.64.

Dehydrochlorination of 4 and the Polymers of the PS Series. A typical procedure is described as follows. To a solution of **4** (150 mg, 0.34 mmol) in DMF (2 mL) was added Et_3N (83 mg, 0.82 mmol) with stirring at room temperature. After 2 h, the reaction mixture was poured into methanol (30 mL) to precipitate (*E,E*)-1,4-bis(2-tosylethenyl)benzene (**5a**) that was dried in vacuo (130 mg, 94%): mp 310 °C (decomposition); ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.41 (s, 6 H, CH_3), 7.47 (d, J = 8.4 Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.54 (d, J = 15.5 Hz, 2 H, $SO_2CH{=}C$), 7.81 (d, J = 15.5 Hz, 2 H, $C{=}CHC_6H_4$), 7.81 (s, 4 H, $C_6H_4CH{=}$), 7.84 (d, J = 8.4 Hz, 4 H, protons on the ortho positions to the sulfonyl groups); IR (KBr, cm^{-1}) 3054, 2924, 2854, 1611, 1596, 1438, 1312, 1304, 1286, 1145, 1084, 964, 846, 817, 778, 656, 555, 507.

Spectroscopic and analytical data of dehydrochlorinated polymers are as follows.

PVS1: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, J = 8.73 Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.65 (d, J = 15.50 Hz, 2 H, $SO_2CH{=}C$), 7.74 (d, J = 15.50 Hz, 2 H, $C{=}CHC_6H_4$), 7.81 (s, 4 H, $C_6H_4CH{=}$), 7.96 (d, J = 8.73 Hz, 4 H, protons on the ortho positions to the sulfonyl groups); IR (KBr, cm^{-1}) 3094, 3054, 1666, 1579, 1487, 1406, 1313, 1300, 1246, 1143, 1085, 973, 874, 838, 787, 689, 570, 516. Anal. Calcd for $(C_{22}H_{16}O_5S_2)_n$: C, 62.25; H, 3.80; S, 15.11. Found: C, 60.69; H, 3.92; Cl, 0.35; S, 14.82.

PVS7: ^{1}H NMR (400 Mhz, DMSO-d_6) δ 7.49 (t, J = 7.75 Hz, 1 H, a proton on C-5 of the 1,3-phenylene group), 7.63 (d, J = 15.32 Hz, 2 H, $SO_2CH{=}C$), 7.68 (d, J = 15.32 Hz, 2 H, $C{=}CHC_6H_4$), 7.76 (d, J = 7.75 Hz, 2 H, protons on C-4 and C-6 of the 1,3-phenylene group), 7.96 (d, J = 8.79 Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.80 (d, J = 8.79 Hz, 4 H, protons on the ortho positions to the sulfonyl groups), 8.20 (s, 1 H, a proton on C-2 of the 1,3-phenylene group); IR (KBr, cm^{-1}) 3097, 3071, 1615, 1579, 1485, 1411, 1318, 1298, 1246, 1144, 1086, 973, 874, 833, 778, 697, 536. Anal. Calcd for $(C_{22}H_{16}O_5S_2)_n$: C, 62.25; H, 3.80; S, 15.11. Found: C, 60.60; H, 3.79; Cl, 0.35; S, 14.69.

PVS8: IR (KBr, cm^{-1}) 3096, 3053, 1615, 1502, 1312, 1230, 1199, 1165, 1122, 972, 839, 794, 778, 655, 618, 556. Anal. Calcd for $(C_{20}H_{14}O_4S_2)_n$: C, 62.81; H, 3.69; S, 16.80. Found: C, 61.51; H, 3.79; Cl, 0.35; S, 16.03.

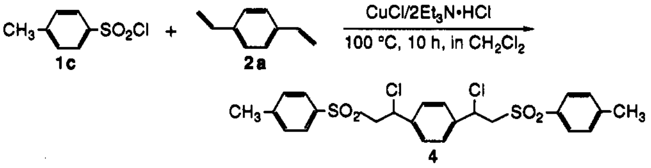
A Method Reaction of 1c with 2b Catalyzed by a Ruthenium Complex. To a solution of **1c** (400 mg, 2.1 mmol) and $RuCl_2(PPh_3)_3$ (19.2 mg, 0.02 mmol) in benzene (3 mL) were added **2b** (130 mg, 1 mmol) and triethylamine (202 mg, 2 mmol) under argon. The mixture was degassed and then sealed under argon. After 60 h at 60 °C with stirring, the reaction mixture was poured into methanol (50 mL) to precipitate a crude product. Recrystallization from ethanol afforded pure (*E,E*)-1,3-bis(2-tosylethenyl)benzene (**5b**) (357 mg, 82%): mp 210–213 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.41 (s, 6 H, CH_3), 7.48 (d, J = 8.2 Hz, 4 H, protons on the meta positions to the sulfonyl groups), 7.54–7.82 (m, 3 H, protons on C-4, C-5, and C-6 of the 1,3-phenylene group), 7.60 (d, J = 15.4 Hz, 2 H, $SO_2CH{=}C$), 7.68 (d, J = 15.4 Hz, 2 H, $C{=}CHC_6H_4$), 7.80 (d, J = 8.2 Hz, 4 H, protons on the ortho positions for the sulfonyl groups), 8.20 (s, 1 H, a proton on C-2 of the 1,3-phenylene group); IR (KBr, cm^{-1}) 3054, 2923, 2820, 1616, 1597, 1313, 1297, 1143, 970, 960, 844, 810, 765, 670, 534.

Polyadditions of 1a to 2b Catalyzed by a Ruthenium Complex. Polymerization of an equimolar amount of each of **1a** and **2b** with a ruthenium complex was carried out in the presence or absence of tri-*n*-butylamine according a procedure similar to that of the model reaction described above; typically, a solution of **1a** (369 mg, 1 mmol), **2b** (130 mg, 1 mmol), $RuCl_2(PPh_3)_3$ (19.2 mg, 0.02 mmol), and n-Bu_3N (371 mg, 2 mmol) in benzene (3 mL) was heated in a sealed tube at 60 °C. After 77 h with stirring, the reaction mixture was poured into methanol (50 mL) to precipitate a light brown polysulfone (PVS14) that was dried in vacuo (434 mg, 87%). The spectroscopic data were identical with those of PVS7 that was prepared by the dehydrochlorination of PS7. Anal. Calcd for $(C_{22}H_{16}O_5S_2)_n$: C, 62.25; H, 3.80; S, 15.11. Found: C, 61.11; H, 4.16; Cl, 1.04; S, 14.69.

Measurements. ^{1}H NMR spectra were obtained on a JEOL GX-400, a Varian Gemini-200, or a Hitachi R-600 spectrometer, using TMS as an internal standard. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR 1600 series. Thermal gravimetric analysis was performed employing a Shimazu TGC-30 TGA system under nitrogen at a heating rate of 10 °C/min. Molecular weights of polymers were estimated by gel permeation chromatography with Tosoh TSK G4000 as a column and DMF containing 0.4% LiBr as an eluent (1 mL/min, 50 °C) on the basis of a calibration curve of polystyrene standards.

Results and Discussion

Polyadditions Catalyzed by Copper(I or II) Chloride. A model reaction for the polymerization, i.e., an addition reaction of *p*-toluenesulfonyl chloride to *p*-divinylbenzene, successfully gave the 2:1 adduct (**4**) in yield of 94% without radical telomerization. Therefore, a similar procedure was applied for the polyaddition of an equimolar amount of each arenedisulfonyl chloride, i.e., bis(*p*-(chlorosulfonyl)phenyl) ether (**1a**) and 1,5-naphthalenedisulfonyl chloride (**1b**), and *p*- or *m*-divinylbenzenes (**2a** or **2b**) (Table I).



The reaction mixtures became heterogeneous in the progress of polymerization except for runs 2–5 and 11. Separation into two immiscible phases, probably a polymer-rich phase and a solvent-rich one, was observed during the polymerization of **1a** (runs 1 and 6–8), while the product polymers precipitated as white powder for **1b** (runs 9 and 10). The product polysulfones, PS1–9, were soluble in polar solvents (e.g., DMF and DMSO). However, no polymer was obtained from the reaction in DMF (run 11).[10]

The addition of $Et_3N{\cdot}HCl$ along with cuprous chloride dramatically promoted the polymerization to give a higher molecular weight polymer, while no polymeric product was obtained in the presence of Et_3N, which assumably deactivated copper(I and/or II) chloride (runs 1–3). As described in the literature,[11] the effect of $Et_3N{\cdot}HCl$ can be explained in connection with the reaction mechanism (Scheme II).

Scheme II

$$ArSO_2Cl + CuCl \rightleftharpoons ArSO_2^{\bullet} + CuCl_2 \qquad (1)$$

$$ArSO_2^{\bullet} + CH_2{=}CHAr' \rightleftharpoons ArSO_2CH_2C^{\bullet}HAr' \qquad (2)$$

$$ArSO_2CH_2C^{\bullet}HAr' + CuCl_2 \rightarrow ArSO_2CH_2CH(Cl)Ar' + CuCl \qquad (3)$$

$Et_3N{\cdot}HCl$ enhanced the solubility of the catalyst by forming an alkylammonium chlorocuprate, which is a more efficient chlorine-transfer agent, to increase the reaction rate of eq 3. Moreover, the polyaddition without $Et_3N{\cdot}HCl$ gave partially dehydrochlorinated polymer that was iden-

Table I
Polyadditions of Arenedisulfonyl Chloride to Divinylbenzene Catalyzed by Copper(I or II) Chloride

run	polymer	monomers[a]	catalyst[b]	solvent	temp, °C	time, h	yield,[c] %	$\bar{M}_w$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	PS1	**1a, 2a**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	100	10	97	80 800[e]	2.75
2	PS2	**1a, 2a**	CuCl	CH_2Cl_2	100	30	72	8 600	1.72
3		**1a, 2a**	CuCl (Et_3N)[f]	CH_2Cl_2	100	30	0		
4	PS3	**1a, 2b**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	60	30	57	4 500	2.81
5	PS4	**1a, 2b**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	80	30	88	8 700	1.77
6	PS5	**1a, 2b**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	100	10	98	27 700	2.96
7	PS6	**1a, 2b**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	100	30	100	117 000	4.96
8	PS7	**1a, 2b**	$CuCl_2/2Et_3N{\cdot}HCl$	CH_2Cl_2	100	30	97	36 400[g]	3.10
9	PS8	**1b, 2b**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	100	10	91	16 300	2.05
10	PS9	**1b, 2b**	$CuCl/2Et_3N{\cdot}HCl$	CH_3CN	100	10	82	12 000	1.90
11		**1b, 2b**	$CuCl/2Et_3N{\cdot}HCl$	DMF	100	10	0		
12	PS10	**3**	$CuCl/2Et_3N{\cdot}HCl$	CH_2Cl_2	100	10	83		

[a] [**1a**] = [**2a**] = 0.4 mol/L, [1] = [**2b**] = 1 mol/L, [3] = 0.8 mol/L. [b] 0.01 equiv for sulfonyl group. [c] Methanol-insoluble polymer. [d] Determined by GPC calibrated with polystyrene standards; eluent, DMF containing 0.4% LiBr. [e] $\bar{M}_n$ = 16 400: calculated by end-group analysis of the ^1H NMR spectrum.[15] [f] Et_3N (2 equiv for **1a**) was added. [g] $\bar{M}_n$ = 13 400: calculated by end-group analysis of the ^1H NMR spectrum.[15]

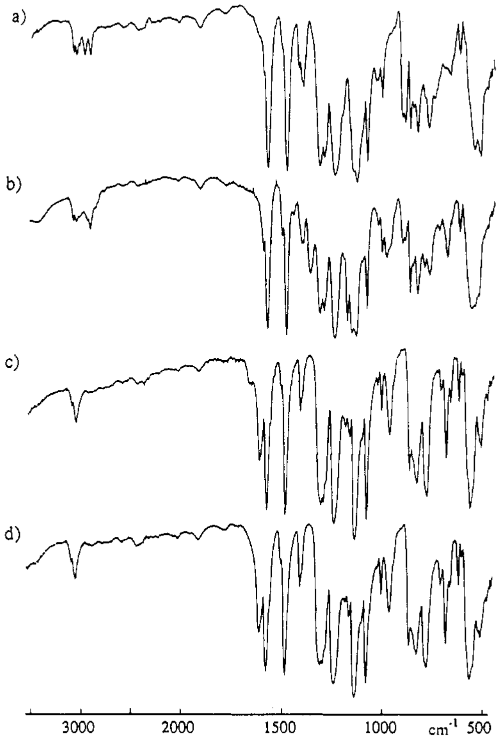


Figure 1. IR spectra of polysulfones: (a) PS1; (b) PS2; (c) PVS1; (d) the resultant polymer after PS1 was heated at 210 °C for 1 h.

tified by spectroscopic methods as well as elemental analysis. IR spectrum of PS2 (run 2) showed an absorption band at 973 cm^{-1} due to the out-of-plane C–H bending vibration of trans vinylene groups, which was not observed in that of PS1 (Figure 1a,b). The extent of dehydrochlorination of PS2 was about 50%, which was calculated on the basis of the ^1H NMR spectrum[12] as well as the elemental analysis.[13]

Higher reaction temperature and longer reaction time increased both the molecular weight and the yield of polymer (runs 4–6 and Figure 2). Figure 2 shows the effects of the reaction time on the polyaddition of **1a** to **2b**. The yield of the polysulfone was over 94 wt % after 5 h, while the values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ increased gradually. The value of $\bar{M}_w/\bar{M}_n$ exceeded the usual one (<2) given by a step polymerization, just after the reaction mixture became heterogeneous (~6.5 h). The higher concentration of the growing chains probably caused a chain-transfer reaction of the radicals to polymer chains and/or a termination reaction between radicals at the polymer ends.

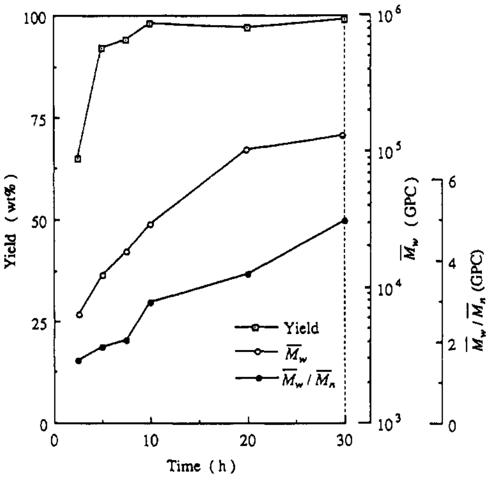
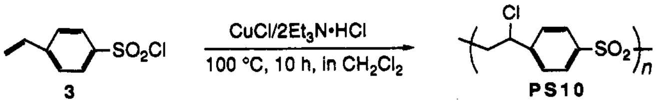


Figure 2. Effects of the reaction time on the polyaddition of **1a** to **2b** ([**1a**] = [**2b**] = 1 mol/L) catalyzed by $CuCl/2Et_3N{\cdot}HCl$ (2 mol % for **1a**) at 100 °C in CH_2Cl_2.

Cupric chloride catalyst was less effective than cuprous chloride (run 8), because it should be reduced in situ to act as the catalyst, probably via a reaction with a vinylic group, which decreased the functionality of divinylbenzene.[14]

$$2CuCl_2 + CH_2{=}CHAr \rightarrow 2CuCl + ClCH_2CH(Cl)Ar$$

A monomer having both a sulfonyl chloride group and a vinyl group, *p*-styrenesulfonyl chloride (**3**), was also polymerized under the same condition (run 12). The product polymer PS10 was only soluble in concentrated H_2SO_4 and its structure was established by IR spectroscopy and elemental analysis.



3 **PS10**

Dehydrochlorination of Polysulfones of the PS Series with a Base. A model compound, **4**, was dehydrochlorinated to (*E,E*)-1,4-bis(2-tosylethenyl)benzene (**5a**) in a yield of 95% by treatment with a small excess of triethylamine at room temperature in DMF solution. Thus, the dehydrochlorination of polymers of the PS series was carried out under the same conditions to give the polysulfones of the PVS series, which have sulfonyl groups between arenylene and vinylene groups (Scheme III and Table II).

The obtained polysulfones PVS1 and 7, were soluble in polar solvents such as DMF and DMSO, whereas PVS8

Scheme III

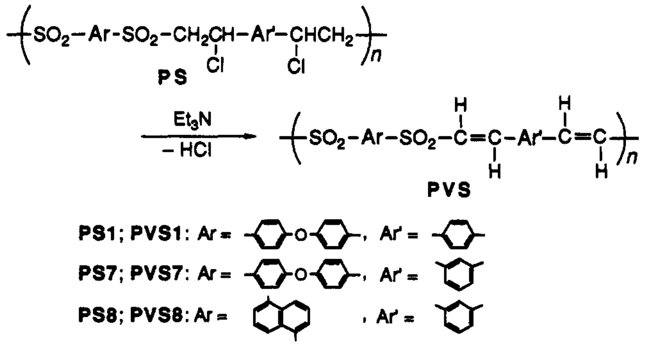


Table II
Dehydrochlorination of Polysulfones of the PS Series by Treatment with Et_3N

	substrate		product			
run	PS	$\overline{DP}$[a]	PVS	yield,[b] %	$\overline{DP}$[a]	Cl, %[c]
1	PS1	32	PVS1	97	28	0.35
2	PS7	27	PVS7	95	29	0.32
3	PS8		PVS8	92		0.35

[a] Degree of polymerization, which was calculated on the basis of the end-group analysis of the ^1H NMR spectrum.[15] [b] Methanol-insoluble polymer. [c] Elemental analysis.

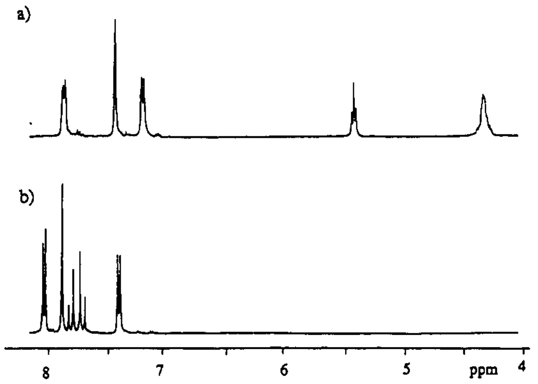


Figure 3. ^1H NMR spectra (400 MHz, DMSO-d_6) of polysulfones: (a) PS1; (b) PVS1.

was insoluble in those solvents. ^1H NMR spectra for PS1 and PVS1 are shown in Figure 3 for contrast. The dehydrochlorination caused the complete disappearance of signals due to chloroethylene protons (δ 4.35 and 5.42) with the appearance of signals due to vinylene protons (δ 7.65 and 7.74). The other signals moved downfield due to the conjugate structure. The coupling constants between two vinylene protons was 15.5 Hz, indicating the trans structure of the vinylene groups. Further support for the dehydrochlorination was obtained from IR spectra. As shown in Figure 1a,c, an absorption band corresponding to the out-of-plane C–H bending vibration of trans vinylene groups was observed at 973 cm^{-1}, whereas the bands corresponding to the C–H stretching vibration of chloroethyl units in the range 2900–3000 cm^{-1} disappeared. Moreover, the chlorine content of the product polysulfones from the elemental analysis, as shown in Table II, indicates that the extent of dehydrochlorination is higher than 98%. On the other hand, the $\overline{DP}$ value of the product polymers is almost equal to that of the original one, so that it is concluded that scission of the polymer main chain has not occurred during the dehydrochlorination.

Polyadditions of 1a to 2b Catalyzed by a Ruthenium Complex. It has been reported that $RuCl_2(PPh_3)_3$ catalyzes the addition reaction of arenesulfonyl chloride to olefins via a free radical redox chain mechanism in the same manner as the copper-catalyzed addition reaction described above.[16] As a model reaction for polymerization, the addition reaction of *p*-toluenesulfonyl chloride with *m*-divinylbenzene was carried out at 60 °C in benzene in the presence of $RuCl_2(PPh)_3$ and Et_3N to give (*E,E*)-1,3-bis(2-tosylethenyl)benzene (**5b**) in a yield of 81%. So, polyaddition of **1a** to **2b** with the catalyst $RuCl_2(PPh)_3$ was attempted.

Scheme IV

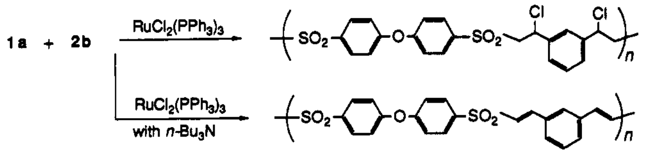


Table III
Polymerizations of 1a with 2b Catalyzed by $RuCl_2(PPh_3)_3$[a]

run	polymer	base[b]	solvent	temp, °C	time, h	yield,[c] %	$\bar{M}_w$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	PS11		benzene	80	72	40	7200	1.62
2	PS12		benzene	100	36	58	8800	2.01
3	PVS13	*n*-Bu_3N	benzene	60	30	70	5900	1.97
4	PVS14	*n*-Bu_3N	benzene	60	77	87	11000	2.30
5	PVS15	*n*-Bu_3N	benzene	100	36	77	8500	1.98
6	PVS16	*n*-Bu_3N	benzene	100	77	76	12000	2.24
7		*n*-Bu_3N	DMSO	100	72	0		
8		*n*-Bu_3N	DMF	100	72	0		

[a] Catalyst, 2 mol % for **1a**; [**1a**] = [**2b**] = 0.33 mol/L. [b] 2 equiv for **1a**. [c] Methanol-insoluble polymer. [d] Determined by GPC calibrated with polystyrene standards; eluent, DMF containing 0.4% LiBr.

Although the copper-catalyzed polyaddition did not proceeded in the presence of the tertiary amine, the ruthenium-catalyzed polyaddition both with and without a tertiary amine gave the polysulfones, which were, however, simultaneously dehydrochlorinated in the presence of the amine (Scheme IV).[17] In addition, the tertiary amine promoted the polyaddition to give the polysulfone having a higher molecular weight in a better yield under milder conditions (Table III).

On the other hand, the polymer prepared in the absence of tertiary amine showed no signals due to the dehydrochlorinated units in the ^1H NMR spectra and the IR spectra, although elemental analysis indicated the dehydrochlorination occurred to a small extent during polymerization. However, the catalytic ability of $RuCl_2(PPh)_3$ was lower than that of $CuCl/2Et_3N{\cdot}HCl$.

Thermal Stability. Thermal gravimetric analysis (TGA) was performed to investigate the thermal degradation of product polysulfones. As typical examples, Figure 4 shows TGA curves for PS1 and PVS1, the latter being prepared by the dehydrochlorination of PS1 with Et_3N. The thermal degradation of PS1 proceeds stepwise, showing two sharp slopes in the TGA curve. The first step is ascribed to the rapid loss of hydrogen chloride because of the following observations. When PS1 was heated at 210 °C for 1 h (weight loss = 12.5 wt %), it became insoluble in any organic solvent but showed the identical IR spectrum with PVS1 (Figure 1c,d). Additionally, elemental contents of this sample (C, 60.66; H, 3.60; S, 14.42; Cl, 0.63) were quite close to those of PVS1 (C, 60.69; H, 3.92; S, 14.82; Cl, 0.35).

The thermal behaviors of the other polymers of the PS and the PVS series were similar to those of PS1 and PVS1, respectively. The results of TGA are summarized in Table IV. The values of T_1 and T_2 represent temperatures at the end points of the first and the second degradation steps, and T_{s1} and T_{s2} represent temperatures at which the first and the second degradation steps start, respectively, as shown in Figure 4. The values of W_1 and W_2 are

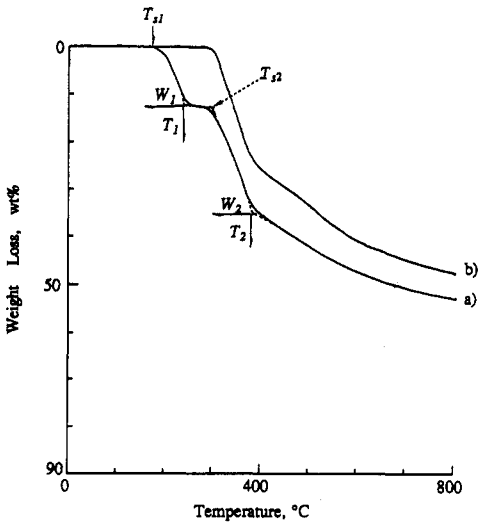


Figure 4. Thermogavimetric curves of polysulfones at a heating rate of 10 °C/min under nitrogen: (a) PS1; (b) PVS1.

Table IV
TGA of Polysulfones of the PS and the PVS Series[a]

polymer	T_{s1}	T_1 (W_1)	T_{s2}	T_2 (W_2)	$W_2 - W_1$	CY
PS1	175	240 (13)	293	385 (35)	22	47
PS2	165	210 (7)	252	380 (28)	21	52
PS7	202	266 (12)	289	382 (34)	22	48
PS9	210	275 (17)	275	386 (36)	19	49
PS10	213	280 (14)	280	382 (42)	28	47
PS12	165	245 (11)	268	390 (31)	30	47
PVS1	289	389 (26)				54
PVS7	287	405 (26)				56
PVS8	284	387 (31)				58
PVS16	255	382 (20)				60

[a] T_{s1} and T_{s2} are the start temperatures of the first and second thermal degradation steps, respectively. T_1 and T_2 represent temperatures at the end points of the first and second thermal degradation steps, respectively. W_1 and W_2 are the weight loss at T_1 and T_2, respectively. The values (wt %) of CY are char yields at 800 °C.

the weight loss at T_1 and T_2, respectively. Each value of W_1 of the polymers of the PS series was almost equal to the (H + Cl) content of the corresponding polymer. Thus, the first thermal degradation step is ascribed to dehydrochlorination. In addition, the second degradation step of PS1 coincided with the first one of PVS1. Furthermore, the values of $W_2 - W_1$ of the PS series polymers and W_1 of the PVS series polymers were close to the SO_2 content (about double the S content) of the corresponding polymer. This fact indicates that escape of SO_2 occurred mainly in the second degradation step of the PS series polymers as well as in the first one of the PVS series polymers.

The T_{s1} values of the PS series polymers were dependent not only on the polymer structure but also on the catalyst system used in the polymerization. With increase of resonance stabilization and the rigidity of the polymer chain, T_{s1} increased in the following order: PS1 < PS7 < PS9 ≤ PS10. Although PS2 and PS12 were prepared from the same combination of the monomers as PS1, their T_{s1} values were lower than that of PS1. It is assumed that the catalyst residue in the isolated polymer, whose amount is dependent on the character of the catalyst, affects T_{s1} values. It was reported that both the copper and ruthenium complexes have the catalytic activity for the dehydrochlorination process.[18,19]

References and Notes

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(12) The extent of dehydrochlorination of PS2 was estimated on the basis of ratio of the relative integration area of a signal at δ 7.80 to that at δ 7.96, which are assignable to aromatic protons in the ortho positions to the sulfonyl groups of the phenylenesulfonylchloroethylene unit and of the phenylenesulfonylvinylene unit, respectively.
(13) PS2: Anal. Calcd for $(C_{22}H_{18}Cl_2O_5S_2)_{0.5}(C_{22}H_{16}O_5S_2)_{0.5}$: C, 57.33; H, 3.72; Cl, 7.69; S, 13.81. Found: C, 58.60; H, 4.20; Cl, 7.94; S, 11.56. The disagreement in sulfur content is assumably due to a little escape of SO_2 during the polymerization.
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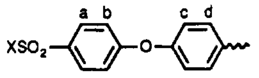

polymer	X	chemical shift, δ H_a	H_b	H_c	H_d
PS1	Cl	7.68	7.02	7.04	7.66
	OH	7.51	7.02	7.04	7.66
PVS1	OH	7.54	7.07	7.18	7.90

Vinylic protons that are capable of another end group, however, were not observed, so that the $\overline{DP}$ value was calculated on the basis of the integral proportion of the above peaks, assuming that both ends of the polymer chain contained the sulfonyl group. It is supposed that the vinylic end groups were consumed by a side reaction, e.g., a homocoupling reaction, at the end of the polymerization.
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Registry No. **1c**, 98-59-9; **2a**, 105-06-6; **2b**, 108-57-6; **4**, 133008-39-6; **5a**, 123147-30-8; **5b**, 132980-85-9; PS1 (copolymer), 132980-90-6; PS1 (SRU), 132980-86-0; PS7 (copolymer), 132980-91-7; PS7 (SRU), 132980-87-1; PS8 (copolymer), 132980-92-8; PS8 (SRU), 132980-88-2; PVS (SRU), 132980-89-3; CuCl, 7758-89-6; $RuCl_2(PPh_3)_3$, 15529-49-4; ClF_2, 7789-19-7.