

Thermal Degradation of Polyarylethersulfones

1. Review of Underlying Chemistry

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The development of composite materials and the appearance of new applications in the aerospace and automotive industries have revived interest in high performance organic polymers, identified as possible matrices for fiber/polymers composites. Polyarylethers, which were some of the first commercialized plastics, are among the polymers being considered. They form a class of polymers that are tough, have a high softening temperature and maintain their mechanical properties for extended periods of time at temperatures over 150°C [1,2,3].

Sulfone-containing polyarylethers generally include one or more aromatic rings linked together by ether and sulfone groups. One class of these polymers also contains isopropylidene linkages. The nature and proportions of the different linkages determine the physical properties of each polymer. Herein we focus attention on polymers with phenyl ether (Ph-O-Ph) and phenyl sulfone (Ph-SO₂-Ph) bonds; we will consider polymers containing the propylidene linkage in a follow-up paper.

The thermoplastic behavior of polyarylethersulfones makes them very attractive for injection molding, forming, pultrusion and other manufacturing techniques in which the raw material is softened by heating in order to be processed. Due to their high softening temperature (glass transition temperature > 195°C), these polymers require processing temperatures of 350 to 400°C. At these temperatures, the chemical bonds within the macromolecules are thermally labile, which can lead to changes in the structure of the polymer. Structural changes can also occur when the polymers are maintained at high operational temperatures (150 to 200°C) for an extended period of time.

The foregoing manufacturing and operational issues have motivated studies of the thermal behavior of the polyarylethersulfones since the early stages of development, and elucidation of the mechanism of degradation has been pursued. The literature in this area is largely experimental and suggests that the thermal decomposition chemistry can cause topological changes leading to altered polymer properties, such as the formation of a gel from a linear polymer. This literature motivated the present work aimed at the development of a molecular model of polymer reaction and diffusion using our recently formulated Monte Carlo approach to the simulation of the reaction of macromolecules.

Most of the experimental work on thermal and radiolytic stability has recently been reviewed by Verma [1]. As is evident in the literature, there is no objective measure of the thermal stability of polyarylethersulfones. If the maximum decomposition temperature is the important parameter, polymers align in the order of increasing stability in one way [5,6,7]. On the other hand, if gel formation is to be avoided (e.g. during injection molding), then stability is ordered in another way [6]. Thus, thermal or radiative stability must be considered in relation to one or more of the polymer's properties when exposed to heat or radiation.

The properties of interest are directly linked to the applications for which the polymers are intended. Polymers may have good stability for certain applications while performing poorly in others. For example, a polymer with a high degradation temperature may exhibit rapid gel formation at processing temperature. The following have been used as a measure of thermal stability: lowest degradation temperature and weight percent loss in vacuum or in air obtained from TGA analysis [5,6,7,10,11,16,17], gel and gas formation [6,7,8,10,11,12,13,18], intrinsic and limiting viscosity of the sol fraction [8,9,10,18,12,13,15], modulus [9], tensile flexural strength [9,13,15] and molecular weight distribution of sol fraction [14,20,21]. Some properties studied in the literature have no direct link to properties necessary for use or manufacturing, but provide clues towards the determination of the underlying phenomena. They include optical density [19], infrared and nmr spectra [6,10,17,18,20] and bond scission and crosslinking rates [8,9].

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The behavior of the polymer depends not only on its chemical composition but on the physical structure as well. Only one recent publication by Nakron and coworkers [19] addresses the influence of initial molecular weight distributions on the thermal reaction of polyarylethersulfones. They show marked differences in the optical densities and oxygen uptake in the degradation of different molecular weight fractions of the chemically identical polyarylethersulfones. Also, Brown et al. [13] have shown large differences in the gel formation during radiolytic degradation of polyarylethersulfones when the reaction temperature is above and below the glass transition temperature.

This explicit relationship between reactivity and structure has prompted the development of the present molecular model of polymer degradation. This model, which incorporates fundamental information concerning the reaction of the polymers' reactive moieties and mobility of the polymer segment, explicitly links the structure of the system to its reactivity and reaction path. The model consists of a Monte Carlo simulation, within a percolation grid, of reaction and segmental mobility of polymer chains.

The framework for this model is the underlying basic chemistry on which it rests. We present the development of the model in two parts. Part 1, the present manuscript, delineates the controlling elementary steps of pyrolysis. These are assembled into a prediction of the reactivity of a model polysulfone in Part 2, when the mechanics of the Monte Carlo simulation of structure, reaction, and diffusion are presented.

Thus our present focus is on basic chemistry. What follows is a result of a thorough review of not only the polyarylethersulfone literature but also the physical and organic chemistry literature of the reactions of polyarylethersulfone-related moieties. Our objective was to discern reaction pathways and kinetics parameters. The former would provide Monte Carlo allowable "transitions" while the latter would provide transition probabilities.

THE THERMAL CHEMISTRY OF POLYETHERSULFONE SYSTEMS

The thermal degradation of polyarylethersulfones was postulated in the original study by Hale et al. [7] to be free radical in nature. This has been probed since in numerous thermal and radiative degradation studies with different formulations of related polyarylethersulfones [4,6,8,10,21]. An important publication by Lyons et al. [22] on the radiative effects on polyarylethersulfones and related model compounds confirmed such an assumption by identifying the presence of several free radicals during ESR monitoring of the reaction.

Although they formulated the main hypothesis behind the degradation process, namely that the "weaker" link breaks and generates radicals, Hale et al. [7] did not account for crosslinking reactions. Their study reports thermal gravimetric experiments that mask the extent of the structural changes occurring in the melt. Their proposed mechanism includes only bond breaking through initiation and bond forming through termination.

Davis [8] was the first to obtain explicit evidence of crosslinking reactions by measuring the gel fraction in the reaction products as a function of time. The experimental curve was similar to the gelation results obtained during copolymerization of polyfunctional monomers [44]. He concluded that crosslinking must occur by addition of polymer radicals to other polymer chains, but did not advance a mechanism for such a process.

A mechanism for crosslinking, involving cyclohexadienyl-type radicals observed by Lyons et al. [22], was later proposed by Danilina et al. [6]. It involves the addition of phenyl radicals, produced by initiation, to the benzene rings in the polymer chains, followed by elimination of hydrogen atoms. More recent publications by Narkon et al. [18] and Kuroda et al. [21] calculate crosslinking and bond scission rates from experimental results, using the Charlesby method for the former and their own novel method for the latter. Their calculations, however, do not take into account the nature of the crosslinking process and only schematic mechanisms of reaction are presented.

It is clear from the literature that structurally significant reactions involved in the radical chains include not only initiation and termination reactions, but also addition steps that can lead to crosslinking. Herein, we reduce the enormous complexity of these types of reactions via their organization into reaction families. Reactions involving radicals are classified into three main groups:

- Initiation reactions, which create radicals from stable molecules;
- Propagation reactions, in which the number of radicals is conserved;
- Termination reactions, which consume radicals.

INITIATION REACTIONS

Hale [7] first proposed that the scission of the "weaker" bonds were responsible for the generation of radicals. Bond dissociation energies identify the carbon-sulfur bond (66 kcal/mole) in the sulfone group.

Although the nature of the initiation has been widely accepted, the mechanism remains a subject of discussion. The dominant view, proposed by Hale et al. [7], consist of a two step initiation mechanism, where the carbon-sulfur bond breaks to produce a phenyl radical and a sulfonyl radical. The Ph-SO₂[•] radical can further decompose to Ph[•] and SO₂ or react with other molecules. This view is shared by Lyons et al. in their radiation damage studied, but no conclusive evidence has been provided in the literature [22].

Ayscough [23] proposed a concerted mechanism in which simultaneous cleavage of adjacent carbon-sulfur bonds occurs.

The fission to Ph[•] and Ph-SO₂[•] described above occurs with $\log_{10}A_1$ (s⁻¹) = 15 and an activation energy equal to the dissociation energy of the carbon-sulfur bond, E₁ = 65 kcal/Mole. For reaction of Ph-SO₂[•] to Ph[•] and SO₂, $\log_{10}A_2$ (s⁻¹) = 15 and E₂ = 45 kcal/Mole is equal to the enthalpy of reaction, for the unimolecular decomposition[†].

The phenyl radicals produced in the initiation steps can either terminate or react with other molecules generating new radicals, which propagate a pseudo kinetic chain. The list of possible radicals participating in radical-molecule reactions is limited to H[•], Ph[•], R-O[•], R-SO₂[•], Cyclohexadienyl radicals, cyclohexenyl radicals and cyclohexyl radicals.

PROPAGATION REACTIONS

Three types of propagation reactions are present in the degradation mechanism: Addition of a radical to benzene rings and double bonds; elimination or β-scission; and hydrogen abstraction by a radical from a stable molecule. We consider each in turn.

Addition Reactions

The work of Danilina et al. [6] suggest that addition reactions to the polymer's benzene ring is the vehicle for crosslinking. Radicals can add to a substituted benzene ring to yield a substituted cyclohexadienyl radical.

These reactions are very fast when the attacking radical is a phenyl radical [24,27,29,30,31,32,34,35,36,39] or a hydrogen atom [25,26,28,37,38]. In the case of phenyl radicals, at 450°C the addition to a benzene ring is 40 times faster than abstraction of hydrogen by the radical from benzene.

Rate constants for addition of hydrogen atoms and phenyl radicals to substituted benzenes have been reported in the synthetic organic chemistry literature[24-39]. Jansen [27] provides a value of 7.8×10^4 M⁻¹ s⁻¹ for the rate constant of addition of phenyl radicals to benzene. Pryor [25] estimated the rate constant for addition of hydrogen to benzene at 10⁹ M⁻¹ s⁻¹ at 35°C. The activation energy for the latter reaction is known to be 3.8 kcal/mole [24,26,37], which implies a $\log_{10}A$ (M⁻¹ s⁻¹) = 11.7. Modelling the transition state for the addition of phenyl radicals provides an estimate of $\log_{10}A$ (M⁻¹ s⁻¹) = 7.7. Combined with the reported rate constant, the activation energy is calculated at E* = 3.83 kcal/moles. This value is very close to the hydrogen value and is consistent with the energetics of the reaction; the estimated enthalpy of reaction for hydrogen and phenyl additions are essentially equal at $\Delta H_R^\ddagger = -24.9$ kcal/moles and 25.1 kcal/mole respectively [25,26].

For all other radicals, the rate constant for addition, in its Arrhenius form, has been estimated from an Evans-Polanyi relationship relating activation energies to heats of reaction. The Evans-Polanyi relationship was used to estimate activation energies (E* = E₀ + α ΔH_R⁰ for exothermic reactions and E* = E₀ + (1-α) ΔH_R⁰ for endothermic reactions).

ΔH_R⁰ is the enthalpy of reaction, E₀ = 16.3 kcal M⁻¹, and α = 0.56. ΔH_R is calculated from the heat of formation of reactant and products determined from literature information or group additivity [41]. Estimated heats of formation are summarized in Table 1. The parameters E₀ and α were determined from the values of the activation energies for the addition of phenyl radicals and the addition of cyclohexadienyl radicals [27,42]. This procedure is described in detail elsewhere.

The pre-exponential factors are assumed to be 5×10^7 M⁻¹ s⁻¹, equal to the one for phenyl radical addition.

The rate constant for addition can also be affected by electronic effects due to the presence of substituents on the reactant molecules. This is particularly true for addition at different positions in substituted benzenes. According to the extensive literature on radical addition to substituted benzene rings [25-39], neutral radicals, such as phenyl radicals, preferentially add to the benzene ring at non-substituted positions. The reasons for such behavior are unclear. A possible ex-

[†] The heat of formation of the sulfonyl radical was calculated from the heat of formation of diphenyl sulfone, ΔH_f = -30.98 Kcal/Mole, and the bond dissociation energy of the C-S bond. Substituent effects, generated by the ether linkages at the para position to the sulfone linkage, have been neglected here.

planation is that for large radicals, the substituent may present an important steric hindrance to ipso-substitution reactions. Because of their size, small hydrogen atoms are assumed to be an exception and are allowed in our reaction scheme to substitute at occupied positions on a benzene ring. For any of the electro-neutral radicals that participate in the reaction mechanism, including the hydrogen atom, the preferred position for addition is ortho to a substituent, followed by the para position and, finally, the usually much less reactive meta position [24,29]. The relative selectivity toward each position is influenced by the electronic characteristics (electron donating or electron withdrawing) of the substituent and the attacking radical [24,29,31].

As an example, the rate constant for addition of a phenyl radical at an ortho position from an NO_2 group is 9 times greater than the rate of addition of the same radical on an unsubstituted benzene [24]. Values of the estimated relative activation energy and rate constant for addition of phenyl radicals, at 425°C, at every position of a substituted benzene to the rate constant of addition to any position in an unsubstituted benzene are summarized in Table 2 for all the possible substituents in the polymer systems considered in this work. Similar studies with other radicals show qualitatively the same results, for electro-neutral radicals [24,29,39]. Quantitatively, the values reported show a stronger influence of the substituents present on the neutral molecule rather than of the nature of the attacking radical. Consequently, the ratios reported in Table 2 are assumed to be the same for all other radicals present during polysulfone degradation.

An analogous reaction is the addition of radicals to the double bonds of cyclohexadiene and cyclohexene, which are not present in the original polymer but can be formed during reaction. Additions to double bonds are similar in nature to the addition to benzenes and consequently the same Evans-Polanyi relation was used to estimate activation energies.

Elimination Reactions.

The reverse reaction to additions are eliminations reactions. They are β -scission reactions in which hydrogen or a substituent are eliminated. The pre-exponential factors for these reactions were estimated at 5×10^{13} when hydrogen is eliminated and 5×10^{12} for elimination of a bulkier substituent. The activation energy, E_β , can be calculated from $E_\beta = E_A - \Delta H_R$, already determined from Table 1.

Hydrogen Abstraction

The last family of radical-molecule reactions is hydrogen abstraction from a stable molecule by any of the radicals. There is very little easily extractable hydrogen in the initial polymer. When the benzyl hydrogen is the one exchanged in this reaction, the rate for the fastest abstraction (by phenyl radicals or H^\bullet) is already several orders of magnitude slower than that for addition to the benzene ring. The only easily abstractable hydrogen in the initial polyethersulfone systems is the phenoxy-H. As the reaction progresses, however, more-saturated cyclohexadienes, cyclohexenes and cyclohexene, as well as a higher number of hydroxy and possible $-\text{SO}_2\text{H}$ groups form and bring an extra source of abstractable hydrogen.

The pre-exponential factor for these reactions was estimated from modelling the transition state at $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ when $\text{R}^\bullet = \text{H}^\bullet$ and $10^8 \text{ M}^{-1} \text{ s}^{-1}$ otherwise. It is comparable with literature values [43]. The activation energy was calculated using the Evans-Polanyi relation.

In this case, $\Delta H_R = d_{\text{R-H}}^0 - d_{\text{R}^\bullet\text{-H}}^0$. The bond energies $d_{\text{R-H}}^0$ and $d_{\text{R}^\bullet\text{-H}}^0$ were found in the literature [[56]] or estimated from group contribution methods. They are summarized in Table 3.

TERMINATION REACTIONS

Radical-radical reactions consume two radical chain carriers. These very fast reactions are responsible for the termination of the kinetic chain. They have kinetics implications, because they eliminate the chain carriers from the reaction mixture, and also structural implications, because they can create bonds.

Recombination Reactions

Recombination of two radicals is the simplest case of termination. Recombination is assumed to be non-activated and with $\log_{10} A (\text{M}^{-1} \text{ s}^{-1}) = 10$ when R_1 or R_2 are hydrogen atoms and $\log_{10} A (\text{M}^{-1} \text{ s}^{-1}) = 9$ $\text{M}^{-1} \text{ s}^{-1}$ otherwise.

Recombination reactions produce an increase in molecular weight but can only be responsible for crosslinking when one of the terminating radicals is a central radical in the polymer chain, such as a phenyl or cyclohexadienyl radical linked to two other benzene rings.

Disproportionation Reactions

Disproportionation reactions can occur, in competition with recombination, when one of the radicals has a donatable hydrogen at the α position. This is the case for cyclohexadienyl, cyclohexenyl or cyclohexyl radicals. From product yields reported in literature [24,26], the rate constant for disproportionation appears to be 3 times smaller than the one for recombination.

SUMMARY

The observed chemistry is the combination of these simultaneous reactions. Their quantitative contributions to the degradation process is a function of their relative rates and their structural significance in the complex mechanism of reaction. The model developed in the following sections incorporates the complete set of elementary steps into a quantitative molecular representation of the polymeric melt. We conclude here with a more quantitative description of the kinetically and structurally significant chemistry.

The thermal reaction begins by fission of the weak Ph-SO₂-Ph bond. The net result is the formation of SO₂ gas and two polymeric phenyl radicals.

The phenyl radicals begin the propagation steps. Phenyl radical addition to a benzene ring affords a substituted cyclohexadienyl (CHD) radical, the key intermediate in the overall chemistry. The CHD radical can add to a neighboring benzene ring, creating a crosslink and a different CHD radical. The CHD radical can also revert to the original phenyl radical and benzene ring, or eliminate a substituent as a radical that can continue the propagation cycle. The CHD radical can also terminate which, when by recombination, will generally lead to another crosslink.

The complexity of this system is that at least seven (7) different radicals can participate in this chemistry. Moreover, the importance of a given reaction depends on whether the radical is at the terminus, or interior of a linear chain, a free low molecular weight radical, or part of a crosslinked polymeric arm. This motivates the use of structure-explicit computer models to track the reaction rates and structural significance. This is the topic of our companion paper to follow.

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Table 2. Substituent Effects for Phenyl Radical Addition to Substituted Benzenes

Substituents	Ortho	Meta	Para
-SO ₂ -†	2.3	1.0	2.1
-O-††	1.2	1.0	1.1
Others†††	1.0	1.0	1.0

† Reactivity towards -SO₂- substituted benzenes was estimated from values for NO₂ substituted benzenes.

†† Reactivity towards -O- substituted benzenes was estimated from values from -O-CH₃ substituted benzenes.

††† Estimated from the values for saturated hydrocarbon.

Table 1. Heat of Formation of Molecules and Radicals [kcal/mol]

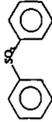
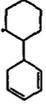
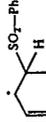
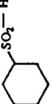
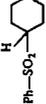
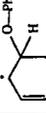
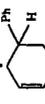
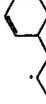
0	H ₂		52.1		-29.3	40.4
19.8			78.6			13
-30.98			43.9	SO ₂		47
8.2	Ph-O-Ph		80.4	SO ₂		45.33
42.92	Ph-Ph		0.65	Ph-O [•]		-23.12
-97.27						12.99
26			43.24	Ph-O-C ₆ H ₁₁		53.17
-0.8			30	Ph-C ₆ H ₁₁		58.94
						24.42

Table 1. Heat of Formation of Molecules and Radicals [kcal/mol]

	18.52		3.39
	-10.76		
	40.4		
	-69.37		
	-40.24		

Table 3. Bond Dissociation Energies [kcal/mol]

H-H	104.2		82.3±1.3
	110.9		83.±3
	86.5		104.4±1
	-66		103.4±1
	66		102.4±1
	86		104.7±1
	73±5		104.7
	95.5		86
	98.2±1		65
	95.1±1		80
	88±1		
	86.3±1.5		