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Mechanism of Poly(*p*-phenylene sulfide) Growth from *p*-Dichlorobenzene and Sodium Sulfide

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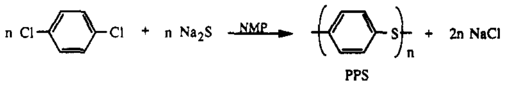
ABSTRACT: The chemistry of poly(*p*-phenylene sulfide) (PPS) growth from Na_2S and *p*-dichlorobenzene in NMP is dominated by the ionic S_NAr mechanism. Consistent with this mechanism are model reactions that obey discrete second-order reaction kinetics in both independent and competition experiments. Reaction rates are as well affected by substituents in a fashion predicted by the S_NAr mechanism. Diagnostic reactions to probe radical mechanisms provide no evidence for radical intermediates with the possible exception of certain anomalous side reactions. The unusual behavior of the growth of high molecular weight PPS at low conversions is totally explained in terms of discrete ionic reaction rates. NMP not only facilitates the S_NAr chemistry through its dipolar aprotic properties but also functions as a catalytic reactant in transforming Na_2S into a soluble nucleophile.

Edmonds and Hill, inventors at will,
How does your polymer grow?
Chemistry radical or ionic, or something exotic,
There are those who predicted we never shall know.
A polymer so tough, simple studies weren't enough,
Models were needed to get in the know.
With second-order rates, and free energies that correlate,
S_NAr we now know is the star of the show.

Introduction

The industrially important semicrystalline polymer poly(*p*-phenylene sulfide) (PPS) is produced commercially from a sodium sulfide equivalent (e.g., an equimolar mixture of sodium hydrosulfide and sodium hydroxide) and *p*-dichlorobenzene (DCB) in *N*-methylpyrrolidinone (NMP) at 200–280 °C (eq 1).[1] At least three different mechanisms have been proposed in the literature for PPS growth by this process (vide infra).[2] To date, compelling experimental evidence that differentiates between the three mechanistic choices has not been reported.



(1)

PPS is insoluble in all common organic solvents below about 200 °C[2-4] and so is extraordinarily difficult to characterize in detail. As a result, molecular weight distributions and end-group types and populations are neither readily discerned nor reliably related to the reaction parameters. The severity of the polymerization conditions poses additional experimental difficulties for mechanistic studies. The polymerization mixture is highly corrosive toward glass and many metals, and polymerizations are generally conducted at temperatures above the boiling point of NMP. Therefore, closed pressure vessels of suitable corrosion-resistant metallurgy are required. These circumstances have made the polymerization process very difficult to study by conventional laboratory techniques. The difficulties in experimental procedures and the uncertainties in experimental interpretations have made the polymerization chemistry a rich subject for speculation.

An enigma that needs to be explained is why does the polymerization *not* exhibit classic condensation polymerization behavior. That is, polymers of higher molecular weight than predicted by the Carother's equation are produced at low conversions[3] and even at unequal DCB to Na_2S ratios.[5] Because the patent literature demonstrates that high molecular weight PPS has been prepared almost exclusively in cyclic amides, another key question to be answered is what unique qualities does NMP possess that makes it such a special reaction medium for the polymerization. Still another unusual feature is that possible initial intermediates in the polymerization, which could distinguish between mechanistic pathways, have yet to be experimentally verified in the literature.

In 1962, Lenz, Handlovits, and Smith studied the self-condensation of sodium 4-chlorobenzenethiolate as a possible route to PPS.[6] On the basis of model compound studies, they concluded the mechanism followed an addition-elimination sequence now commonly referred to as an S_NAr mechanism (they also readily excluded "benzyne" and catalytic mechanisms). This is a very well-established mechanism in organic chemistry and has been thoroughly reviewed in Miller's monograph.[7] If the same mechanism is operative in the commercial PPS synthesis, it can be conceptually displayed for a growth step as in Scheme I. Subsequent publications by Brady[8] and Sergeev and Nedelkin[9] also suggest the S_NAr mechanism.

The second proposal is that the polymerization occurs by a one-electron-transfer process with radical cations as reactive intermediates. This proposal was published by Koch and Heitz from 1983–85[10,11] and for convenience is referred to herein as the radical-cation mechanism. It is unique in that no "stable" oligomeric intermediates (with the single exception of 4-chlorothiophenol) are formed in the polymerization process; high molecular weight polymer is produced directly via a continuously propagating polymer chain growth process involving radicals. This mechanism was proposed in an attempt to rationalize (a) the formation of polymers of higher molecular weight than predicted at low conversions, (b) the formation of disulfides in model compound studies, and (c) the high stability of the radical cations of PPS oligomers in mass spectral analyses. This mechanism is outlined in Scheme II. Because it is a new mechanistic concept for "nucleophilic" aromatic substitution, its general characteristics and responses to reaction variables have not been established.

The third is Bunnett's radical-anion mechanism[12] ($S_{RN}1$), which was applied to PPS polymerization by Annenkova et al. in 1986.[13,14] Interestingly, oligomeric PPS has been successfully synthesized via the $S_{RN}1$ mechanism at room temperature from sodium 4-bromobenzenethiolate in dimethyl sulfoxide (DMSO) solvent with

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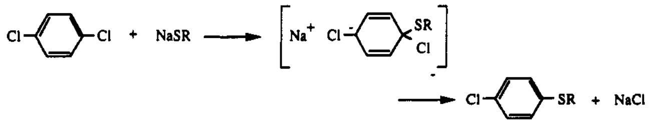
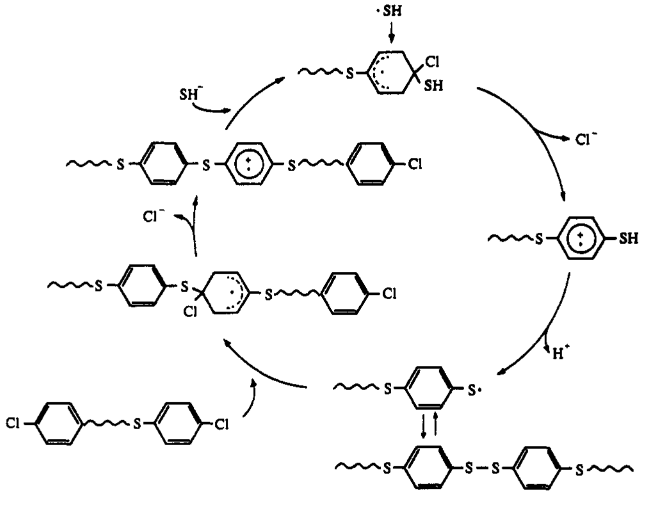
Scheme I[a]
S_NAr Mechanism for PPS Growth Step

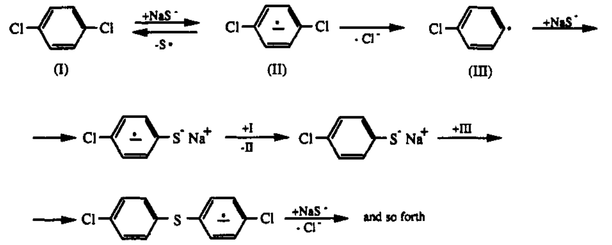


[a] R = H, $(C_6H_4S)_nC_6H_4Cl$.

Scheme II
Radical-Cation Mechanism for PPS Growth (Redrawn from Reference 11)

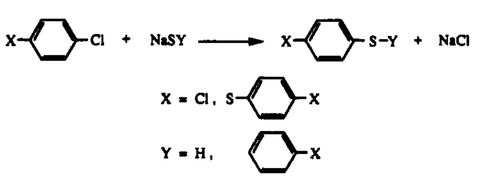


Scheme III
$S_{RN}1$ Mechanism for PPS Growth (Redrawn from Reference 14)



diazonium salts as radical initiators.[15] However, the operability of the $S_{RN}1$ mechanism in the high-temperature commercial reaction, eq 1, remains an open question. Scheme III presents a conceptual illustration of the mechanism as applied to an initial stage of PPS synthesis. Although this is also a radical chain process, there are no intermediates in common with the radical-cation mechanism. Characteristics of reactions occurring by $S_{RN}1$ mechanisms include an initiation process, a preference for polar non-hydrogen-donating solvents, rate laws that are sometimes complex, and inhibition of the radical chain by hydrogen-donating or electron-accepting reagents.[16] The inhibiting reagent, however, may not be universal to all $S_{RN}1$ reactions.[16] In addition, direct disubstitution of dihaloarenes is commonly observed by this mechanism.[12,16]

Model compound reactions were studied to establish the mechanistic aspects of PPS synthesis, while circumventing the polymer analytical difficulties. A premise upon which the present study is based is that the mechanism of the polymer growth steps, generalized in eq 2, will be the same as that of discrete model compound reactions. To this end, a study of aryl chloride substitutions by organosulfur anions under reaction conditions approximating PPS synthesis has been undertaken. The conclusion from these studies is that polymer growth occurs principally by the S_NAr mechanism.



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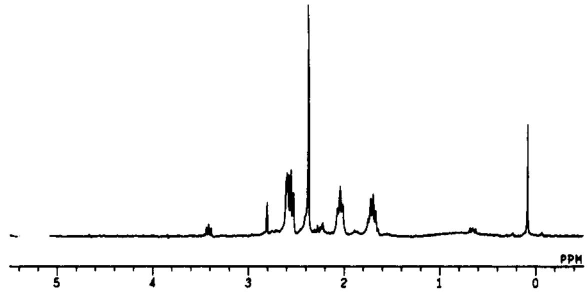


Figure 1. ^1H NMR spectrum (270 MHz) of SMAB–NaSH in DMSO-d_6 at 90 °C. Full assignments of SMAB–NaSH and SMAB resonances in their ^1H and ^{13}C NMR spectra in both D_2O and DMSO-d_6 are presented in Table I. In the spectrum shown, minor resonances at 2.75, 1.90, 0.65, and 0.08 ppm due to the reference material, sodium 3-(trimethylsilyl)-1-propanesulfonate, and at 3.42, 2.82, 2.25, and 1.90 ppm due to residual NMP are also apparent.

Table I
NMR Chemical Shifts of SMAB and the SMAB–NaSH Mixture[a]

	in D_2O		in DMSO	
	SMAB	SMAB–NaSH	SMAB	SMAB–NaSH
		^1H NMR		
N*H*			2.61 (b)	2.60 (b)
NCH_2	2.61 (t)	2.68 (t)	2.56 (t)	2.57 (t)
NCH_3	2.40 (s)	2.45 (s)	2.39 (s)	2.38 (s)
COCH_2	2.29 (t)	2.29 (t)	2.02 (t)	2.04 (t)
$COCH_2CH_2$	1.80 (m)	1.84 (m)	1.68 (m)	1.72 (m)
S*H*				0.8 (b)
		^{13}C NMR		
*C*O	184.3	183.9	177.2	177.8
$NHCH_2$	51.2	50.9	52.1	52.1
NCH_3	36.3	36.2	36.2	36.2
$COCH_2$	35.4	35.1	36.0	36.0
$COCH_2CH_2$	26.4	25.8	26.5	26.6

[a] Values are reported in ppm, referenced at 0.08 ppm with the trimethyl protons of sodium 3-(trimethylsilyl)-1-propanesulfonate. Abbreviations used are t for triplet, s for singlet, m for multiplet, and b for broad. Relative integrated peak areas of ^1H NMR spectra are consistent with the peak assignments.

Results and Discussion

Reactants. The PPS polymerization reactants are formally accounted for in eq 1; however, the identities of the "reactive" sulfur species and the function of NMP are problematic. During polymerizations, the only groups that can be assigned to the ends of growing polymer chains with a high degree of confidence are 4-chlorophenyl. The precise nature of reactive sulfur species (i.e., –SH, –S•, –S⁻, or –SNa) on chain ends is not easily assumed.

When hydrated Na_2S dissolves in NMP at elevated temperatures, a chemical reaction occurs, yielding an isolable product with the empirical formula $Na_2S·NMP·H_2O$.[17] The ^1H and ^{13}C NMR spectra (Figure 1 and Table I) of this product clearly reveal that the NMP ring has been hydrolytically opened to yield sodium 4-(*N*-methylamino)-butanoate (SMAB).[17] The broad resonance at 0.8 ppm in Figure 1 is assigned to the hydrogen of NaSH. This product is therefore more precisely named as a SMAB–NaSH mixture (same empirical formula). Separation of NaSH from SMAB could not be achieved by recrystal-

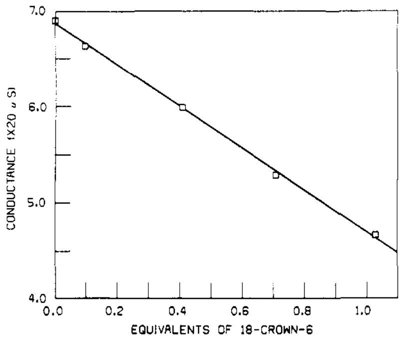


Figure 2. Conductance titration of 3.9 M SMAB–NaSH in NMP at 150 °C with 18-crown-6.

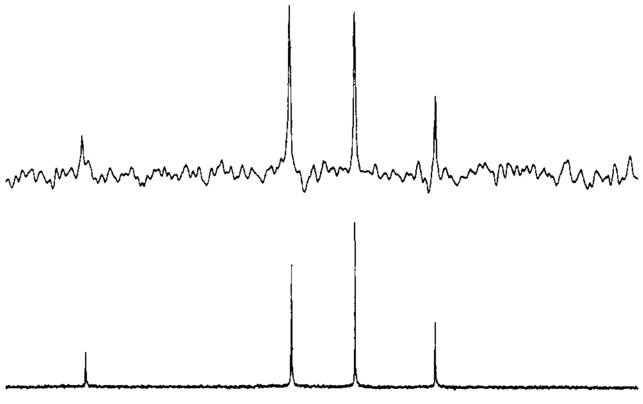


Figure 3. ^{13}C NMR spectra of sodium benzenethiolate plus water in NMP at 25 °C (bottom) and 250 °C (top).

lization; an equimolar mixture precipitated.[17] The same SMAB–NaSH mixture can be prepared by treating SMAB with NaSH or by heating NaSH, NaOH, and NMP together. The SMAB–NaSH mixture is soluble in warm NMP, while, in stark contrast, anhydrous Na_2S and NaSH are virtually insoluble. SMAB alone is readily prepared from NaOH and NMP at elevated temperatures.[18] Its ^1H and ^{13}C NMR spectra are also reported in Table I for comparison. There are no remarkable differences between the NMR spectra of SMAB and SMAB–NaSH. Shifts in resonances of the carbonyl carbon and the α hydrogens between the two solvents suggest the electronic environment about the carbonyl group is solvent dependent. In order to investigate whether any complex ion association existed between SMAB and NaSH in NMP, a conductometric titration was performed on 3.9 M SMAB–NaSH in NMP with 18-crown-6 at 150 °C. The negative slope of the conductance with added crown ether (Figure 2) indicated solvent-separated ion pairs, at least for one of the sodium ions. While a more precise description of the sulfur nucleophile in solution is desirable, further details are not available.

The nature of the sulfur end groups, whether arenethiol or arenethiolate, on growing polymer chains has been addressed with model compounds. The relative importance of these two sulfur types was assessed by reacting equimolar amounts of thiophenol and NaOH in NMP and observing the equilibrium between thiophenol + NaOH and sodium benzenethiolate + water at 25 and 250 °C. As shown in Figure 3, the ^{13}C NMR spectra are identical at both temperatures and the chemical shifts are those of the benzenethiolate ion rather than thiophenol.

In most of the work to be described, the reactions selected for study were chosen because they were believed to simulate the polymer growth steps closely. Further, complete identifications of reactants, stable intermediates, and products were possible in most experiments. Throughout the remainder of this report, "Na_2S" designates that hydrated Na_2S or NaSH/NaOH were charged to the reaction and that the SMAB–NaSH mixture is the actual reactant, as indicated vide supra.

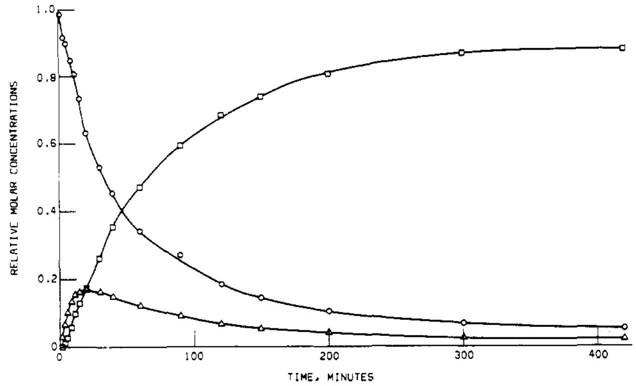
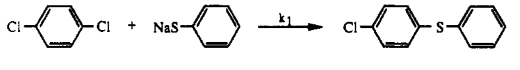
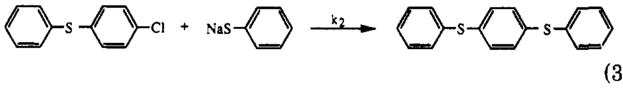


Figure 4. Relative molar concentrations of DCB (○), 1-chloro-4-(phenylthio)benzene (△), and 1,4-bis(phenylthio)benzene (□) vs time during the reaction of 0.400 M sodium benzenethiolate with 0.200 M DCB in NMP at 200 °C.

Selectivity. The selectivity of the substitution process was examined through a careful GC/MS analysis of the products obtained upon treating DCB with 2 equiv of sodium benzenethiolate in NMP at 200 °C (eqs 3a and 3b). The concentrations of DCB, 1-chloro-4-(phenylthio)benzene, and 1,4-bis(phenylthio)benzene as a function of time are illustrated in Figure 4. Figure 4 presents data for a reaction in which air was carefully excluded. In this case, no side products or isomeric analogues could be found. However, when oxygen was not rigorously excluded or temperatures greater than 200 °C were used, various side products could be observed.

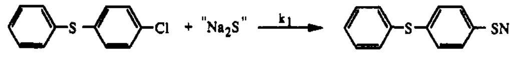


(3a)

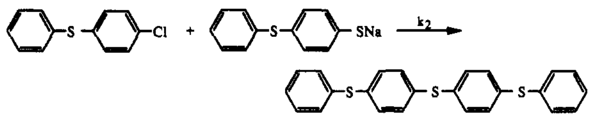


(3b)

A similar study of the reaction of Na_2S with 2 equiv of 1-chloro-4-(phenylthio)benzene (eqs 4a and 4b) was also undertaken. When the same attention to experimental detail was taken and when the reaction aliquots were maintained under argon until acidification and GC analysis, only 1-chloro-4-(phenylthio)benzene, 4-(phenylthio)thiophenol, and bis(4-phenylthiophenyl) sulfide were observed (see Figure 5). However, if air was not excluded from the raw aliquots, the GC analysis showed varying amounts of bis(4-phenylthiophenyl) disulfide in place of 4-(phenylthio)thiophenol. The oxidation of mercaptans in air is well-known and accounts for the occurrence of any disulfides.



(4a)



(4b)

The formation of high molecular weight PPS demands that each individual growth step be a highly selective process. This is precisely the finding of the model

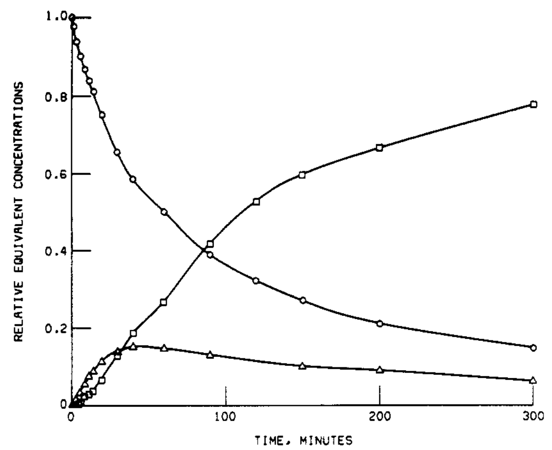


Figure 5. Relative equivalent concentrations of 1-chloro-4-(phenylthio)benzene (○), 4-(phenylthio)thiophenol (after acidification) (△), and bis(4-phenylthiophenyl) sulfide (□) vs time during the reaction of 0.100 M "Na_2S" with 0.200 M 1-chloro-4-(phenylthio)benzene in NMP at 200 °C.

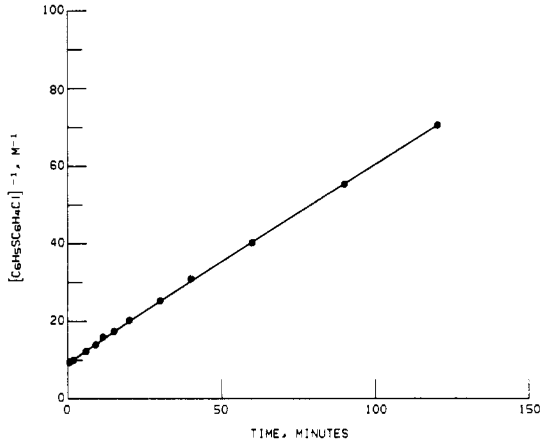


Figure 6. Second-order rate plot for the equimolar reaction of sodium benzenethiolate with 1-chloro-4-(phenylthio)benzene in NMP at 200 °C.

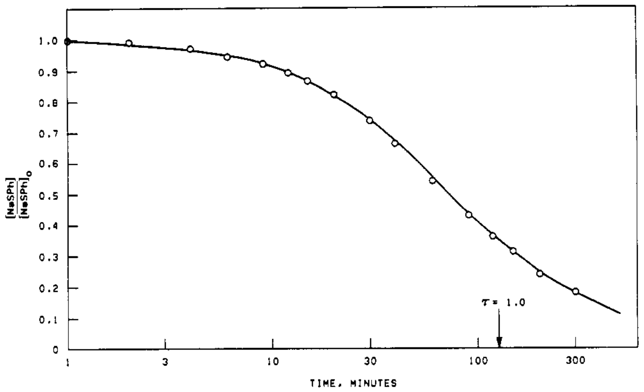


Figure 7. Graphical analysis of the consecutive second-order reaction of 0.200 M sodium benzenethiolate with 0.100 M DCB in NMP at 200 °C. The circles are experimental data points while the solid line is the theoretical curve for $k_2/k_1 = 3.8$. The position for $\tau = 1.0$ is fixed by the theoretical curve. Rate constants were calculated by using the time where $\tau = 1.0$ (see ref 20 for details).

Table II
Comparison of Second-Order Rate Constants for Aryl Chloride Displacements by Sulfur Nucleophiles in NMP at 200 °C Measured by Various Methods[a]

	rate constant value, L mol^{-1} s^{-1}		
reaction	A	B	C
C_6H_5Cl + NaSPh	2.6×10^{-5}		2×10^{-5}
p-ClC_6H_4Cl + NaSPh		1.6×10^{-3}	1.75×10^{-3}
p-$C_6H_5SC_6H_4Cl$ + NaSPh		6.1×10^{-3}	6.0×10^{-3}
p-$C_6H_5SC_6H_4Cl$ + "Na_2S"		3.5×10^{-3}	4.0×10^{-3}

[a] Method A is a conventional second-order integrated rate analysis of a reaction using equimolar amounts of the coreactants. B is a graphical analysis of a consecutive reaction using stoichiometric amounts of the coreactants.[20] C is a pseudo-first-order analysis of a reaction using a 100-fold excess of the aryl halide.

reactions. An ionic S_NAr substitution pathway could well be expected to exhibit this high selectivity. A lower selectivity might be expected in radical processes, since the intermediates could be capable of abstracting hydrogen atoms from NMP. Yet, the unusually high reactivity of arenethiolates toward aryl radicals[19] might make the $S_{RN}1$ mechanism a very selective process also. Examples of $S_{RN}1$ reactions exhibiting high selectivity are known.[16]

The radical-cation mechanism was proposed in large part based on the observance of a disulfide intermediate in the reaction of 1-chloro-4-(phenylthio)benzene with Na_2S.[10,11] As mentioned above, we observed the disulfide intermediate in this same reaction only when air was allowed to contact samples withdrawn from the reaction mixture. Under anaerobic work-up conditions, the disulfide *was not produced.* As a result, there is no compelling need at this point to invoke arylthio radical intermediates in the reaction mechanism.

Kinetics. The reaction of sodium benzenethiolate with either chlorobenzene or 1-chloro-4-(phenylthio)benzene obeyed classic second-order kinetics through at least 90% conversion of the reactants at 200 °C in NMP. Conventional second-order plots like that shown in Figure 6 were typically obtained. For the disubstitution processes in eqs 3a,b and 4a,b, a straightforward mathematical analysis was not possible because the rate equation for a consecutive second-order process could not be integrated by exact methods. However, rate constants could be determined by using a graphical method (see Figure 7).[20] The value of k_2 in eq 4b determined by the graphical analysis of the reaction of Na_2S with 1-chloro-4-(phenylthio)benzene closely matched that obtained in the direct reaction of sodium 4-(phenylthio)benzenethiolate with 1-chloro-4-(phenylthio)benzene. Several reactions were also run under pseudo-first-order conditions. Plots of the limiting reagent with time followed classic first-order behavior. The second-order rate constants from these studies agreed with those determined by conventional second-order studies. Rate constants determined in these studies are listed in Table II.

In either of the disubstitution processes in eqs 3a,b and 4a,b, the ratios of the two rate constants could be calculated from component concentrations determined in samples taken during experiments (using eq 33–27 in ref 21). In each case examined, this ratio remained constant throughout the experiment, indicating a constant stepwise substitution process. Furthermore, in pseudo-first-order reactions of DCB with excess sodium benzenethiolate, the ratios of the monosubstituted to disubstituted product were identical with respect to DCB conversion at 0.001 00 M DCB as well as at concentrations 1000-fold higher. Thus, chloride substitution by a sulfur anion occurs stepwise with discrete rate constants over a 1000-fold concentration range of the aryl halide. This behavior strongly indicates an S_NAr rather than an $S_{RN}1$ process. For example, under $S_{RN}1$ conditions, the initial ratio of disubstitution to monosubstitution products in the reaction of 1,3-dichlorobenzene with diethyl phosphite ion increases with increasing dilution—a logical consequence of the electron-transfer kinetics of the $S_{RN}1$ mechanism.[22]

Table III
Reaction Rate Comparisons for Aryl Chloride Displacements by Sulfur Nucleophiles in NMP at 200 °C in Independent and Competition Experiments

	relative reactivities	
reaction	separately	in competition
p-$C_6H_5SC_6H_4Cl$ + "Na_2S"/ NaSPh	1/1.5	1/1.5
NaSPh + C_6H_5Cl/p-ClC_6H_4Cl	1/67	1/51
NaSPh + p-ClC_6H_4Cl/ p-$C_6H_5SC_6H_4Cl$	1/3.4	1/3.7
$NaSC_6H_4Cl$ + p-ClC_6H_4Cl/ p,p'-$ClC_6H_4SC_6H_4Cl$	1/15	1/12

Competitive vs Separate Relative Reactivities. The relative reactivities (ratio of rate constants) of two pairs of aryl halides toward sodium benzenethiolate were determined independently and in competition experiments. Similarly, the relative reactivities of a pair of sulfur anion reagents toward 1-chloro-4-(phenylthio)benzene were measured both in separate and competition experiments. The results of these experiments are displayed in Table III. The agreement between the relative rates observed in the two environments is remarkably close.

These results are again consistent with the S_NAr but not the $S_{RN}1$ mechanism. Relative reaction rates in $S_{RN}1$ processes generally differ significantly when they are determined in competition vs independent experiments. For example, the relative reactivities of a series of substituted aryl iodides toward pinacolone enolate ion were found to differ by a factor of nearly 400 in independent experiments.[23] In competitive experiments this factor was less than 2.[23] This is because $S_{RN}1$ processes comprise initiation, propagation, and termination steps. When two substrates react competitively, the sum of the initiation/termination steps is different from when they react independently.[23]

Effect of Radical Inhibitors/Initiators in Model Reactions. The influence of special reagents that may act as initiators, electron traps, or hydrogen atom transfer agents in radical processes was screened in reactions of DCB and 1-chloro-4-(phenylthio)benzene with sodium benzenethiolate. It was hoped that the reagents screened would be otherwise inert to the strongly basic, high-temperature reaction conditions.

When oxygen, a potential radical initiator or scavenger in $S_{RN}1$ processes,[16,24] was rigorously excluded from the reaction of 1-chloro-4-(phenylthio)benzene with sodium benzenethiolate, the reaction was readily analyzable by second-order methods, yielding reproducible rate constants. If the reaction was not rigorously deoxygenated, the observed second-order rate constants varied by a factor of 2. This peculiar behavior was further probed by repeating these experiments in the presence of 10% toluene, a potential hydrogen-transfer agent. The deoxygenated experiment was normal, but the one that was not deoxygenated displayed nonlinear kinetics reacting at a higher rate early compared to the latter stages of the reaction (see Figure 8). When this same experiment was conducted at 240 °C instead of 200 °C, the halide disappearance was again erratic and far slower than a conventional deaerated experiment (see also Figure 8).

The influence of three other reagents was tested in the reaction of DCB or of 1-chloro-4-(phenylthio)benzene with sodium benzenethiolate. Because the course of these reactions was readily analyzed by either the graphical integration method or by conventional second-order methods, the effects of added reagents were easily evaluated. The presence of 1.0 or 10 mol % (relative to DCB) of galvinoxyl or of 5.0 or 50 mol % (relative to 1-chloro-4-(phenylthio)benzene) of di-*tert*-butylnitroxyl, both stable free radicals, had no perceptible effect on the reactions. The galvinoxyl was detected by GC in reaction aliquots, and its concentration gradually decreased throughout the experiment. The third reagent tested was nitrobenzene at 10 and 100 mol % relative to DCB. Only the higher concentration experiment was affected. After 300 min, the DCB conversion was less than expected. However, the sodium benzenethiolate conversion was greater than expected. Furthermore, some of the nitrobenzene was consumed during the experiment. Graphical analysis for only the first 15 min of data yielded rate constants in agreement with those obtained in the absence of nitrobenzene. Both reactants initially were consumed at a normal rate. However, sodium benzenethiolate apparently slowly reacted with nitrobenzene, resulting in a faster sodium benzenethiolate consumption than in the conventional experiment. Because the sodium benzenethiolate was being partially depleted in a side reaction, the conversion of aryl chlorides actually slowed.

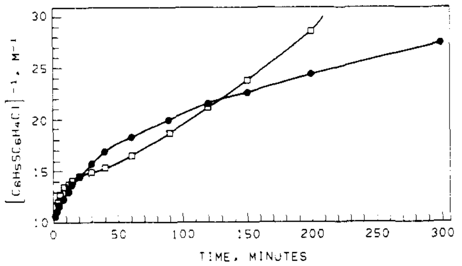


Figure 8. Second-order rate plots for the equimolar reactions of 0.100 M sodium benzenethiolate with 0.100 M 1-chloro-4-(phenylthio)benzene in 90/10 NMP–toluene at 200 °C (●) and at 240 °C (□).

Effect of Radical Inhibitors/Initiators in Polymerizations. Russian workers[13,14] have reported that the polymerization reaction is slowed if oxygen or hydroquinone is present and that it is *totally inhibited* when tetracyanoethylene is present. They interpreted this behavior as indicative of an $S_{RN}1$ polymerization mechanism. While both hydroquinone and tetracyanoethylene are often useful radical inhibitors, their use in PPS polymerization studies is problematic due to their expected deprotonation and nucleophilic substitution, respectively, by sulfur anions. To examine the effect of a potential inhibitor in our laboratories, polymerizations in the presence of a significant amount of tetracyanoethylene were conducted by M. D. Herd. As shown in Figure 9, the DCB conversion was somewhat less after 40 min when tetracyanoethylene was present, but polymer was still produced. Furthermore, the tetracyanoethylene was completely consumed in these experiments. Unlike the Russian work, Herd's polymerizations with tetracyanoethylene did not lead to compelling evidence for an $S_{RN}1$ mechanism.

Because of the effectiveness of di-*tert*-butylnitroxyl as an $S_{RN}1$ inhibitor,[16] polymerizations in the presence and absence of 1.0 mol % of di-*tert*-butylnitroxyl revealed that it had little influence on the extent of conversion or the product molecular weight. Also, no aliphatic C–H stretching vibrations were observed in the IR spectrum of the product, indicating the absence of the trapping agent.

Effect of Substituents on Reaction Rates. Aryl chloride substitutions by sodium benzenethiolate in NMP are very sensitive to other substituents on the aromatic ring. A comparison of second-order rate constants determined in our laboratory for variously substituted aryl chlorides is displayed in Table IV. On a relative rate per chloride basis, the range of reactivities spans over 3 orders

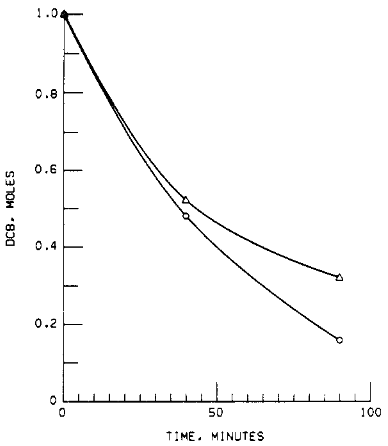


Figure 9. DCB conversion during polymerization in the presence (△) and absence (○) of 0.20 mol of tetracyanoethylene. The polymerization consisted of 1.00 mol each of DCB and Na_2S in 3.5 mol of NMP at 235 °C.

Table IV
Effect of Substituents on Reactivities of Aryl Chlorides toward Sodium Benzenethiolate in NMP at 200 °C

aryl chloride	2nd order k, L mol^{-1} s^{-1}	relative rate per Cl
p-$CH_3NHC_6H_4Cl$	too slow to measure	
C_6H_5Cl	2.6×10^{-5}	1
p-ClC_6H_4Cl	1.75×10^{-3}	34
m-$C_6H_5SC_6H_4Cl$	1.0×10^{-3}	38
m-ClC_6H_4Cl	1.0×10^{-2}	190
p-$C_6H_5SC_6H_4Cl$	6.0×10^{-3}	230
p-$C_6H_5SO_2C_6H_4Cl$	too fast to measure	

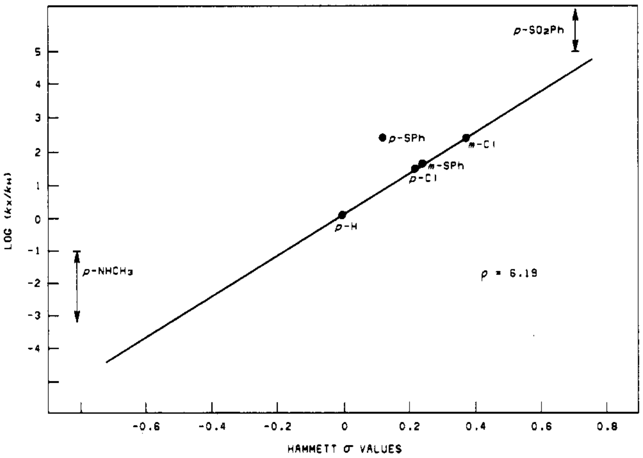
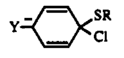


Figure 10. Relative rates of substituted aryl chloride displacements by sodium benzenethiolate in NMP at 200 °C plotted vs Hammett σ values.

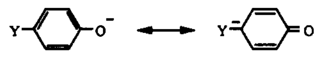
of magnitude for the substrates selected.

A plot of the relative rates vs Hammett σ values provides the correlation shown in Figure 10. The data point for the p-SPh substituent falls above the correlation, indicating an unexpected activating effect. If the mechanism is S_NAr, a comparison of relative reaction rates with equilibrium constants for phenol ionizations would be far more appropriate. The resonance stabilization of phenoxide ion offered by substituents (eq 5b) involves an



(5a)

vs.



(5b)

equivalent resonance structure to the S_NAr intermediate

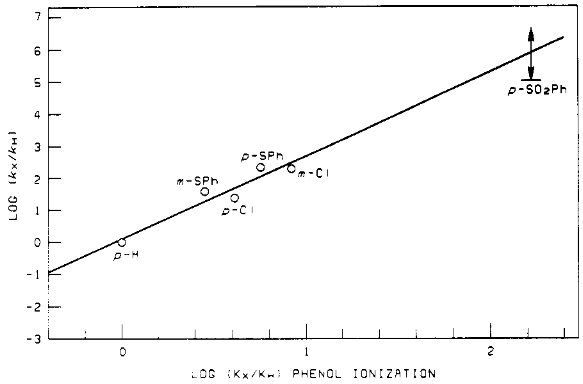


Figure 11. Relative rates of substituted aryl chloride displacements by sodium benzenethiolate in NMP at 200 °C plotted vs substituted phenol ionization constants.

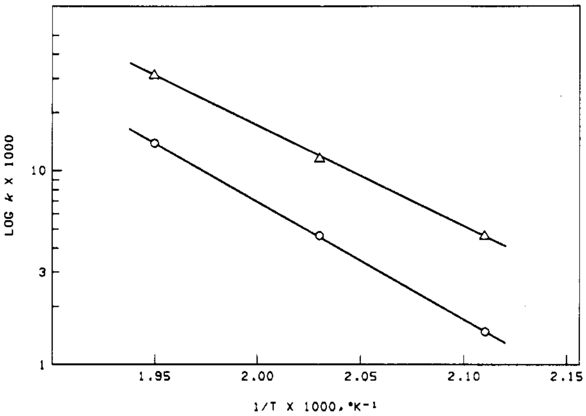


Figure 12. Arrhenius plots for the reactions of sodium benzenethiolate in NMP with 1-chloro-4-(phenylthio)benzene (top) and with DCB (bottom).

Table V
Activation Parameters for Aryl Chloride Displacements by Benzenethiolate

reaction	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/K·mol	$\Delta G^\ddagger$, kcal/mol
p-ClC_6H_4Cl + NaSPh	25.8	−19.0	35.1
p-$C_6H_5SC_6H_4Cl$ + NaSPh	21.7	−24.1	33.6

(eq 5a). A plot of this type, Figure 11, yields a reasonable correlation for all substituents, including p-SPh.

The ρ value of 6.19 is significantly large, indicating a high degree of negative charge buildup in the transition state. Comparable ρ values have been found in both S_NAr and $S_{RN}1$ processes.[7,12,23] However, for $S_{RN}1$ reactions, this was true only when rates were measured in independent rather than competitive environments.

Effect of Temperature. Reaction rates of model compounds increase predictably with temperature. Arrhenius plots of reaction rates over 200–240 °C were linear (e.g., Figure 12), allowing E_a values to be determined. Activation parameters calculated from E_a and 220 °C rate constant values are listed in Table V. As expected, the $\Delta H^\ddagger$ and $\Delta G^\ddagger$ values are larger than those for S_NAr displacements of more strongly activated aryl halides by thiolates.[25] Furthermore, the $\Delta S^\ddagger$ values are large and negative, indicative of a high degree of order in the transition state, and are comparable to those for S_NAr displacements of strongly activated aryl halides by thiolates.[25] At the higher temperatures, very small amounts of side products were observed.

Conclusions. A great deal of effort was required to establish the mechanistic path for the deceptively simple condensation of Na_2S and DCB shown in eq 1. The evidence presented herein supports the conclusion that the predominant mechanism for chain growth in PPS polymerizations is the ionic S_NAr process.

There is no compelling evidence in support of the radical-cation mechanism proposed by Koch and Heitz. That mechanism was proposed in large part to explain disulfide content in model compound reactions; however, replication of their experiments under rigorously anaerobic conditions did not produce disulfides. The incompatibility of radical cations with a strongly basic, electron-rich reaction medium also makes this proposal unattractive.

The radical anion, $S_{RN}1$, mechanism for sulfur displacement of halogen in PPS synthesis cannot be dismissed as easily. The possibility for thermal initiation of an $S_{RN}1$ process does exist, and such a reaction pathway can be very selective—a requirement for the growth of high molecular weight product. In fact, the low-temperature radical-initiated polymerization of sodium 4-bromobenzenethiolate in DMSO to oligomeric PPS[15] convinces one that such a mechanism is viable. Also the mobility of halogen in PPS synthesis follows the same order expected in $S_{RN}1$: $Cl < Br < I$. However, the $S_{RN}1$ process is diagnostically inhibited by radical scavengers or electron traps. Our work showed that the addition of several possible inhibitors failed, especially when accounting for the reactivity of the inhibitor with nucleophilic monomer. The kinetics observed in model compound reactions are most compatible with a simple ionic S_NAr mechanism in that discrete, stepwise rate constants could be obtained that were insensitive to dilutions or competing reactions with homologues. In addition, reaction rates were affected by substituents in a predictable fashion using a free-energy correlation with Hammett σ^- values.

The observations reported herein bear many similarities to the displacements of halobenzenes by alkyl thiolates in hexamethylphosphoramide (HMPT) solutions reported by Tiecco and co-workers.[26] They observed a qualitatively similar dependence of halogen mobilities, of rate on halobenzene substituents, and of indifference to radical inhibitors. They also concluded that these reactions proceeded by an S_NAr mechanism. Even more closely related studies of substituted bromobenzene displacements by sodium benzenethiolate in NMP exhibited similar relative rates and led to the same mechanistic conclusion.[27]

A key element in the successful attainment of high molecular weight polymer is the use of NMP as the reaction medium.[28] The ability of NMP, when used as a solvent, to facilitate S_NAr processes is well documented.[29-31] The conductometric experiments reported herein reinforced the concept that NMP effectively dissociates ion pairs. It is likely that the hydrogen atom donating properties of NMP actually terminate $S_{RN}1$ processes. However, the special qualities that NMP brings to the process go well beyond that of a conventional solvent. As discussed, part of the NMP is converted into the aminocarboxylate SMAB, which serves both to solubilize NaSH and act as a proton acceptor.

In PPS synthesis, the fact that unexpectedly high molecular weight polymer is produced early in the polymerization or that high molecular weight polymer is formed even with one of the monomers in large excess has been termed "preferential polymer formation"[6] and "reactive intermediate polycondensation".[10] This behavior can now be understood; it is a natural consequence of the sensitivity of the S_NAr mechanism to the substituents on the aryl chloride and to the nucleophilicity of the sulfur anion for each individual growth step. Most of the growth steps have rate constants larger than that for condensation of the two monomers.[32] More specifically, the enhanced activating ability of a para sulfur substituent relative to chlorine (Figure 10 is particularly demonstrative) provides the driving force for growth of high molecular weight at low conversions.

While it appears that the dominant chain-growth mechanism is S_NAr, anomalies in the synthesis of PPS should not be overlooked. Support for a minor competing $S_{RN}1$ component that might underlie the S_NAr mechanism is found when PPS polymerizations are carefully analyzed. Hydrogen atom end groups on PPS can be detected, suggesting that a small amount of reductive dehalogenation occurs. This and other reaction paths that are set apart from the dominant and selective S_NAr pathway should be considered as undesirable side reactions.

Experimental Section

Most commercially available compounds were used as received. NMP and thiophenol were distilled before use. Sodium benzenethiolate and sodium 4-chlorobenzenethiolate were prepared by dissolving NaOH and the appropriate thiophenol in methanol under argon and evaporating the solution to dryness. Alternatively, the thiolate salts were sometimes prepared in situ. The thiols and their salts, NaSH, and Na_2S are very susceptible to air oxidation, so they were handled under argon or nitrogen. 1-Chloro-4-(phenylthio)benzene was synthesized by the treatment of bis(4-chlorophenyl) disulfide with phenylmagnesium bromide in ether and was purified by distillation: bp 155–156 °C (2.5 mm). This route yielded a higher purity distilled product than the literature method employing (4-chlorophenyl)magnesium bromide and diphenyl sulfide.[33] Procedures patterned after those of Koch and Heitz[10] were used in the preparation of 1,4-bis(phenylthio)benzene [mp 81 °C (lit.[10] mp 82 °C)], bis(4-bromophenyl) sulfide [mp 111–112 °C (lit.[34] mp 112 °C)], and bis(4-phenylthiophenyl) sulfide [mp 108 °C (lit.[10] mp 111 °C)]. All synthesized compounds displayed the expected IR, ^1H and ^{13}C NMR, and mass spectra. NMR spectra were obtained on a JEOL JNM-GX270 FT-NMR spectrometer fitted with a high-temperature, high-resolution ^{13}C probe custom built by Doty Scientific. Details of this equipment and its operation are reported elsewhere.[35]

Apparatus. Rate studies and polymerizations were performed in Autoclave-Engineers 300-mL and 1-L autoclaves constructed of 316 S.S. or titanium metallurgies. Each reactor was equipped with a mechanical stirrer, a thermowell, a gas outlet, a gas/liquid inlet, and, in most cases, a sampling tube. Pressurized vessels connected in series were used to add coreactants and additional solvent to the autoclave to initiate reactions. Reactor temperatures were controlled to within ±2 °C (usually ±1 °C) following initial excursions when adding coreactants.

Rate Studies. A typical pseudo-first-order kinetic experiment is described. An autoclave was charged with 0.600 g (15.0 mmol) of NaOH, 1.650 g (15.0 mmol) of thiophenol, 1.0 g of H_2O, and 116 g of NMP under a flow of argon. The apparatus was assembled and flushed with argon. In most cases, the autoclave was heated to 155 °C, the vent tube was opened and a slow flow of argon was passed through the autoclave as the temperature was increased 1 °C/min until an amount of water sufficient to effect a dehydration had distilled out. The vent was closed, and the temperature of the autoclave was increased to a few degrees higher than the desired run temperature. A deaerated, heated solution of 0.02205 g (0.150 mmol) of DCB and 0.15 g of biphenyl in 15 g of NMP was added from the first charge vessel. Immediately thereafter, 15 g of deaerated heated NMP was added from the second vessel through the first, and the autoclave pressure was increased to 300 psig with argon. About 15 s elapsed during these operations, and the temperature would dip several degrees below the set point. At preselected intervals, 3-mL samples were withdrawn via the sampling tube (discarding a 1–2-mL forerun) under argon. Later, the pH of each sample was adjusted to 4.0 with aqueous HCl followed by extraction (3×) with ether. The three ether extracts were combined and analyzed by GC. Contact of the samples with air occurred only during the ether extraction process.

GC analyses were performed on a 6 ft × 0.25 in. (3-mm-i.d.) glass column packed with 3% OV-1 on 80/100 Chromosorb W-HP that was temperature programmed from 75 to 350 °C. Peak identities were assigned by GC/MS and in most cases by spiking with authentic samples. Component concentrations were calculated on the basis of peak areas relative to the internal standard (biphenyl) with corrections for relative detector responses.

Preparative Polymerizations. A general procedure is described. Into a 1-L autoclave were charged 93.3 g (1.00 mol) of NaSH hydrate (nominally 60%), 40.4 g (1.01 mol) of NaOH, and 247.8 g of NMP. The autoclave was closed and flushed with N_2. The mixture was dehydrated by distilling away the water at temperatures of 150–210 °C. This was followed by the addition of 148.5 g (1.01 mol) of DCB, any test reagents, and 99.0 g of NMP. Polymerizations were typically conducted for 1 h at 235 °C followed by 2 h at 265 °C, after which the reactor was cooled. The product was recovered by submitting the contents to several hot water washes (ca. 80 °C) and then drying the polymer at 100 °C in a vacuum oven.

Conductometric Titration. A YSI microconductance probe (cell constant = 1.0/cm) connected to a YSI Model 32 conductance meter was used to measure conductance. The solution temperature was maintained at 150 °C with a thermostated bath. Conductance measurements were made on a stirred 3.9 M solution of the SMAB–NaSH mixture in NMP to which weighed quantities of solid 18-crown-6 were added. Conductance was then plotted versus equivalents of 18-crown-6 added (Figure 2); the correlation coefficient was greater than 0.99.

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References and Notes

(1) PPS has been produced commercially since 1973 by the Phillips Petroleum Co. under the registered trademark Ryton.
(2) Reviews: (a) Geibel, J. F.; Campbell, R. W. In *Comprehensive Polymer Science. Volume 5. Step Polymerization*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P. Eds.; Pergamon Press: Oxford, 1989; pp 543–560. (b) Fradet, A. *Bull. Soc. Chim. Belg.* **1989**, *98*, 635–641.
(3) Lopez, L. C.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29* (1), 83–151.
(4) The insolubility, high strength, and temperature stability of PPS make it an attractive engineering thermoplastic. See: Geibel, J. F.; Campbell, R. W. *Encyclopedia of Chemical Processing and Design*, in press.
(5) Campbell, R. W. (Phillips Petroleum Co.). U.S. Patent 3 919 177, 1975.
(6) Lenz, R. W.; Handlovits, C. E.; Smith, H. A. *J. Polym. Sci.* **1962**, *58*, 351–367.
(7) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier Publishing Co.: Amsterdam, The Netherlands, 1968.
(8) Brady, D. G. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1981**, *36*, 231–239.
(9) Sergeev, V. A.; Nedelkin, V. I. *Makromol. Chem., Macromol. Symp.* **1989**, *26*, 333–346.
(10) Koch, W.; Heitz, W. *Makromol. Chem.* **1983**, *184*, 779–792.
(11) Koch, W.; Risse, W.; Heitz, W. *Makromol. Chem. Suppl.* **1985**, *12*, 105–123.
(12) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413–420.
(13) Annenkova, V. Z.; Antonik, L. M.; Vakul'skaya, T. I.; Voronkov, M. G. *Dokl. Akad. Nauk SSSR* **1986**, *286*, 1400–1403.
(14) Annenkova, V. Z.; Antonik, L. M.; Shafeeva, I. V.; Vakul'skaya, T. I.; Vitkovskii, V. Yu.; Voronkov, M. G. *Vysokomol. Soed., Ser. B* **1986**, *28*, 137–140.
(15) Novi, M.; Petrillo, G.; Sartirana, M. L. *Tetrahedron Lett.* **1986**, *27*, 6129–6132.
(16) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph Series 178; American Chemical Society: Washington, DC, 1983.
(17) First discovered by R. W. Campbell and J. C. Randall at Phillips Petroleum Co. in 1973.
(18) Campbell, R. W. (Phillips Petroleum Co.). U.S. Patent 3 867 356, 1975.
(19) Ciminale, F.; Bruno, G.; Testaferri, L.; Tiecco, M.; Martelli, G. *J. Org. Chem.* **1978**, *43*, 4509–4512.
(20) Pannetier, G.; Souchay, P. *Chemical Kinetics*; Gesser, H. D., Emond, H. H., English translators; Elsevier Publishing Co., Ltd.: Amsterdam, The Netherlands, 1967; pp 196–200. Individual α vs τ plots for specific k_2/k_1 ratios were generated by a computer integration method.
(21) Capellos, C.; Bielski, B. H. J. *Kinetic Systems*; John Wiley and Sons, Inc.: New York, 1972; pp 100–103.
(22) Bunnett, J. F.; Shafer, S. J. *J. Org. Chem.* **1978**, *43*, 1877–1879.
(23) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 2604–2608.
(24) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449–1457.
(25) Reference 7; pp 190–192.
(26) Cogolli, P.; Maiolo, F.; Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Org. Chem.* **1979**, *44*, 2642–2646.
(27) Stock, L. M.; Mayers, C. J., private communication, University of Chicago. Mayers, C. J. Thesis, The University of Chicago Libraries.
(28) Edmonds, J. T., Jr.; Hill, H. W., Jr. (Phillips Petroleum Co.). U.S. Patent 3 354 129, 1967.
(29) Miller, J.; Parker, A. J. *J. Am. Chem. Soc.* **1961**, *83*, 117–123.
(30) Cox, B. G.; Parker, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 408–410.
(31) Campbell, J. R. *J. Org. Chem.* **1964**, *29*, 1830–1833.
(32) For example, bis(4-chlorophenyl) sulfide is 14 times more reactive than DCB toward "Na_2S" at 200 °C.
(33) Wiegand, G. H.; Peterson, J. R.; Yu, S.-L. *Int. J. Sulfur Chem., A* **1972**, *2*, 294–295.
(34) Montaudo, G.; Bruno, G.; Maravigna, P.; Finocchiaro, P.; Centineo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 65–79.
(35) Wade, B.; Abhiraman, A. S.; Wharry, S. M.; Sutherlin, D. M. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1990**, *28*, 1233–1249.