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A Remarkably Thermally Stable, Polar Aliphatic Polysulfone

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ABSTRACT: A polar ester-functionalized aliphatic polysulfone with an odd-number of linking carbon atoms possessing remarkable thermal stability, degrading at 100 °C above previously prepared polysulfones, was prepared in conjunction with the proposal of a novel concept for polar organic polymers. The synthesis involved polyaddition of vinyl sulfone and *tert*-butyl ethyl malonate in the presence of an amidine base and catalytic amount of water, followed by decarbo-*tert*-butoxylation. The polymers were characterized by infrared and nuclear magnetic resonance spectroscopies, elemental analysis, gel permeation chromatography, differential scanning calorimetry, and thermogravimetric analysis. Characterization results compared well with model compounds. Poly-decarbo-*tert*-butoxylation was achieved by exposure to trifluoroacetic acid, followed by treatment with copper(I) oxide, affording a soluble polar polysulfone, which could be cast into homogeneous films.

Introduction

Polar organic polymers have become an appealing and promising new class of materials with a large variety of applications such as piezoelectrics, pyroelectrics, ferroelectrics, etc.[1] The prime example of such materials is the ferroelectric poly(vinylidene fluoride) (PVDF).[2,3] PVDF films can be forced into the highly polar β-phase by stretching and poling. In this phase, the all-*trans* chains are packed with a parallel alignment of like electric dipoles.[2] Considering the local fields induced by each dipole, a parallel arrangement of adjacent electric dipoles is energetically unfavorable. In this paper, we propose a new concept for polar organic polymers that may spontaneously adopt a polar structure without the need for poling. This may be achieved by designing polymer chains that bear coupled sets of antiparallel electric dipoles possessing different magnitudes. Such ordering is found in ferrielectric materials.[4,5] The spontaneous formation of a polar structure may then arise from an energetically preferred ferroelectric coupling of ferrielectric chains. Analogous strategies were successfully realized in case of magnetic materials.[6,7] Assuming an all-*trans* polymer chain, a ferrielectric dipole arrangement may be obtained by placing a strongly electron-withdrawing group (SEWG) in alternating sequence with a weakly electron-withdrawing group (WEWG) at every fourth carbon atom along the polymer chain (Figure 1a). Taking into consideration the magnitude of dipole moments of certain functional groups and chemical feasibility, we chose the sulfone moiety $-SO_2-$ ($\mu \approx 4.5$ D) as SEWG and an ester group $-COOR$ ($\mu \approx 1.8$ D) for the WEWG (Figure 1b) and intended the synthesis of odd-numbered aliphatic polysulfones starting from vinyl sulfone and a malonic ester.[8,9] Investigations of the thermal properties of aliphatic polysulfones through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were reported for even-numbered polysulfones.[10,11] However, to the best of our knowledge, odd-numbered aliphatic polysulfones have not been characterized by DSC and TGA to date.

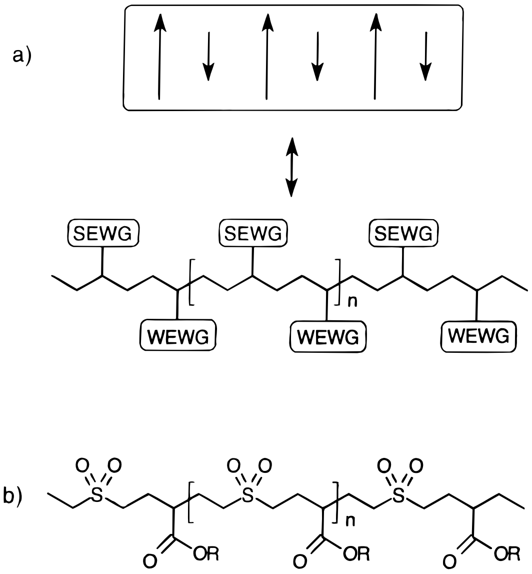

Figure 1. Envisioned ferrielectric dipole alignment along the polymer chain: (a) schematic illustration of a ferrielectric polymer chain (SEWG, strongly electron-withdrawing group; WEWG, weakly electron-withdrawing group); (b) Suggested polymer structure.

In this article, we comment on the preparation and characterization of polar ester-functionalized, odd-numbered aliphatic polysulfones and their model compounds. These polysulfones are potential candidates for new polar polymers. Emphasis is devoted to both synthesis and thermal characterization of these novel materials.

Experimental Section

Measurements. Melting points were determined with a Buchi melting point apparatus (Dr. Tottoli). IR spectra were recorded on a Mattson Galaxy FTIR 3000 spectrometer. ^1H NMR spectra were acquired with a Varian Gemini 200 instrument using TMS as internal standard. Mass spectra were recorded on a VG70SE double focusing sector mass spectrometer equipped with a xenon saddle field FAB gun. Gel

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permeation chromatography (GPC) was carried out on a Wyatt Technology system equipped with two Phenogel columns (5 μm, 10^5 Å, and 10^3 Å), a DAWN DSP laser photometer, and an OPTILAB DSP interferometric refractometer; the eluent was 0.1 M LiBr in dimethylformamide (DMF). Differential scanning calorimetry (DSC) was performed under nitrogen flow with a Perkin-Elmer DSC 7 instrument, which was calibrated with indium and zinc standards. The heating rate was 10 K/min; cooling rate was 5 K/min. Thermogravimetric analyses (TGA) were conducted under nitrogen flow on a Perkin-Elmer TGA 7 analyzer at a heating rate of 20 K/min. This instrument was calibrated with alumel, nickel, and perkalloy standards. Elemental analyses for C, H, and S were performed by Atlantic Microlab, Inc. (Norcross, GA); Cu analyses were carried out by Galbraith Laboratories (Knoxville, TN).

Materials. Copper(I) oxide (97%), 1,8-diazabicyclo[5.4.2]-undec-7-ene (DBU, 98%), methyl vinyl sulfone (98%), 1,1,1-trichloroethane (99%, ACS reagent grade), and trifluoroacetic acid (TFA, ACS reagent grade) were used as received from Aldrich. Vinyl sulfone and *tert*-butyl ethyl malonate were purified by distillation prior to use. Acetonitrile was distilled over calcium hydride. All reactions were carried out under an argon atmosphere.

5-*tert*-Butoxycarbonyl-2,8-dithia-5-ethoxycarbonylnonane 2,2,8,8-Tetraoxide (1). To a solution of methyl vinyl sulfone (7.272 g, 69 mmol) and *tert*-butyl ethyl malonate (5.368 g, 29 mmol) in acetonitrile (20 mL) was added dropwise DBU (4.479 g, 29 mmol) over a period of 10 min while the reaction was being cooled with an ice bath. After 30 min, the cooling was removed and the mixture allowed to warm to room temperature overnight. Monitoring the reaction by TLC revealed full conversion of the malonate by the next morning. The solvent was evaporated under reduced pressure and the residual oil dissolved in methylene chloride. After extraction (three times) with dilute aqueous HCl, the organic layer was washed with water, dried ($MgSO_4$) and concentrated in a vacuum to give a brown, viscous oil (11.51 g). Recrystallization from refluxing toluene afforded an off-white solid. Yield: 11.05 g (95% based on the limiting reagent, *tert*-butyl ethyl malonate). Mp: 66−67 °C. IR (KBr, cm^{-1}): 2981, 2936 (C−H), 1737 (C=O), 1370 (*tert*-butyl), 1303, 1137 (O=S=O). ^1H NMR ($CDCl_3$, 200 MHz): δ 4.25 (q, 2H), 3.17−3.08 (m, 4H), 2.96 (s, 6H), 2.37−2.29 (m, 4H), 1.48 (s, 9H), 1.30 (t, 3H). FAB−MS (NBA) (*m/z*): 345 ($M^+ - C_4H_8$, 73), 327 ($M^+ - C_4H_8 - H_2O$, 100), 253 ($M^+ - C_2H_4 - CO_2 - C_4H_8 - H_2O$, 24). Anal. Calcd for $C_{15}H_{28}O_8S_2$: C, 45.00; H, 7.00; S, 16.00. Found: C, 44.82; H, 7.10; S, 16.14.

5-Carboxy-2,8-dithia-5-ethoxycarbonylnonane 2,2,8,8-Tetraoxide (2). Compound **1** (4.654 g, 11.6 mmol) was dissolved in TFA (50 mL) and stirred at 60 °C for 4.5 h. The solvent was removed in a vacuum and the residue recrystallized from ethyl acetate to give a fine, white powder. Yield: 3.35 g (84%). Mp: 154−156 °C. IR (KBr, cm^{-1}): 3250−3050 (O−H), 2993, 2930 (C−H), 1753, 1728 (C=O), 1142 (O=S=O). ^1H NMR (py-d_5, 200 MHz): δ 4.21 (q, 2H), 3.83−3.76 (m, 4H), 3.17 (s, 6H), 3.03−2.95 (m, 4H), 1.11 (t, 3H). FAB−MS (NBA) (*m/z*): 345 (M^+, 100), 327 ($M^+ - H_2O$, 94), 253 ($M^+ - H_2O - CO_2 - C_2H_4$, 19). Anal. Calcd for $C_{11}H_{20}O_8S_2$: C, 38.37; H, 5.81; S, 18.61. Found: C, 38.44; H, 5.89; S, 18.55.

2,8-Dithia-5-ethoxycarbonylnonane 2,2,8,8-Tetraoxide (3). In a glovebox, a three-necked flask was loaded with compound **2** (1.000 g, 3.0 mmol) and anhydrous copper(I) oxide (0.022 g, 0.15 mmol). Acetonitrile (7 mL) was added by a syringe via a septum and the mixture stirred at 80−85 °C overnight. After evaporation of the solvent at reduced pressure, the residual oil was dissolved in methylene chloride and extracted three times with diluted aqueous HCl, followed by washing with water and drying with $MgSO_4$. The organic phase was concentrated at reduced pressure. Slow addition of petroleum ether afforded fine, white needles that were filtered off and washed with petroleum ether prior to drying in a vacuum. Yield: 555 mg (62%). Mp: 97 °C. IR (KBr, cm^{-1}): 3008, 2933 (C−H), 1720 (C=O), 1313, 1127 (O=S=O). ^1H NMR (py-d_5, 200 MHz): δ 4.08 (q, 2H), 3.52−3.44 (m, 4H), 3.17 (s, 6H), 2.96 (m, 1H), 2.47−2.29 (m, 4H), 1.07 (t, 3H). FAB−MS (NBA) (*m/z*): 301 (M^+, 77), 255 ($M^+ - C_2H_4 - H_2O$, 100). Anal. Calcd for $C_{10}H_{20}O_6S_2$: C, 40.00; H, 6.67; S, 21.33. Found: C, 39.94; H, 6.74; S, 21.42.

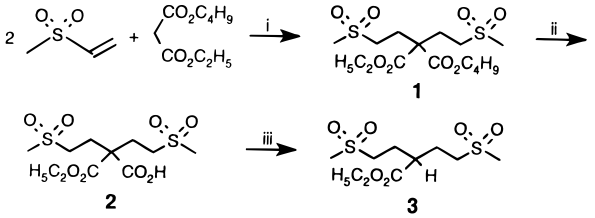
Polymer Synthesis. Polymer from Vinyl Sulfone and *tert*-Butyl Ethyl Malonate (4). (a) Standard Procedure. Vinyl sulfone (4.731 g, 40.04 mmol) and *tert*-butyl ethyl malonate (7.536 g, 40.04 mmol) were placed in a three-necked flask equipped with a stir bar and reflux condenser. After dilution with 1,1,1-trichloroethane (20 mL), the solution was chilled with an ice bath. DBU (0.463 g, 3 mmol) was added dropwise within 10 min by a syringe, which triggered the spontaneous, exothermic polyaddition reaction concomitant with a rapid increase in the mixture's viscosity. After 30 min, the cooling bath was removed, and the mixture was allowed to warm to room temperature and stirred for 2 days. Chloroform was added to dilute the solution, which was then added dropwise into vigorously stirred methanol (2 L). Large, off-white flakes precipitated and were collected by filtration, dried in a vacuum and dissolved in chloroform for reprecipitation in methanol. The 3-fold precipitated polymer was dried in a vacuum for 2 days. Yield: 3.23 g (26%). IR (KBr, cm^{-1}): 2982, 2940 (C−H), 1727 (C=O), 1371 (*tert*-butyl), 1150 (O=S=O). ^1H NMR ($CDCl_3$, 200 MHz): δ 4.25 (q, 2H), 3.13 (m, 4H), 2.34 (m, 4H), 1.48 (s, 9H), 1.30 (t, 3H). Anal. Calcd for $C_{13}H_{22}O_6S$: C, 50.97; H, 7.19; S, 10.46. Found: C, 49.96; H, 7.17; S, 11.25.

(b) Polymerization in Dried Solvent upon Addition of Water. Vinyl sulfone (5.322 g, 45.04 mmol) and *tert*-butyl ethyl malonate (8.472 g, 45.01 mmol) were loaded into a three-necked flask equipped with a stir bar, condenser, and septum. Dried methylene chloride (10 mL) was added by a syringe as the solvent and the flask was chilled with an ice bath. DBU (1.02 g, 7 mmol) was added dropwise over a period of 10 min using a syringe. No hints for polymerization were observed (cf. method a). The mixture was stirred for 10 min, and then the ice bath was removed. After 10 h of stirring at room temperature, the mixture's viscosity was still unchanged. A TLC developed in iodine vapor showed three spots corresponding to the two starting materials and DBU. Then, a few drops of water were added to the reaction mixture, upon which the viscosity increased very rapidly. To minimize phase separation, the mixture was heated to reflux overnight. After the reaction was cooled to room temperature, methylene chloride was added for dilution and the orange solution added dropwise to vigorously stirred methanol (1 L). The off-white precipitate was separated by filtration, dried in a vacuum, and dissolved in chloroform for reprecipitation. The 2-fold precipitated polysulfone was dried in a vacuum for 2 d. Yield: 4.33 g (31%). IR (KBr, cm^{-1}): 2981, 2940 (C−H), 1725 (C=O), 1372 (*tert*-butyl), 1152 (O=S=O). ^1H NMR ($CDCl_3$, 200 MHz): δ 4.25 (q, 2H), 3.13 (m, 4H), 2.33 (m, 4H), 1.47 (s, 9H), 1.30 (t, 3H). Anal. Calcd for $C_{13}H_{22}O_6S$: C, 50.97; H, 7.19; S, 10.46. Found: C, 49.97; H, 7.08; S, 11.93.

De-*tert*-butylation of Polymer 4 (5). Polymer **4** (3.300 g, 11 mmol) was dissolved in TFA (30 mL) and stirred at 80−85 °C for 8 h. The solvent was evaporated and the residue dried in a vacuum to give a brown solid foam, which was dissolved in DMF and added dropwise to vigorously stirred water. The off-white precipitate was separated, washed with methanol−water and dried in a vacuum for 2 d. Yield: 2.65 g (97%). IR (KBr, cm^{-1}): 3250−3050 (O−H), 2982, 2940 (C−H), 1730 (C=O), 1127 (O=S=O). ^1H NMR (py-d_5, 200 MHz): δ 4.26 (m, 2H), 3.86 (m, 4H), 2.98 (m, 4H), 1.16 (br t, 3H).

Decarboxylation of Polymer 5 (6). In a glovebox, polymer **5** (1.300 g, 5.2 mmol) and anhydrous copper(I) oxide (0.067 g, 0.5 mmol) were weighed into a three-necked flask, which was equipped with a stir bar, condenser, and septum. After addition of acetonitrile (10 mL) via a syringe, the turbid brown mixture cleared upon stirring at 80−85 °C overnight. Once at room temperature, the solution was acidified with aqueous HCl with a concomitant color change to yellow. The solvent was evaporated under reduced pressure, and the residue dissolved in pyridine. This solution was added dropwise into vigorously stirred water; the precipitate was sepa-

Scheme 1. Synthesis of Model Compounds 1−3[a]



[a] Key: i, DBU, MeCN, 0 °C → room temperature (95%); ii, TFA, 60 °C (84%); iii, catalytic Cu_2O, MeCN, 80−85°C (62%).

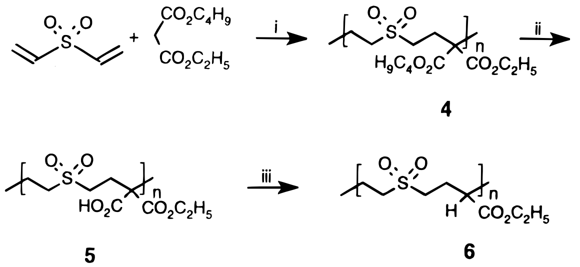
rated and dried in a vacuum for 2 d to give a mint-green polymer. Yield: 0.96 g, (89%). Further purification from copper contamination was achieved by redissolving the product in pyridine and adding this solution to a mixture of water/methanol (3/1) for slow reprecipitation affording a slightly mint-green polymer after drying in a vacuum. Recovery yield: 42−55%. IR (neat, cm^{-1}): 2988, 2978 (C−H), 1721 (C=O), 1314, 1121 (O=S=O). ^{1}H NMR (py-d_5, 200 MHz): δ 4.14 (m, 2H), 3.54 (m, 4H), 3.01 (m, 1H), 2.42 (m, 4H), 1.15 (m, 3H). Anal. Calcd for $C_8H_{14}O_4S$: C, 46.59; H, 6.80; S, 15.54; Cu, 0.00. Found: C, 45.86; H, 6.50; S, 16.05; Cu, 0.14.

Results and Discussion

Synthesis of Compounds 1−3. The three model compounds 5-*tert*-butoxycarbonyl-2,8-dithia-5-ethoxycarbonylnonane-2,2,8,8-tetraoxide (**1**), 5-carboxy-2,8-dithia-5-ethoxycarbonylnonane 2,2,8,8-tetraoxide (**2**), and 2,8-dithia-5-ethoxycarbonylnonane 2,2,8,8-tetraoxide (**3**) were synthesized according to Scheme 1. The diester **1** was obtained smoothly by conjugate addition of 1 equiv of *tert*-butyl ethyl malonate to slightly more than 2 equiv of methyl vinyl sulfone in the presence of DBU.[12] The model reaction was performed in acetonitrile because the polar solvent was expected to accelerate the reaction and the product was soluble in it. Similar yields were obtained in the actual polymerization solvents (methylene chloride and 1,1,1-trichloroethane). We hoped that the decarbo-*tert*-butoxylation of **1** to **3** would occur in one step by treatment with TFA at elevated temperatures.[13] In principle, the decarboxylation of **2** representing a β-oxo carboxylic acid derivative should be readily accomplished.[14] Unfortunately, treatment of **1** with TFA at elevated temperatures only effected de-*tert*-butylation, yielding half-ester **2**, **without** decarboxylation, to give **3**. The observed difficulty likely stems from the α,α-bisalkyl functionalization in **2**, which may conflict with stabilization of carbanionic intermediates through resonance or inductive effects and thereby effectively retards decarboxylation.[15,16] Rigorous reaction conditions, not acceptable for polymer analogous reactions, would therefore be necessary for such systems.[15−18] A method employing hot DMSO as the decarboxylation medium also met with failure.[17,18] Resorting to catalytic decarboxylation conditions using copper(I) reagents,[19−21] we found that treatment of half-ester **2** with catalytic amounts of copper(I) oxide in acetonitrile smoothly provided compound **3**. These conditions were considered reasonable for the decarboxylation of polymer **5**.

Synthesis of Polysulfones 4−6. The polymers **4**−**6** were prepared as illustrated in Scheme 2. We assumed that polymerization in acetonitrile would lead to precipitation of the product polymer, whereas polymerization in chlorinated solvents would produce viscous solutions, which was in fact observed for methylene chloride and 1,1,1-trichloroethane. The diester polymer **4** was obtained by polyconjugate addition of a malonate ester and vinyl sulfone.[8,9] Polymerization in acetonitrile led to precipitation of product; further, our experiments unveiled that the polyaddition of *tert*-butyl ethyl malonate and vinyl sulfone in the presence of an amidine base such as DBU or tetramethyl guanidine required the cocatalysis of water. When impure starting materials (95−97% purity grade) were subjected to the polyaddition reaction, the mixture polymerized immediately in an exothermic reaction and rapidly became viscous. Because of the known problems associated with step-growth linear polymerizations,[22] absolute reaction conditions and exact one-to-one mole ratios of the reactants were employed to maximize the degree of polymerization. Surprisingly, no polymerization was observed under those absolute conditions, and the starting materials were recovered. Variation of reaction parameters such as amount of DBU, polarity of solvent, or reaction temperature was fruitless until a couple of drops of water were added, when polymerization was triggered instantaneously. Too much water, in turn, limited the degree of polymerization as revealed by GPC. The best conditions for the polyaddition reaction, with respect to the degree of polymerization, polydispersity, and product purity, were found to be freshly distilled starting materials, 7.5 mol % DBU, of reagent grade 1,1,1-trichloroethane (containing about 0.1% of water) as the solvent, and external ice-bath cooling during the addition of DBU.

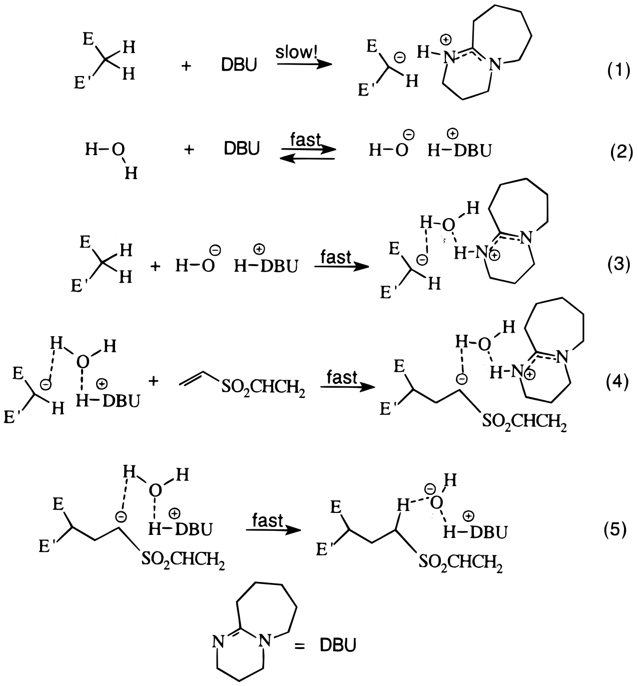
Scheme 2. Synthesis of Polymers 4-6[a]



As shown in Scheme 3, we believe the catalytic effect of water is dual: (a) it initiates the Michael-type addition (reactions 2 and 3) and (b) it prevents cross-linking by fast proton transfer to the intermediate α sulfonyl carbanion (reaction 5). Proton transfer from carbon to nitrogen (reaction 1) is kinetically less favored than reaction 2. Thus, DBU initially deprotonates water forming DBU−H$^{(+)}$ $^{(-)}$OH (reaction 2). Though we show only reaction 2 as an equilibrium, reactions 1−3 are expected to be equilibria but “far to the right”. As a strong, small base, the hydroxide rapidly deprotonates the malonic ester (reaction 3), the carbanion then adds, as a potent nucleophile, to vinyl sulfone in a Michael-type reaction (reaction 4). The difference in pK_a values between the α-methylene groups of the sulfone (pK_a: 20−25) and the malonic ester (pK_a: 12−13) leads to rapid proton transfer within the initial addition product−DBU−H$^{(+)}$ $^{(-)}$OH complex, liberating hydroxide for the generation, once again, of malonate. The proton transfer in reaction 5 can be either from [DBU−H]$^+$ or the complexed water.

Surprisingly, the expected formation of six-membered rings from vinyl sulfone and the malonic ester was not observed; even efforts to intentionally synthesize cyclic species failed. In the presence of excess *tert*-butyl ethyl malonate, we apparently synthesized some oligomeric polysulfones of type **4** as well as tiny amounts of cyclic

Scheme 3. Role of Water in the Polymerization Reaction



oligomers, but we were unable to characterize these materials unambiguously. In case of the cyclic oligosulfones, mass spectroscopy provided hints for the formation of tetra- and pentamers, but the presence of six-membered rings could be ruled out. The reluctance of vinyl sulfone toward ring formation was noted before by others.[23,24]

Conversion of **4** to the half-ester polymer **5** was accomplished in excellent yield by treatment with TFA at moderately elevated temperatures and subsequent precipitation from DMF into water. TGA measurements revealed a two-step degradation behavior for **4**, with the first step corresponding to 29% weight loss at an onset temperature of 202−215 °C closely matching the loss of isobutylene and carbon dioxide (see below). This encouraged us to attempt the thermal conversion of **4** and **5** to **6**. We heated dilute solutions of **4** or **5** to temperatures between 130 and 180 °C under argon. Additionally, neat samples of **4** and **5** were heated to temperatures ranging from 165 to 215 °C under argon or vacuum. The brown solids isolated after each of these thermal treatments were completely insoluble in all solvents, including DMF or *N*-methyl-2-pyrrolidinone (NMP) at elevated temperatures, which is indicative of cross-linked material. Exposure of **4** or **5** to heat can generate reactive decomposition intermediates, which react further, giving cross-linked products.[25,26] These findings are consistent with the thermal instability discovered for model compound **2** (see above). However, our target polysulfone **6** was accessible by exposure of **5** to copper(I) oxide under similar conditions as mentioned above for the preparation of **3**. But owing to its polar nature, polymer **6** served as a potent complexing agent for copper cations. Hence, **6** was contaminated with copper salts that imparted a mint color. Attempts to circumvent this problem by reducing the amount of copper(I) catalyst failed because at least 18 mol % copper(I) species were required to drive the decarboxylation to completion. Polymer **6** was readily soluble only in polar solvents such as DMF, NMP, or pyridine. Extraction with aqueous HCl, a procedure successful in the case of model compound **3**, was therefore not an option. Hence, we attempted complexation of the copper cations away from the polymer in two different ways: In a first approach, we treated DMF solutions of the decarboxylation product of **5** with hydrogen sulfide gas to form insoluble, black copper sulfide,[27] but separation of copper sulfide particles from the polymer solution failed. Therefore, complexation and separation of copper ions was attempted by addition of strong nitrogen-based ligands such as ammonia, pyridine, or triethylamine[27] to solutions of the decarboxylation product and then adding these solutions to water or water/methanol. Best results were achieved by dissolving the decarboxylation product of **5** in pyridine and adding this solution dropwise to a neutral mixture of methanol and water for slow precipitation. The copper contamination was thereby reduced to 0.14−0.30%. Addition of dilute hydrogen peroxide to the pyridine solution prior to precipitation to ensure the existence of solely copper(II) ions gave identical results.

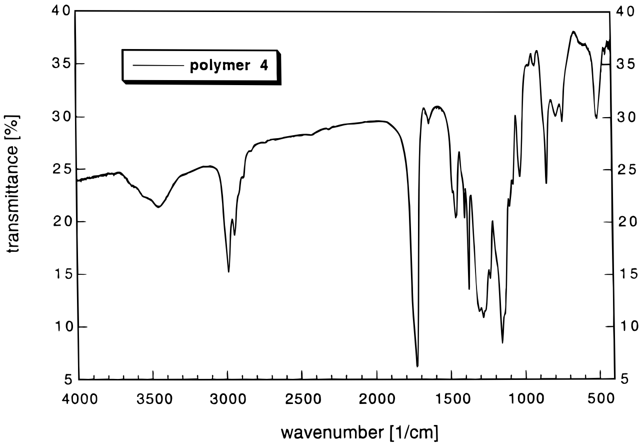


Figure 2. FTIR spectrum of polysulfone **4** in KBr mull.

Polymer Characterization. The structures of the polysulfones **4**−**6** were established through FTIR, NMR, and elemental analyses and by comparison with the unambiguously characterized model compounds **1**−**3**. For instance, conversion of **4** via **5** to **6** was evident in both ^{1}H NMR and FTIR spectroscopy. The *tert*-butyl peak in the ^{1}H NMR spectrum of polymer **4** at $\delta = 1.30$ ppm disappeared almost completely upon treatment with TFA; a residual amount of about 2% *tert*-butyl moiety could not be eliminated as determined by ^{1}H NMR spectroscopy of both **5** and **6**. The characteristic *tert*-butyl signal at $\nu = 1371$ cm^{-1} was very strong in the FTIR spectrum of **4** (Figure 2) but greatly reduced for **5** and **6** (Figure 3). In addition, the intensities of the C−H bands of **5** and **6** were significantly reduced compared to those of **4**. A strong OH-band indicative of the carboxylic acid group was found for **5** but was missing in the FTIR spectra of **4** and **6**. Further spectroscopic evidence for decarboxylation was a signal corresponding to the methine proton detected in the ^{1}H NMR spectrum of **6** at $\delta = 3.01$ ppm. Since no end groups were detected for any of the polysulfones by NMR spectroscopy, we can surmise that the molecular weight was in the high range determined by GPC (see below). All spectroscopic data collected for the polymers **4**−**6** matched closely with that obtained for the model compounds **1**−**3**.

Polymer **4** was an off-white solid and showed excellent solubility in a variety of different media such as

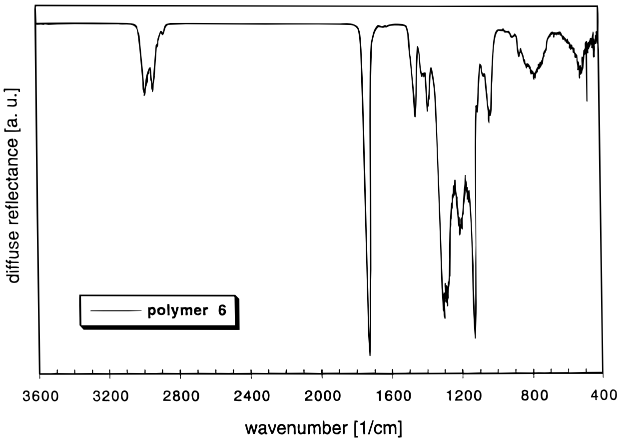


Figure 3. FTIR spectrum of neat polysulfone **6**.

Table 1. Characterization of Polysulfones 4 and 6 by GPC

polymer	M_n[a]	M_w[b]	M_w/M_n[c]	X_n[d]
4	31 900	56 570	1.77	100
6	21 870	30 410	1.39	105

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] Polydispersity. [d] Degree of polymerization.

chlorinated solvents, THF, cyclopentanone, *m*-cresol, DMF, and NMP. The off-white polymer **5** was readily soluble only in polar solvents such as DMF, NMP, pyridine, TFA, DMSO, and THF, somewhat soluble in aqueous base with concomitant foam formation, and insoluble in chlorinated solvents. Polymer **6** was soluble in DMF, NMP, pyridine, cyclopentanone, and warm acetonitrile but was insoluble in THF and chlorinated solvents.

The molecular weights (M_n and M_w), degrees of polymerization (X_n), and polydispersities of the polysulfones were determined by GPC with light scattering detector and refractive index measurements (Table 1). Depending upon the polyaddition conditions, the degrees of polymerization for polymer **4** varied from $X_n = 40$ to $X_n = 515$. Three-fold precipitation (overall yield: 60%) reduced the polydispersities of **4** from PD = 1.87−3.15 to PD = 1.11−1.37. In the case of polymer **6**, the degrees of polymerization correlated closely with those of the precursor polymer **4**. For instance, starting from **4** with $X_n = 100$ and PD = 1.77 led to **6** with $X_n = 105$ and PD = 1.39. These results indicate that the polymer analogous reactions performed on **4** and **5** did not significantly affect the molecular weights. The polydispersities, in turn, were slightly reduced in almost all cases, most likely due to repeated precipitations.

Transparent, clear films were cast from 10 to 20 wt % solutions of polysulfone **4** in different solvents such as chloroform, *m*-cresol, THF, and cyclopentanone onto either glass slides or polyethylene (PE) sheets. Upon standing for a few days, all these originally homogeneous films gradually turned opaque and formed cracks. When completely dry, the films became brittle. These glassy films did not show any mechanical strength. This behavior was not dependent upon the material's molecular weight. Characterization of this glassy, brittle film material by FTIR, NMR, X-ray, elemental analysis, GPC, DSC, and TGA revealed unmodified, recovered starting material **4**. The observed film behavior may be related to restricted chain flexibility and mobility due to the steric bulk introduced by the *tert*-butyl ester in conjunction with the stiffening effect that the $-SO_2-$ unit imparts on the polymer.[28] The embrittlement was likely due to solvent evaporation. To support this hypothesis, blending with diisooctyl phthalate as plasticizer greatly reduced the embrittlement and glassy properties, affording stable, clear, transparent, and rather flexible films.

Table 2. Thermal Characterization of Polysulfones 4 and 6 by DSC and TGA

polymer	T_g[a] (°C)	TGA[b] (°C)	TGA[c] (°C)
4	88	202;[d] 368[e]	204
6	67	376	332

[a] Glass transition temperature, determined from second heating scans (DSC). [b] Onset temperatures for degradation. [c] 5% weight loss. [d] First weight loss. [e] Second weight loss (see Figure 4).

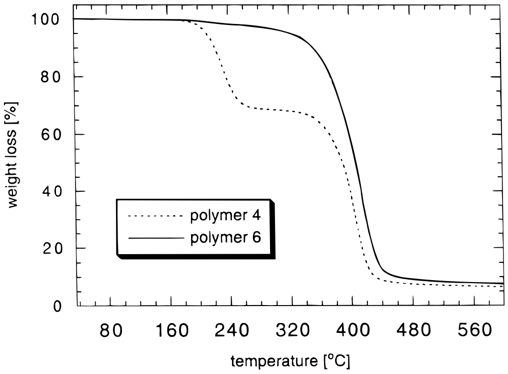


Figure 4. TGA traces of polysulfones **4** and **6** at a heating rate of 20 K/min.

The target polymer **6** exhibited quite different film properties. Homogeneous, stable, transparent, mint-colored films were cast from 10−12 wt % solutions in cyclopentanone onto PE sheets or glass slides. These films, once easily removed from the PE support, were flexible and showed fair mechanical strength. They recovered from slight stretching and mechanical deformation and have not shown hints for degradation or aging on exposure to air for a few months. However, even dry films strongly adhered to glass upon contact and had to be immersed in water to be lifted off without cracking.

The thermal properties of the polymers **4** and **6** were investigated by both DSC and TGA (Table 2, Figure 4). Neither polymer **4** nor **6** showed any crystalline properties in DSC analyses. The glass transition temperatures were determined to be between $T_g = 75$ and 100 °C for **4** and $T_g = 65$ to 70 °C for **6**, increasing with the material's molecular weight. The higher T_g's observed for **4** are in agreement with the assumed limited flexibility and mobility of the rigid polymer chains compared to **6** (see above). TGA measurements of polymer **4** showed a clean two-step degradation curve; 5% weight loss was reached between 200 and 210 °C (Figure 4). The first step corresponding to a weight loss of 29% matched well with the loss of isobutylene and carbon dioxide. Significant weight loss was also detected at 370−380 °C, the onset temperature for the second step, indicating decomposition of the remaining product. To the best of our knowledge, all aliphatic polysulfones prepared and characterized to date were found to exhibit relatively low thermal stability and decomposed with onset temperatures below 280 °C.[11] TGA traces acquired for polymer **6** reflected a one-step degradation profile and revealed unprecedented thermal

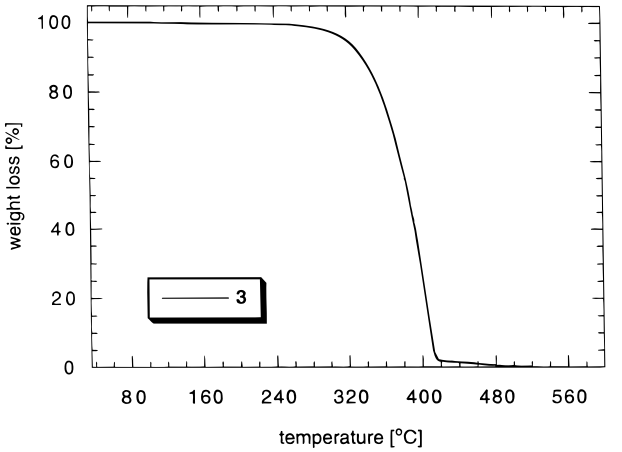


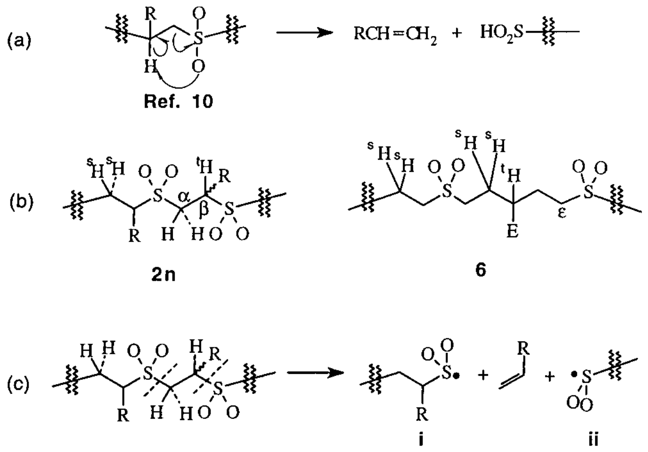
Figure 5. TGA trace of model compound **3** at a heating rate of 20 K/min.

stability with respect to weight loss (Figure 4). The curves showed a straight horizontal line up to 200 °C, where the slope became somewhat negative with an inflection point at about 225 °C. The characteristic 5% weight loss was reached at 320–330 °C. The onset temperature for degradation was determined to be 375–385 °C and correlated closely with the onset temperatures for the second step as measured in TGA traces of **4** (Figure 4). For comparison, the TGA trace of model compound **3** showed a one-step degradation curve with an onset temperature of 350 °C (Figure 5). Higher gain TGA scans of polysulfone **6** revealed a tiny step amounting to 1–2% weight loss between 200 and 250 °C. Taking into consideration a residual amount of about 2% *tert*-butyl ester in **6** (see above), thermal decarbo-*tert*-butoxylation *could* account for approximately 1% weight loss in that particular temperature range. Two-step degradation processes with a minor but clear weight loss preceding the major step were published for other aliphatic polysulfones.^{10} However, the first weight loss detected in those materials was much more significant than in **6**. The degradation profile of **6** was therefore viewed as a one-step process.

To detect possible cross-linking reactions of polymer **6** during heating, we stopped the TGA runs at about 330 °C and treated the brownish residues with small amounts of DMF; all material dissolved. The same experiments conducted with **4** resulted in completely insoluble material (see above). When DSC traces of **6** were run up to 400 °C, no hints for cross-linking reactions could be detected, whereas similar measurements with **4** unveiled an exothermic peak ($\Delta H = -160$ J/g) at about 180 °C onset temperature, which is indicative of cross-linking. Furthermore, the reproducible glass transitions detected in repeated DSC runs of polymer **4** between ambient temperature and 170 °C completely vanished in the second and subsequent heating scans if the sample was heated beyond 250 °C during the first data collection. These findings are in accord with thermally induced cross-linking in case of polymer **4**, but suggest no significant cross-linking reactions for polymer **6**.^{29}

Schoene and Noether studied even-numbered ($2n$), aliphatic polysulfones with 2n carbon atoms linking the sulfone units in the main chain.^{8,9,30} They did their investigations before the advent of modern techniques such as DSC and TGA. Later, Gipstein et al. proposed a degradation mechanism for $2n$ aliphatic polysulfones,^{10,31} based on GC–MS and DTA–TGA investigations and proposed a cyclic mechanism, shown in Scheme 4a, to explain the low thermal stability (onset above 250 °C)^{10,11} of the polyolefin sulfones. The same authors^{10,31} showed the formation of α-olefins and sulfur dioxide as main decomposition products. The occurrence of minor decomposition products was ascribed to free radical processes following decomposition of the sulfinic acid shown in Scheme 4a, affording ethylene, conjugated oligoenes and sulfur dioxide as stable products. The ultimate cause for the thermal instability of poly olefin sulfones was ascribed by these researchers to the low bond dissociation energy of the C–S bond (55–60 kcal/mol).^{10} Polymer **6**, an odd-numbered ($2n + 1$) aliphatic polysulfone revealed a dramatic shift in thermal stability of at least 100 °C toward higher temperatures (onset above 375 °C). The enhanced thermal stability of **6** leads us to conclude that the accepted degradation mechanism, ascribed to Gipstein, et al, is definitely not a universal mechanism. In Scheme 4 we show a comparative sketch of the $2n$ and $2n + 1$ backbones. Several important differences and similarities become immediately apparent.

Scheme 4. Schematic Representation of Proposed Thermal Decomposition Pathways for Polysulfones



1. Considering the SO_2 moiety, in the 2n polymers, there are only two secondary β hydrogens (^{s}H) and one tertiary β hydrogen (^{t}H), whereas in polymer **6** there are **four secondary** β hydrogens and one tertiary γ hydrogen. By analogy to the "ref 10" picture (Scheme 4a), the γ hydrogen atom could be engaged in a six-membered cyclic decomposition path.
2. The γ (^{t}H) in polymer **6** is acidic (pK_a ca. 25), as is the ^{t}H in the $2n$ polymers (pK_a ca 25).
3. The $2n$ polymers are poly β-disulfones, whereas polymer **6** has α,ϵ-disposed sulfone groups.
4. Both types of polymer have as their weakest bond the C–S bond.

In view of the above, the following points can be made. (i) If the accepted path of ref 10 were correct, polymer **6** should be even **more thermally labile** than $2n$ polymers because it has the same weakest link **and** has statistically twice as many β hydrogens as $2n$ polymers. (ii) If the accepted path were correct, polymer **6** should also be **more thermally labile** than $2n$ polymers because the olefin fragment produced can, by simple prototropy, lead to a very stable ester-conjugated alkene. We conclude from the above comparisons and especially point 3, above, that the cyclic degradation mechanism is either applicable only when a β tertiary hydrogen is available or, more likely and contrary to the accepted cyclic mechanism, the 2*n* polymers decompose by predominant cleavage of the α,β-disposed sulfones as shown in Scheme 4c where the fragments **i** and **ii** would further splinter into smaller pieces rapidly by the same process. Clearly this is a course of events not available to polymer **6**.

Summary

We proposed a novel strategy for polar organic polymers and designed both odd-numbered aliphatic polysulfones **4**−**6** and the corresponding model compounds **1**−**3**. Compounds **3**−**6** exhibit unexpected thermal stability. The polyaddition of vinyl sulfone and *tert*-butyl ethyl malonate in the presence of an amidine base to afford precursor polysulfone **4** required the co-presence of small amounts of water. Decarbo-*tert*-butoxylation was achieved by exposure of **1** or **4** to TFA, followed by treatment with copper(I) oxide; the uncatalyzed decarboxylation reaction failed for both the model compound and the polymer. Films of polysulfone **4** became brittle and glassy with time but flexibility could be recovered upon addition of a plasticizer. Polymer **6** produced homogeneous, flexible, and mechanically, as well as temporally stable films.

In due time we will report on our current investigations of the crystal structure of **3**, the dielectric and mechanical properties of films prepared from polysulfone **6**, and our efforts on improving the synthesis of **6** and related polymers.

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