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Mechanisms of Thermal Decompositions of Polysulfones: A DFT and CBS-QB3 Study

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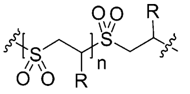
ABSTRACT: The thermal stabilities of polysulfones with different lengths of the carbon-linker between sulfone groups have been explored. B3LYP and CBS-QB3 calculations on possible thermal decomposition mechanisms of model compounds show that even carbon-linked polysulfones—copolymers of alkenes and SO_2—decompose by a radical chain mechanism involving facile depolymerization after initial homolysis. Sulfinate impurities [$-S(=O)-O-CH_2-$], formed as a minor component in polysulfone synthesis, can serve as good initiators for the radical mechanism. Polysulfones with odd-carbon linkers do not readily depolymerize in this fashion owing to high barriers of depropagation; these polymers undergo thermal degradation by the slower cyclic β-elimination processes.

Introduction

Polysulfones are copolymers of alkenes and SO_2 that are widely used as engineering materials because of their numerous desirable properties.[1] Polysulfones are generally synthesized by the copolymerization of alkenes with sulfur dioxide, or by oxidation of polysulfides, prepared by condensation polymerizations of dimercaptans with dihalides or the radical addition of dimercaptans to alkenes. Polysulfones produced in this way have two carbon atoms in repeating units between the sulfone groups, as in **1**.



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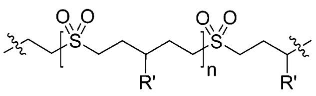

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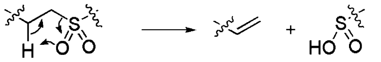
The principal drawback of these polysulfones as engineering materials is their relatively low thermal decomposition temperatures (~135 °C, R = −Et, PBS), which is below the polymer melt temperature.[1] Recently Schmidt-Winkel and Wudl prepared an ester-functionalized polysulfone (R′ = $-CO_2Et$, SWWP), **2**, with a five-carbon linker between sulfone groups.[2] This polymer exhibits remarkable thermal stability, degrading at temperatures more than 100 °C above those of the previously reported polysulfones.

The depolymerization of polysulfones has long been considered to occur by a concerted β-elimination mechanism (Scheme 1). Such a decomposition path, independent of lengths of the carbon-linkers, should occur qualitatively equally well for both the polysulfones **1** and **2**. We have explored the mechanisms of decompositions of polysulfones with quantum mechanical methods. An explanation of the enhanced stability of **2** has been found which should aid in the further development of thermally resistant polysulfones.

Scheme 1. Concerted β-Elimination of Sulfones



(1)

Polysulfones undergo thermal decomposition to afford assorted decomposition products, including sulfur dioxide and alkenes. Kinetic studies of the decompositions of polysulfones began in the 1950s.[3−5] Activation energies, determined by various means and dependent on temperature ranges, for the copolymers of SO_2 and vinyl monomers range from 18 to 48 kcal/mol.[5−9] The weakest bond in a polysulfone chain is the C−S bond, which has a bond strength variously quoted at 55−65 kcal/mol. Because the measured activation energies are considerably lower than the C−S bond energy, Wellisch et al.[6] proposed a mechanism in which bond-breaking and bond-making occur in a concerted fashion at high temperature (275 °C) (Scheme 1). This retro-ene type process generates a vinyl sulfone and a sulfinic acid. The sulfinic acid product then loses SO_2.

Polymer **2**, with 1,3-situated sulfone groups, could react by a similar mechanism. Since **2** is much more stable than **1**, an alternative mechanism is necessary, or else the SO_2 substituent in **1** is exerting a powerful substituent effect on the retro-ene type process. Schmidt-Winkel and Wudl have presented arguments against the concerted β-elimination:[2] (a) If a concerted β-elimination occurred, the five-carbon sulfone, **2** (R′ = $-CO_2Et$), which has more acidic β-hydrogens than **1** (R = −Et), should be the more labile. (b) The 5-carbon sulfone, **2**, could produce an alkene that could tautomerize to a very stable ester-conjugated alkene.

The two mechanisms, C−S bond homolysis and β-elimination, or a combination thereof,[10] have been invoked to account for the experimental observations, usually in terms only of the initiation step. The kinetics of depolymerization must include both propagation and termination steps in addition to initiation (the C−S bond cleavage). Bowden et al. have analyzed the entire decomposition process in terms of all three processes that occur in a chain depolymerization.[8] In contrast to Bowden's reported activation energy (12-14 kcal/mol) at low temperature (<200 °C), Yang and co-workers in-

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Table 1. Calculated Energies, ZPEs, and Entropies of Relevant Species in Polysulfone Depolymerization, with the CBS-QB3 Method (Energies in Atomic Units, 1 hartree = 627.5095 kcal/mol)

	E (au)	ZPE (au)	*S* (eu)	
$CH_3^{\bullet}$	−39.74172	0.029 29	50.1	
SO_2	−548.03454	0.006 80	59.3	
$CH_3CH_2^{\bullet}$	−78.96756	0.058 41	61.4	
$CH_2{:}CH_2$	−78.41357	0.050 30	55.1	
$^{\bullet}CH_2CH_2^{\bullet}$ (triplet)	−78.30705	0.044 84	59.5	
$^{\bullet}CH_2CH_2CH_2^{\bullet}$ (triplet)	−117.53076	0.072 53	76.6	
$CH_3CH{:}CH_2$	−117.64211	0.078 52	63.3	
$CH_3CH_2CH_2^{\bullet}$	−118.19135	0.086 96	68.7	
$CH_3SO_2^{\bullet}$	−587.80355	0.044 30	71.4	
CH_3SO_2H	−588.42422	0.054 89	72.0	
$CH_3SO_2CH_3$	−627.65874	0.084 68	77.0	
$CH_3SO_2CH_2CH_3$	−666.88487	0.112 14	85.0	
$CH_3S({=}O)OCH_2CH_3$	−666.86468	0.112 14	88.1	
$CH_3SO_2^{\bullet}\ {}^{\bullet}CH_2CH_3$ (triplet)	−666.77044	0.103 22	119.5	
$CH_3SO_2CH{:}CH_2$	−665.66949	0.088 94	81.6	
$CH_3SO_2CH_2CH_2^{\bullet}$	−666.22346	0.097 47	87.6	
$CH_2{:}CHCO_2CH_3$	−305.98516	0.093 98	80.2	
$^{\bullet}CH_2CH_2CO_2CH_3$	−306.53475	0.101 75	86.6	
$CH_3SO_2CH_2CH{:}CH_2$	−704.89730	0.116 86	90.7	
$CH_3SO_2CH_2CH_2CH_2^{\bullet}$	−705.44704	0.125 50	96.3	
$CH_3SO_2CH_2CH_2SO_2^{\bullet}$	−1214.28410	0.111 62	109.4	
$CH_3SO_2CH_2CH_2SO_2CH_3$	−1254.14128	0.150 14	112.4	
$CH_3SO_2CH_2CH_2CO_2CH_3$	−894.45308	0.154 76	113.0	
$CH_3SO_2CH_2CH_2CH_2SO_2CH_3$	−1293.36358	0.178 22	120.5	
$CH_2{:}CHCH(COCH_3)CH_3$	−309.27845	0.143 67	90.8	
$CH_2CH_2CH(COCH_3)CH_3$	−309.82969	0.152 19	96.1	
$CH_3SO_2CH_2CH_2CH(COCH_3)CH_3$	−897.74801	0.205 07	119.2	
$CH_3SO_2^{\bullet}\ {}^{\bullet}CH_2CH_2SO_2CH_3$ (triplet)	−1254.04148	0.144 59	127.1	
transition states				
$CH_3SO_2CH_2CH_3$ (β- TS)	−666.79900	0.104 87	84.5	Figure 1
$CH_3SO_2CH_2CH_2SO_2CH_3$ (β- TS)	−1254.06133	0.143 11	110.0	Figure 2
$CH_3SO_2CH_2CH_3$ (C−S TS)	−666.78331	0.107 74	88.1	Figure 3
$CH_3SO_2CH_2CH_2^{\bullet}$ (C−S TS)	−666.20960	0.097 18	89.8	Figure 4
$[CH_3SO_2^{\bullet}\ CH_3SO_2CH_2CH_2^{\bullet}] \rightarrow RSO_2H + RSO_2CH{:}CH_2$ (Hydrogen abstraction)	−1254.03249	0.142 34	111.6	Figure 5
$CH_2CH_2CH_2 \rightarrow CH_2CH{:}CH_3$	−117.52456	0.072 48	62.9	

vestigated the early stage (<0.5 wt % decomposition) of the thermal degradation of poly(1-butene sulfone) at low temperatures (110−130 °C, below the onset temperature) by using a pH meter, resulting in a much higher activation energy of 64.6 kcal/mol.[11]

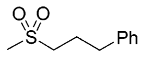
Results and Discussions

To explore how these decompositions occur, a series of model calculations were conducted to mimic the bond cleavages in the depolymerization of polysulfones. Optimized geometries of reactants, products, transition states, and reaction intermediates were obtained with density functional theory, using the B3LYP functional and the 6-31G* basis set in GAUSSIAN 98 and 03.[12] This is a robust level for a variety of organic reactions, although energetics become more problematical with heteroatoms, especially sulfur, using such a small basis set.

To obtain accurate energies, we were guided by the results of Martin,[13] who has proposed the heat of atomization energy of sulfur trioxide as a benchmark for computational thermochemistry. Various otherwise robust methods give rather large errors in prediction of the heat of atomization of SO_3. Petersson's theoretical model CBS-QB3, implemented in the Gaussian programs, gives an error of only 0.2 kcal/mol for the ΔH_f of SO_3,[14] and has an average error of only 1 kcal/mol for a large experimental data set.[14−20] The method was used in the present investigation.

The calculated energies, zero-point energies, and entropies (298 K) are summarized in Table 1, and energies and entropies of reaction are shown in Table 2. These CBS-QB3 energies were employed to deduce the overall activation energy of the radical chain depolymerization, according to a kinetic analysis based on the steady-state hypothesis.

Decomposition of Ethyl Methyl Sulfone. We explored concerted elimination and homolysis mechanisms theoretically for ethyl methyl sulfone. During the course of this investigation, Cubbage et al. reported the first theoretical and experimental information on the degradation of a nonpolymeric sulfone: the β-elimination of ethyl methyl sulfone and related molecules.[21] They investigated reactions of **3**, **4**, and **5** experimentally in the gas phase at 490−550 °C. The experimental activation enthalpies for decomposition of **3**, **4**, and **5** are 53.5 ± 1.0, 52.5 ± 1.6, and 47.0 ± 1.8 kcal/mol, respectively. The lower activation energy for **5** was attributed to the substituent effect of the phenyl group. This was regarded as evidence for concerted β-elimination besides the isotopic effect, since no effect of the phenyl group would be anticipated for a C−S homolysis.



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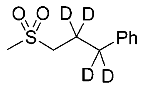

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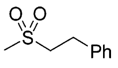

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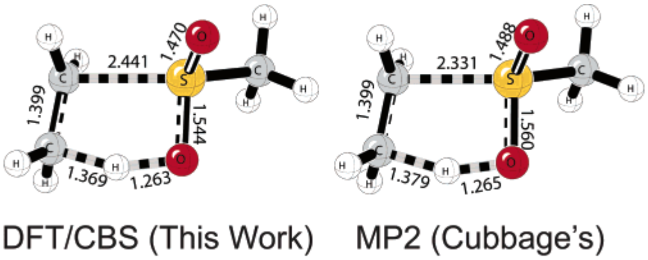
Cubbage et al. also conducted MP2/6-311+(3df,2p)//MP2/6-31G(dp) and CASSCF calculations on an ethyl methyl sulfone model; they obtained $\Delta H^{\pm} = 54.5$ and $\Delta H_{\text{rxn}} = 35.7$.[21] These computed activation energies are

Table 2. Calculated Reaction and Activation Enthalpies, Free Energies (298 K, in kcal/mol), and Entropies (eu) with the CBS-QB3 Method[a]

	ΔH	ΔG	ΔS
β-elimination			
a. $CH_3SO_2CH_2CH_3 \rightarrow CH_3SO_2H + CH_2{:}CH_2$	30.2	17.6	42.1
b. $CH_3SO_2(CH_2)_2SO_2CH_3 \rightarrow CH_3SO_2H + CH_2{:}CHSO_2CH_3$	30. 5	18.1	41.2
c. $CH_3SO_2(CH_2)_2CH(COCH_3)SO_2CH_3 \rightarrow CH_3SO_2H + CH_2{:}CHCH(COCH_3)CH_3$	29.1	16.0	43.6
d. $CH_3SO_2(CH_2)_3SO_2CH_3 \rightarrow CH_3SO_2H + CH_2{:}CHCH_2SO_2CH_3$	27.0	14.4	42.3
C−S rupture			
e. $CH_3SO_2CH_2CH_3 \rightarrow CH_3SO_2^{\bullet} + CH_3CH_2^{\bullet}$	72.0	57.6	48.2
f. $CH_3SO_2CH_2CH_3 \rightarrow CH_3SO_2^{\bullet}\ {}^{\bullet}CH_2CH_3$[b]	71.8	61.5	34.5
g. $CH_3SO_2CH_2CH_2SO_2CH_3 \rightarrow CH_3SO_2^{\bullet} + {}^{\bullet}CH_2CH_2SO_2CH_3$	72.3	58.3	47.0
h. $CH_3SO_2(CH_2)_3SO_2CH_3 \rightarrow CH_3SO_2^{\bullet} + CH_3SO_2CH_2CH_2CH_2^{\bullet}$	71.5	57.3	47.6
i. $CH_3SO_2CH_2CH_2CH(COCH_3)CH_3 \rightarrow CH_3SO_2^{\bullet} + {}^{\bullet}CH_2CH_2CH(COCH_3)CH_3$	72.6	58.1	48.8
C−O rupture			
j. $CH_3S(=O)O{-}CH_2CH_3 \rightarrow CH_3SO_2^{\bullet} + CH_3CH_2^{\bullet}$	59.3	43.9	45.1
two-bond homolysis			
k. $CH_3SO_2CH_2CH_2SO_2CH_3 \rightarrow 2\ CH_3SO_2^{\bullet} + CH_2{:}CH_2$	76.9	51.1	86.3
l. $CH_3SO_2CH_2CH_2^{\bullet} \rightarrow CH_3^{\bullet} + CH_2{:}CH_2 + SO_2$	22.2	−0.3	76.9
m. $CH_3SO_2CH_2CH_2SO_2CH_3 \rightarrow CH_3SO_2CH_3 + CH_2{:}CH_2 + SO_2$	22.7	−0.5	79.0
complexation:			
n. $CH_3SO_2^{\bullet} + CH_3SO_2CH_2CH_2^{\bullet} \rightarrow [CH_3SO_2^{\bullet}{-}{-}{-}CH_3SO_2CH_2CH_2^{\bullet}]$	9.7	−0.2	−31.9
termination:			
o. $[CH_3SO_2^{\bullet\bullet}CH_2CH_2\ SO_2CH_3] \rightarrow CH_3SO_2H + CH_2{:}CHSO_2CH_3$	−41.9	−40.3	−5.4
	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
activation energetics			
p. ${}^{\bullet}CH_2CH_2CH_2^{\bullet} \rightarrow CH_2CH{:}CH_3$	3.9	8.0	−13.6
q. $CH_3SO_2CH_2CH_2^{\bullet} \rightarrow CH_3SO_2^{\bullet} + CH_2{:}CH_2$ (C−S TS)	8.7	8.0	2.2
r. $CH_3SO_2CH_2CH_3 \rightarrow CH_3SO_2H + CH_2{:}CH_2$ (β-TS)	53.9	54.0	−0.5
s. $CH_3SO_2CH_2CH_2SO_2CH_3 \rightarrow CH_3SO_2H + CH_2{:}CHSO_2CH_3$ (β − TS)	50.2	50.9	−2.4
t. $CH_3SO_2CH_2CH_3 \rightarrow CH_3SO_2^{\bullet} + {}^{\bullet}CH_2CH_3$ (C−S TS)	63.7	62.8	3.1
u. $[CH_3SO_2^{\bullet}\ {}^{\bullet}CH_2CH_2\ SO_2CH_3] \rightarrow CH_3SO_2H + CH_2{:}CHSO_2CH_3$ (termination)	5.6	10.3	−15.4

[a] β-TS ≡ β-elimination transition state; C−S TS ≡ homolytic transition state. [b] Formation of lowest-lying triplet.



DFT/CBS (This Work) MP2 (Cubbage's)

Figure 1. Calculated transition states of β-elimination of $CH_3SO_2CH_2CH_3$ (left, with the CBS-QB3 method that was a B3LYP/CBSB7 optimization; right, data from Cubbage et al. with MP2).[22]

in excellent agreement with experiment and show that the concerted β-elimination occurs for this reaction.

We also explored this reaction theoretically with density functional theory (DFT) and Complete Basis set (CBS) methods. B3LYP geometry optimizations followed by CBS-QB3 energetic evaluations gave $\Delta H^{\ddagger} = 54.1$ kcal/mol and $\Delta H_{rxn} = 30.2$ kcal/mol. To compare the accuracy of different methods, the MP2/6-311+(3df,2p)//MP2/6-31G(dp) calculations, as Cubbage et al. used for locating transition states of cyclic β-elimination, were carried out for the heat of atomization of sulfur trioxide; an error of −23 kcal/mol was obtained, as contrasted with the 0.2 kcal/mol error for CBS-QB3. The CBS-QB3 numbers are more reliable, but in any case are in reasonable agreement with Cubbage's reports for the $\Delta H^{\ddagger}$ for the elimination. The transition state for the β-elimination is shown in Figure 1. The C−S bond breaking is substantial, with a length of 2.44 Å in the transition state. The hydrogen is also appreciably transferred, with a forming O···H bond length of 1.26 Å and the breaking C···H of 1.37 Å.

The CBS-QB3 calculation for the C−S homolysis of $CH_3SO_2CH_2CH_3$ to form $CH_3SO_2^{\bullet} + CH_3CH_2^{\bullet}$ results in $\Delta H_{rxn} = 72.0$ kcal/mol. No matter whether the 55−65 kcal/mol range measured experimentally or 72 kcal/mol calculated, the homolysis of these simple sulfone compounds is substantially higher in energy than the thermal decomposition of polysulfones with two-carbon linkers reported in the literature (less than 48 kcal/mol).

Substituent Effects on Concerted *β*-Eliminations. The effects of altering the number of carbon atoms in the sulfone linker, of a neighboring sulfone group on the ease of elimination, and of the ester function of the Schmidt-Winkel and Wudl polymer on the rates of each of these decomposition mechanisms were investigated with the model compounds $CH_3SO_2(CH_2)_2SO_2CH_3$, $CH_3SO_2(CH_2)_3SO_2CH_3$, and $CH_3SO_2(CH_2)_2CH(CO_2CH_3)SO_2CH_3$. The results in Table 2, entries a−d, show that elimination reactions of odd- and even-linked disulfones have reaction free energies of 14−18 kcal/mol, and the length of the tether between sulfones or the nature of the substituent has only a minor effect on the heat of reaction. Alkyl substituents are likely to stabilize the product and make the elimination less endothermic (compare entries a and b to c and d in Table 2). All of these processes are endergonic at room temperature but have favorable free energies at high temperatures, as discussed later.

A β-sulfone lowers the activation energy for the concerted β-elimination (compare reactions r and s in Table 2) by about 3−4 kcal/mol, relative to that of ethyl methyl sulfone, because of the more labile β-H atoms. From two-carbon linker (**6**, 50.2 kcal/mol, CBS-QB3) to three-carbon linker (**7**, 48.7 kcal/mol, CBS-QB3), the activation energy decreases by an additional 1.5 kcal/mol. As shown in Table 2, entries e−g, the energetics of C−S scission are not influenced by the substitu-

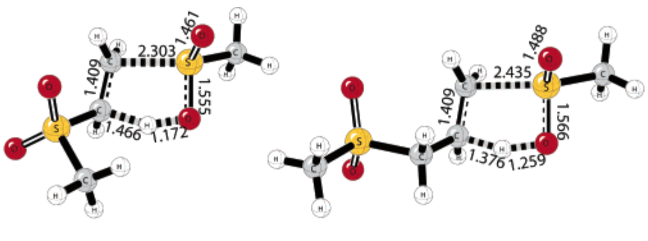


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Figure 2. Calculated transition structures of β-eliminations for disulfone model with two-carbon and three-carbon linkers (CBS-QB3).

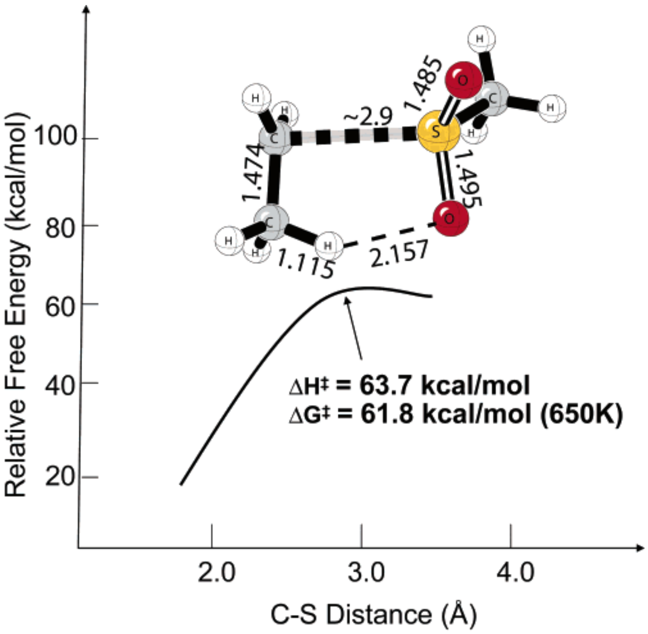
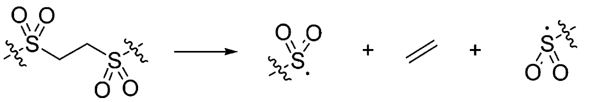


Figure 3. Calculated activation energy for the C−S homolysis, determined by an energy scan with (U)B3LYP/6-31G(d) and then by CBS-QB3 corrections of Energy.

ents for these systems to a large extent. For these systems, the ΔH_{rxn} values for homolysis are all about 72 kcal/mol. The activation free energy of a homolysis reaction may be less than the reaction enthalpy, since $\Delta S^{\ddagger}$ increases along the reaction path.[23−25] All the $\Delta G^{\ddagger}$ maxima can occur before the bonds are fully broken. The activation energy of the C−S scission, determined by locating the maximum free-energy at 650 K, is about 63.7 kcal/mol with $CH_3SO_2CH_2CH_3$ model, where the free energy reaches the highest plateau in the potential energy surface, with a partially breaking C−S bond length of about 2.9 Å. Calculations showed that the activation energy of the homolysis changes little in the experimental temperature range ($\Delta G^{\ddagger}_{298\mathrm{K}}$ = 62.8 kcal/mol). This energy is close to the activation energy of 64.6 kcal/mol measured by Tsay et al. at the early stage of thermal degradation of poly(1-butene sulfone) at 110−130 °C.[11] The energy of the two-bond homolysis reaction, shown in the following equation, was also computed.



(2)

This reaction was modeled with $CH_3SO_2CH_2CH_2SO_2CH_3$. The one-bond homolysis has ΔH_{rxn} = 72.3 kcal/mol and ΔG_{rxn} = 58.0 kcal/mol (reaction g), while two-bond scission has ΔH_{rxn} = 76.9 kcal/mol and ΔG_{rxn} = 51.1 kcal/mol at 298 K (reaction k). Note that the second bond scission to form ethylene requires only 4.6 kcal/mol in enthalpy.

Kinetics of Radical Chain Depolymerization. The analysis is based largely on the work of Bowden et al., the most recent and thorough study of the decomposition kinetics of polysulfones.[8] These authors studied the depolymerization of the copolymer of 1-butene and SO_2 with thermogravimetic analysis; the kinetic data were analyzed according to the comprehensive treatment by Reich and Stivala.[26]

The kinetics of depolymerization is expressed in terms of random initiation, presumably the homolysis of the C−S bond, followed by depropagation and bimolecular termination.

Initiation step:

$$\text{polysulfone} \xrightarrow{k_i} R_c^{\bullet} + R_s^{\bullet} \tag{3}$$

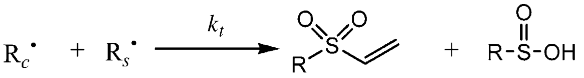
where $R_c^{\bullet}$ and $R_s^{\bullet}$ are alkyl and sulfonyl radicals generated by the C−S homolytic cleavage, respectively.

Propagation step:

$$R_c^{\bullet} \xrightarrow{k_d^{c}} R_s^{\bullet} + CH_2{:}CH_2 \tag{4}$$

$$R_s^{\bullet} \xrightarrow{k_d^{s}} R_c^{\bullet} + SO_2 \tag{5}$$

Termination step:



(6)

This termination reaction is believed to be most probable for involving a stable sulfonyl radical; it has large exothermicity, a low activation barrier, and a favorable entropy since two molecules are produced in contrast to biradical combinations.

The steady-state hypothesis can be applied to the alkyl and sulfonyl radicals, both of which are present at very low concentrations. The polymer is assumed to be present at a constant concentration (of unity). The steady-state equations for alkyl and sulfonyl radicals are

$$\frac{\mathrm{d}[R_c^{\bullet}]}{\mathrm{d}t} = k_i - k_d^{\,c}[R_c^{\bullet}] + k_d^{\,s}[R_s^{\bullet}] - k_t[R_c^{\bullet}][R_s^{\bullet}] = 0$$

and

$$\frac{\mathrm{d}[R_s^{\bullet}]}{\mathrm{d}t} = k_i + k_d^{\,c}[R_c^{\bullet}] - k_d^{\,s}[R_s^{\bullet}] - k_t[R_c^{\bullet}][R_s^{\bullet}] = 0$$

From the above two equations, we can easily deduce that

$$[R_c^{\bullet}] = \sqrt{\frac{k_i}{k_t}\frac{k_d^{\,s}}{k_d^{\,c}}} \quad \text{and} \quad [R_s^{\bullet}] = \sqrt{\frac{k_i}{k_t}\frac{k_d^{\,c}}{k_d^{\,s}}}$$

Thus, an expression for the measurable weight-loss rate in the depolymerization can be obtained by computing the total release rate of $CH_2{:}CH_2$ and SO_2

monomers in the reaction cycle (MW: molecular weight):

$$v_t \equiv -\frac{\mathrm{d}W}{\mathrm{d}t} = k_d^{\,c}[R_c^{\bullet}]\mathrm{MW}_{\mathrm{CH_2:CH_2}} + k_d^{\,s}[R_s^{\bullet}]\mathrm{MW}_{\mathrm{SO_2}} = \mathrm{MW}_{\mathrm{CH_2:CH_2}}\sqrt{\frac{k_i k_d^{\,c} k_d^{\,s}}{k_t}} + \mathrm{MW}_{\mathrm{SO_2}}\sqrt{\frac{k_i k_d^{\,c} k_d^{\,s}}{k_t}} = (\mathrm{MW}_{\mathrm{CH_2:CH_2}} + \mathrm{MW}_{\mathrm{SO_2}})\sqrt{\frac{k_i k_d^{\,c} k_d^{\,s}}{k_t}}$$

and therefore, the total rate constant can be given in a Arrhenius equation:

$$k = \sqrt{\frac{k_i k_d^{\,c} k_d^{\,s}}{k_t}} = \sqrt{\frac{A_i A_d^{\,c} A_d^{\,s}}{A_t}}\sqrt{\frac{\mathrm{e}^{-E_i/RT}\mathrm{e}^{-E_d^c/RT}\mathrm{e}^{-E_d^s/RT}}{\mathrm{e}^{-E_t/RT}}} = \sqrt{\frac{A_i A_d^{\,c} A_d^{\,s}}{A_t}}\,\mathrm{e}^{-(E_i+E_d^c+E_d^s-E_t)/2RT}$$

Alternatively, the observed Arrhenius coefficient (A) and activation energy (E_{tot}) will be

$$A = \sqrt{\frac{A_i A_d^{\,c} A_d^{\,s}}{A_t}} \quad \text{and} \quad E_{\mathrm{tot}} = \frac{E_i + E_d^{\,c} + E_d^{\,s} - E_t}{2}$$

where the E's are defined as follows:

E_{tot}: experimentally measured Arrhenius activation energy

E_i: activation energy for initiation

E_d^c: activation energy for SO_2 release

E_d^s: activation energy for alkene release

E_t: activation energy for termination

Activation Energies of Radical Chain Depolymerization. Now we can turn to practical computation of the activation energy of each step in radical chain depolymerization. The experimental Arrhenius activation energy (E_a) for depolymerization of poly(1-butene sulfone) has been measured to be 46.8 ± 1.2 kcal/mol.[8] The early literature tried to rationalize this with an estimate of 33.8 kcal/mol[8] of activation energy for the depropagation (E_d), according to the activation energy of 5 kcal/mol for polymerization (E_p, as a retro-reaction) and polymerization energy (ΔH_{gc}) of 28.8 kcal/mol (corresponding to reaction energy in the gas phase of ca. 22.7 kcal/mol of model reaction m in Table 2, with a differentiation of 6.1 kcal/mol caused by heat of phase change).

However, the real reaction goes through a radical chain cycle involving the two-step propagation, in which the activation energy cannot be estimated in the same way as for one-step propagation. Thus, the previous equation, $E_{\mathrm{tot}} = {}^1/_2(E_i - E_t) + E_d$, is improper for the two-step depropagation of depolymerization. Instead, the new equation of $E_{\mathrm{tot}} = {}^1/_2(E_i + E_d^s + E_d^c - E_t)$ should be applied here, or alternatively, the "overall E_d" can be expressed as ${}^1/_2(E_d^s + E_d^c)$. With this expression, the values obtained by Bowden and co-workers can be compared to values calculated here. From Table 2, the C−S homolytic cleavage has a predicted E_i of 63.7 kcal/mol, quite close to the early estimate of 63 kcal/mol. CBS-QB3 calculations agree well with the Bowden results if the initiation step is C−S rupture. The activation energies for C−S bond homolysis are about 10 kcal/mol higher than those for β-elimination of both the simple sulfone compounds and other modeling calculations in this work.

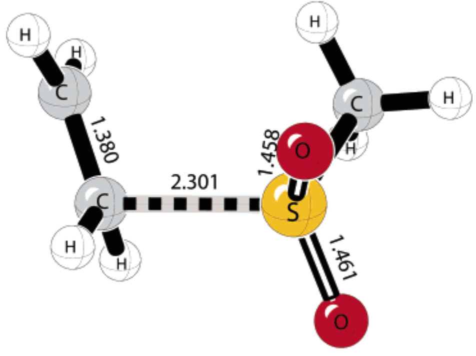


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Figure 4. Calculated transition state for modeling the depropagation process in the radical chain depolymerization (CBS-QB3).

The activation barriers for depropagation steps, involving loss of ethylene and SO_2 were also computed separately with the CBS-QB3 method:

$$\mathrm{CH_3SO_2CH_2CH_2^{\bullet}} \rightarrow \mathrm{CH_3SO_2^{\bullet}} + \mathrm{CH_2{:}CH_2} \quad \Delta E = 4.0\ \text{kcal/mol},\quad \Delta E^{\ddagger} = 8.7\ \text{kcal/mol}\ (E_d^{\,c}) \tag{7}$$

$$^{\bullet}\mathrm{O_2SCH_2CH_3} \rightarrow \mathrm{SO_2} + {}^{\bullet}\mathrm{CH_2CH_3} \quad \Delta E = 17.1\ \text{kcal/mol},\quad \Delta E^{\ddagger} = 17.1\ \text{kcal/mol}\ (E_d^{\,s}) \tag{8}$$

Thus, the activation barrier for overall depropagation (E_d) in the gas phase is 12.9 kcal/mol [$E_d = {}^1/_2(E_d^s + E_d^c)$]. The propagation step of polymerization (opposite direction) has activation energy (E_p) of 4.7 kcal/mol. The calculated E_p is consistent with the experimental value of 5 kcal/mol in the polymerization by Dainton et al.[4] The termination step of radical-chain degradation is an H-abstraction:

$$\mathrm{RSO_2^{\bullet}} + \mathrm{RSO_2CH_2CH_2^{\bullet}} \rightarrow \mathrm{RSO_2H} + \mathrm{RSO_2CH{:}CH_2} \tag{9}$$

This reaction is exothermic by 41.8 kcal/mol in the gas phase (R = CH_3-, CBS-QB3). The H-abstraction involved precursor formation of a hydrogen-bonded (S=O- - -HC) complex [$RSO_2^{\bullet}$- - -$RSO_2CH_2CH_2^{\bullet}$] that has a computed binding energy of 9.7 kcal/mol (R = CH_3−, CBS-QB3):

$$\mathrm{CH_3SO_2^{\bullet}} + \mathrm{CH_3SO_2CH_2CH_2^{\bullet}} \rightarrow [\mathrm{CH_3SO_2^{\bullet}}\text{- - -}\mathrm{CH_3SO_2CH_2CH_2^{\bullet}}] \tag{10}$$

The precursor complex then undergoes hydrogen transfer from the alkyl radical to the sulfonyl radical, with an activation energy of 5.6 kcal/mol (CBS-QB3), generating the stable termination products, a sulfinic acid, and a vinyl sulfone:

$$[\mathrm{CH_3SO_2^{\bullet}}\text{- - -}\mathrm{CH_3SO_2CH_2CH_2^{\bullet}}] \rightarrow \mathrm{CH_3SO_2H} + \mathrm{CH_3SO_2CH{:}CH_2} \tag{11}$$

Because the termination is a bimolecular reaction, there is an unfavorable activation entropy of 47 esu in

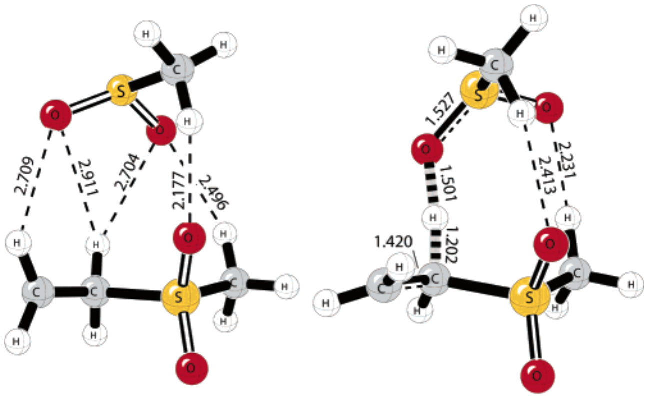

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Figure 5. Calculated lowest-energy radical pair complex and the transition state for termination (CBS-QB3).

the gas phase (CBS-QB3), corresponding to 23.5−35 kcal/mol in the experimental temperature range of 200−475 °C. Therefore, the termination step is dependent on the experimental temperature: the higher the experimental temperature, the more difficult to terminate radical degradation. This affects the preexponential A_t in the Arrhenius equation, but not the activation energy (E_{tot}).

The kinetic Arrhenius expression gave the observed activation energy in terms of these computed reaction parameters:

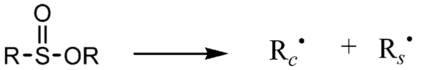
$$E_a = E_{\mathrm{tot}} = {}^1\!/_2(E_i + E_d^{\,c} + E_d^{\,s} - E_t) = {}^1\!/_2[63.7 + 8.7 + 17.1 - (5.6 - 9.7)] = 46.7\ \mathrm{kcal/mol}$$

This agrees astonishingly well with the measured value of 46.8 ± 1.2 kcal/mol![8]

The radical chain mechanism of decomposition thus differs for the even- and odd-linked polysulfones significantly. For a normal, even-linked polysulfone, the reaction involves homolytic initiation, followed by stepwise loss of SO_2 and ethylene. After the onset temperature [135 °C, PBS], where the termination is suppressed and the radical chain degradation become dominant, the calculated overall activation barrier is 46.7 kcal/mol, lower than that of the concerted β-elimination (49−54 kcal/mol).

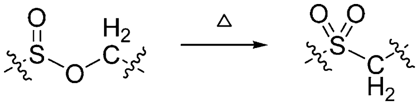
The traditional even-linked polysulfones, including longer conjugated alkene linker [$-CH_2-(CH{:}CH)_n-CH_2-$], will benefit from the low barriers to lose of conjugated alkenes $CH_2{:}(CH-CH)_n{:}CH_2$. The depolymerization follows a route exactly opposite to the radical copolymerization reactions of conjugated alkenes and sulfur dioxide.

There is an additional mode to initiate depolymerization. An impurity in polysulfone, the sulfinate [$-S(=O)-O-C-$] structure is generally generated in the copolymerization process by reaction of $RSO_2^{\bullet}$ with alkene. Before the temperature reaches the onset for C−S rupture, the unstable sulfinate can undergo more facile O−C scission toward the same alkyl and sulfonyl radicals. With this O−C rupture serving as a more accommodating initiator for radical chain depolymerization, the overall activation energy will decrease by $^1/_2\Delta$BDE of 6.4 kcal/mol [BDE(C−O), 59 kcal/mol; BDE(C−S), 72 kcal/mol, based on the CBS-QB3 model reactions e and j in Table 2], leading to a nonlinear relationship in the Arrhenius plot for untreated polysulfones.



$$R{-}\overset{\overset{O}{\|}}{S}{-}OR \longrightarrow R_c^{\bullet} + R_s^{\bullet} \qquad (12)$$

Preheating (annealing) at a relative low temperature for a while can consume these unstable species, e.g., by sulfinate reorganization into the normal stable structure of polysulfone.[8] Such exogenous initiators, possibly also including remaining radical initiators from the previous polymerizations, do perturb the experimental measurement on Arrhenius activation energy of polysulfone depolymerization, leading to a diversity of experimental data (18−48 kcal/mol) in the literature.[5−9]



$$\Delta H_{\mathrm{rxn}} = -12.7\ \mathrm{kcal/mol} \qquad (13)$$

For odd-linked sulfones, including the Schmidt-Winkel and Wudl polymer discussed earlier, a concerted elimination mechanism occurs. The homolysis is feasible but unproductive, since the depolymerization does not ensue. The odd-linked alkyl radical cannot produce alkene directly, but would produce alkyl diradical instead.

Model calculations indicate that this endothermic step requires 70 kcal/mol (CBS-QB3, reaction **14**), implying that E_{tot} is at least as high as 78.7 kcal/mol if other parameters are identical to the even-linked polysulfones. Thus, the radical chain pathway is insignificant in the odd-linked polysulfones.

$$CH_3SO_2CH_2CH_2CH_2^{\bullet} \rightarrow CH_3SO_2^{\bullet} + {}^{\bullet}CH_2CH_2CH_2^{\bullet} \quad \Delta E = 69.6\ \mathrm{kcal/mol}\ (\sim E_d^{\,c}) \qquad (14)$$

The findings also rationalize the fact that, in cases of special poly(styrene-sulfone)s that were prepared by adding an excess amount of styrene monomers in polymerization, the activation energy increased with the content of styrene in the polymer significantly, since forming longer alkyl linkers may increase chances to inhibit a radical propagation.[27]

The carbon-centered and sulfonyl radicals have been detected in even-linked polysulfone by ESR spectroscopy at room temperature; Vogel and co-workers have found that a trace amount of the radicals in poly(methylidenecyclopentane−sulfone) catalyze alkene isomerization.[28]

Conclusions

Even-linked polysulfones, including those with conjugated linkers [$-CH_2-(CH{:}CH)_n-CH_2-$], can decompose by homolysis of C−S bonds, or lower-energy C−O bonds if the sulfinate structure is present as impurity in the polymers, followed by facile radical chain paths that depolymerize the polysulfones via alternating loss of alkene and sulfur dioxide. Heat treatment can reorganize the weak C−O bond to a normal C−S bond in the polysulfones. This process increases the onset temperature of the thermal degradation of the conventional alkene−SO_2 copolymers, e.g., PBS. Because of the nature of radical chain depolymerizations, such polysulfones always suffer from a low onset temperature (typically, 135 or 200 °C for untreated and heat-treated PBS, respectively, lower than its melting point) and relatively low activation energy (less than 47 kcal/mol).

When the polysulfone contains an odd number of carbon atoms, there is no such low-energy radical path for decomposition available to the alkyl radical formed from C−S cleavage in polysulfones. They cannot depolymerize by the low-energy free radical mechanism. These polymers depolymerize by the cyclic β-elimination mechanism with the relatively higher activation energy (∼54 kcal/mol, e.g., SWWP), basically independent of the nature of functional linkers. Such polymers have been found to be thermally stable up to 375 °C.[2]

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Supporting Information Available: Tables of comparisons of decomposition of disulfones with alkyl linkers of odd- and even-number carbons and *xyz*-coordinations of critical points in the mechanisms (CBS-QB3), and a figure showing details of the free energy maximum method for C−S ruptures. This material is available free of charge via the Internet at http://pubs.acs.org.

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