3. The ratio of C_s/C_{pa} is important. It controls both the number of charged sites that can be formed on a polymer molecule in solution and the degree of polymer coil expansion.

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Studies of Sulfonyl Radicals. 6.[1] Chain-Transfer Constants of Some Sulfonyl Chlorides in Styrene and Methyl Methacrylate Polymerizations

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ABSTRACT: Chain-transfer constants (C_{tr}) of arene- and alkanesulfonyl chlorides at 60 °C in styrene and methyl methacrylate (MMA) polymerizations have been determined using the conventional $\bar{P}_n$ (degree of polymerization)–C_{tr} relationship. Large C_{tr} values for the polystyryl radical were obtained with the sulfonyl chlorides (0.1–2.6) compared to that with CCl_4 (0.01). A Hammett plot for substituted benzenesulfonyl chlorides gave $\rho = 0.86$, which may be explained by the contribution of a charge-transferred resonance form ($ArSO_2^- Cl\ ^+CH(Ph)CH_2{\sim}$) in the transition state. On the other hand, C_{tr}'s for poly(MMA) radical were found to be $(5–9) \times 10^{-4}$ with arenesulfonyl chlorides.

In connection with the propagation mechanism of radical copolymerization[2] of vinyl monomers with sulfur dioxide, we have been investigating the chemistry of sulfonyl radicals. We have already reported that sulfonyl radicals have a strong electron-accepting and electrophilic nature,[3] and the elimination of SO_2 from sulfonyl radicals and the recombination rate constants for these radicals have also been investigated.[4,5] With respect to chain-transfer reactions concerned with sulfone compounds, relatively large transfer constants (C_{tr}) for polystyryl radical with azosulfones were observed in our laboratory.[6]

In this study, the chain-transfer reaction of various sulfonyl chlorides, as shown in eq 1, has been investigated.

$$ {\sim}P\cdot(\text{polymer radical}) + RSO_2Cl \rightarrow {\sim}PCl + RSO_2\cdot \qquad (1)$$

Although similar processes were involved in the mechanism of the adduct formation of sulfonyl chlorides with alkenes,[7] no chain-transfer constant of sulfonyl halides has been reported so far, as far as we know, and this reaction may be expected to show a strong polar effect due to the formation of electron-accepting sulfonyl radicals.

Polymerizations of styrene and methyl methacrylate (MMA) were carried out in the presence of sulfonyl chlorides at 60 °C using azobis(isobutyronitrile) (1.2×10^{-2}M) and stopped at a low conversion. Conversion was measured gravimetrically. The polymerization rates of styrene and MMA were not changed by the addition of a small quantity of sulfonyl chlorides in this experiment. Molecular weights were evaluated from the intrinsic viscosities of benzene solutions of polystyrene[8] and poly(MMA).[9]

Figure 1 shows that the plots of $1/\bar{P}_n$ vs. [S]/[M] are straight lines according to

$$1/\bar{P}_n = 1/\bar{P}_o + C_{tr}[S]/[M] \qquad (2)$$

where $\bar{P}_n$ and $\bar{P}_o$ are the degrees of polymerization in the presence and the absence of sulfonyl chlorides, and [S] and

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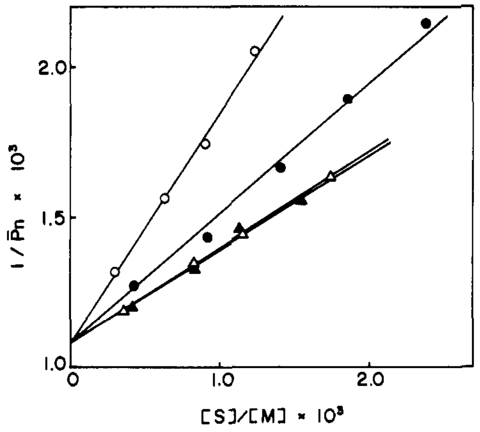

Figure 1. Plots of $1/\bar{P}_n$ vs. [S]/[M] for the chain-transfer reaction of substituted benzenesulfonyl chlorides [*p*-chlorobenzenesulfonyl chloride(○), benzenesulfonyl chloride(●), *p*-methylbenzenesulfonyl chloride (△), *p*-methoxybenzenesulfonyl chloride(▲)] and styrene, respectively.

Table I
Chain-Transfer Constants (C_{tr}) of Sulfonyl Chlorides for Poly(MMA) Radical at 60 °C

sulfonyl chloride	C_{tr}	k_{tr}, M^{-1} s^{-1} [c]
benzenesulfonyl chloride	0.433	76
p-chlorobenzenesulfonyl chloride	0.765	140
p-methylbenzenesulfonyl chloride	0.318	56
p-methoxybenzenesulfonyl chloride	0.311	55
phenylmethanesulfonyl chloride[a]	0.319	56
methanesulfonyl chloride	0.118	21
PMC[b]	2.76	490

[a] Phenylmethane-α,α-d_2-sulfonyl chloride was found to have the same C_{tr} value. [b] α-Phenyl-β-(methanesulfonyl)ethanesulfonyl chloride. [c] k_{tr} was calculated from the C_{tr} value and $k_p = 176$ M^{-1} s^{-1}.[13]

[M] are the concentrations of sulfonyl chlorides and monomer, respectively. C_{tr}'s thus obtained are summarized in Tables I (styrene) and II (MMA), together with chain-transfer rate constants k_{tr} which are evaluated from $C_{tr} = k_{tr}/k_p$ and the reference values for propagation rate constants k_p.

C_{tr} values of sulfonyl chlorides for polystyryl radical in Table I are strikingly large (0.1–2.6), compared with the values of CCl_4 (0.007–0.015 at 60 °C)[10] and of $C_6H_5CCl_3$ (0.00575 at 60 °C),[10] in which a similar chlorine abstraction process is involved. On the other hand, the values for poly(MMA) radical in Table II are small and of the same order of magnitude as the value of CCl_4 ((0.925–5) × 10^{-4} at 60 °C).[10] The Hammett plot for para-substituted benzenesulfonyl chlorides in Figure 2 gives $\rho = 0.86$ for polystyryl radical, suggesting that electron-withdrawing substituents accelerate the reaction. The contribution of a charge-transferred resonance form in the transition state (II in eq 3) would be a reasonable explanation for the polar

$$\sim CH_2CH(Ph)\cdot + RSO_2Cl \rightarrow$$
$$[\underset{\text{I}}{\sim CH_2CH(Ph)\cdot\ \dot{C}l\ \cdot O_2SR} \leftrightarrow \underset{\text{II}}{\sim CH_2\overset{+}{C}H(Ph)\ \dot{C}l\ \overset{-}{O}_2SR}]$$
$$\rightarrow\ \sim CH_2CH(Ph)Cl + RSO_2\cdot \quad (3)$$

character of this reaction. The strong electron-accepting character of sulfonyl radicals[3] may be responsible for the large contribution of the resonance form II and for lowering the energy level of the transition state. Electron-withdrawing substituents may stabilize sulfinate anions in the resonance form II and facilitate the reaction. Small C_{tr} values (or k_{tr} values in Table II) for poly(MMA) radical can be explained by decreased contribution of the charge-transferred structure II, in which the cation is unstable due to the presence of the electron-withdrawing ester group.

Table II
Chain-Transfer Constants (C_{tr}) of Sulfonyl Chlorides for Poly(MMA) Radical at 60 °C

sulfonyl chloride	C_{tr} × 10^4	k_{tr}, M^{-1} s^{-1} [a]
benzenesulfonyl chloride	5.16	0.27
p-chlorobenzenesulfonyl chloride	8.56	0.44
p-methylbenzenesulfonyl chloride	4.06	0.21

[a] k_{tr} was calculated from the C_{tr} value and $k_p = 515$ M^{-1} s^{-1}.[13]

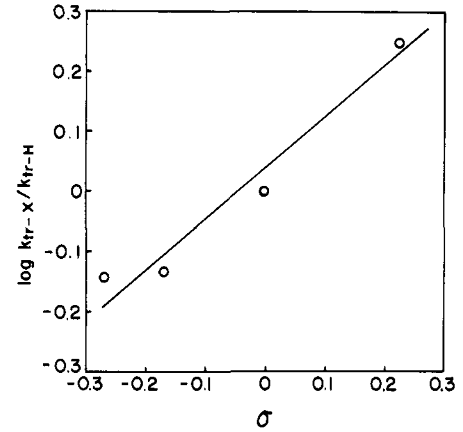

Figure 2. Hammett plot for the chain-transfer reaction of substituted benzenesulfonyl chlorides with polystyryl radical.

Unexpectedly, a similar substituent effect ($\rho = 0.8$) on C_{tr} for poly(MMA) radical to that ($\rho = 0.86$) for polystyryl radical was observed. From the discussion above, this cannot be attributed to a similar contribution of structure II in eq 3. The small transfer constants but similar ρ value for poly(MMA) may be due to a more product-like transition state.[11]

The importance of the contribution of the resonance form II may be shown in the explanation for the difference of C_{tr} between methane- and phenylmethanesulfonyl chloride. Namely, the electron-withdrawing phenyl group may stabilize the sulfinate anion in II and increase the reaction rate.

$PhCD_2SO_2Cl$ has the same C_{tr} value as that for $PhCH_2SO_2Cl$ in Table I, indicating that the transfer reaction is chlorine abstraction but not hydrogen abstraction.

It is interesting to compare C_{tr} (0.118) for $PhCH_2SO_2Cl$ to that (2.76) for $CH_3SO_2CH_2CH(Ph)SO_2Cl$ (PMC)[12] which has the SO_2 unit at the antepenultimate position. A large C_{tr} value for PMC may be attributed to the unstability of PMC due to the electronic repulsion between the SO_2 groups. Relief from this electronic repulsion in the transition state, in which simultaneous elimination of SO_2 ($-SO_2Cl$) may occur,[12] would facilitate the reaction.

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(12) α-Phenyl-β-(methanesulfonyl)ethanesulfonyl chloride (PMC) was prepared by using the method of T. B. Johnson and J. M. Sprague, *J. Am. Chem. Soc.*, **58**, 1348 (1936). PMC was found to be rather unstable even at room temperature, decomposing with evolution of SO_2. It was purified by a low-temperature recrystallization from CH_2Cl_2 and stored in a refrigerator. Anal. Calcd for $C_9H_{11}ClO_4S_2$: C, 38.22; H, 3.92; Cl, 12.53; S, 22.68. Found: C, 38.02; H, 4.09; Cl, 12.40; S, 22.20. NMR measurements for the decay of PMC in the absence of AIBN give a half-life > 300 min over the concentration range from 6×10^{-4} to 3×10^{-3} M used in the C_{tr} experiment; decomposition during the polymerization (<80 min) is therefore neglected.
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Reversible Cationic Polymerization of Trioxepane Resulting in Establishment of Stationary Concentrations of Three Monomers. Calculation of the Stationary Concentrations and of the Frequency of Various Triads

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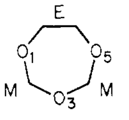
ABSTRACT: Cationic polymerization of 1,3,5-trioxepane proceeds without termination and yields living polymers. The propagation is accompanied by depropagation that prevents quantitative conversion of the monomer into polymers. Unusual complexity of this system is caused by the occurrence of alternative modes of depropagation that generate dioxolane and formaldehyde in addition to dioxepane. These act then as monomers in their own right converting the polymerization into a kind of copolymerization. Eventually, the system reaches a stationary state, and the concentrations of all three monomers then remain constant. Distinction is made between the equilibrium concentrations and stationary concentrations of the monomers. The former are determined by the free energies of the monomer and monomeric segment of regular polymers, whereas the values of the latter are proportional to the mole fractions of living polymers terminated by specific sequences of units. Treatment developed here allows the calculation of the pertinent mole fractions of polymers with specific terminal sequences of units and subsequently the stationary concentrations of the monomers as well as the frequencies of various triads in the polymer chains. The mole fractions, the stationary concentrations of the monomers, and frequencies of various triads depend on the composition of the polymers, i.e., on the ratio of $-OCH_2CH_2-$ units to $-OCH_2-$ units in the formed macromolecules.

An interesting paper describing cationic polymerization of 1,3,5-trioxepane was published recently by Schulz et al.[1] The following conclusions were derived from their observations:



1,3,5-trioxepane

(1) The investigated polymerization proceeds without termination, i.e., it yields living polymers.

(2) Both propagation and depropagation participate in the process. Consequently, the conversion of the monomer into polymers is not quantitative, and eventually its concentration reaches a stationary value when the rate of propagation is exactly balanced by the rate of depropagation.[2]

(3) The composition of the polymer differs from that of the monomer.

(4) The residual unpolymerized material is a mixture composed not only of the original monomer, trioxepane, but also of 1,3-dioxolane, which polymerizes or copolymerizes under conditions of Schulz's experiments. Dioxolane is formed in the course of polymerization, and its concentration reaches, simultaneously with trioxepane, a stationary value.

(5) Extensive NMR analysis of the polymers revealed the presence of triads such as $-OCH_2{\cdot}OCH_2{\cdot}OCH_2-$, denoted as –MMM–, and $-OCH_2{\cdot}OC_2H_4{\cdot}OCH_2-$, denoted as –MEM–.

These observations imply that two modes of trioxepane propagation are involved in the process. The $-O{=}CH_2^+$ group always is the reactive end group of these polymers, and it is denoted as $\sim\!\sim M^+$. The $-OCH_2CH_2^+$ group ($\sim\!\sim E^+$) is never formed, neither through propagation nor by depropagation. Propagation involving an attack on oxygen

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