tributions from the tlc together with the GPC results cited earlier. There is certainly qualitative though not quantitative agreement here.

Comparing the tlc and GPC results, we notice that the former always predicts much narrower distribution than does the latter. Previous reports[13,14] showed good agreement between the two results at least for polystyrenes. The disagreement found here for a narrow distribution polystyrene, PS-355, is presumably due to the observation mentioned earlier that polystyrene developed by H_4furan–CH_3OH system migrated toward the glass-silica gel interface becoming hardly visible from the silica gel side. On the other hand, the disagreement found for various SBRs and polybutadienes may be partly due to the undeveloped residue at the origin. The amount of the residue is substantially larger in this H_4furan–CH_3OH system than in the $CHCl_3$–CCl_4 system.

Several comments are necessary here. First, no corrections for dispersion have been made and there would certainly seem to be upward tailing. Furthermore our calibration standards are much better at higher styrene than at lower styrene levels. Specifically we had to narrow distribution polybutadienes at our disposal. This will probably lead to greater errors in polybutadienes and low styrene SBRs. The H_4furan–CH_3OH system shows a large dependence of R_f on X. This could be improved by employing a more adequate system probably consisting of three or four solvent mixtures.

Concluding Remarks

Copolymers may be separated by tlc according to composition or molecular weight. We have in this paper developed tlc techniques for separating one particular copolymer system, butadiene–styrene, which had industrial importance. It was shown that using elution gradient techniques based upon relatively nonpolar solvents leads to separation according to composition by an adsorption mechanism. Use of very polar solvent-nonsolvent mixtures leads to separation primarily according to molecular weight. By suitable calibration the tlc smears may be interpreted quantitatively as compositional heterogeneity and molecular weight distribution. This procedure should be applicable to other copolymer systems.

Acknowledgments. Dr. G. Kraus and the Phillips Petroleum Co. kindly made available to us four samples of narrow molecular weight and compositional distribution butadiene–styrene copolymer. This work was supported in part under National Science Foundation Grants GK 11035 and 18897.

Induced Decomposition of Some Azo Sulfones with Polymer Radicals and Telomerization with Azo Sulfones

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Received August 9, 1973

ABSTRACT: Radical polymerizations of styrene and of methyl methacrylate (MMA) initiated by some azo sulfones were investigated to determine chain-transfer constants to azo sulfones with polystyryl and poly(MMA) radicals, respectively; with the former radical the constants at 70° were found to be 9.7 (*p*-methoxyphenyl phenylazo sulfone) to 23.4 (methyl phenylazo sulfone, MPAS) comparable to those of mercaptans, but with latter radical, the constant was practically zero. Thus, the relative rate constants for induced decomposition of azo sulfones with the polystyryl radical at 70° were correlated with Hammett's σ values of $\rho = +0.5$. Telomerizations of styrene, 1-hexene, and MMA, except a phenyl phenylazo sulfone (PPAS)-1-hexene system, were also studied by using an excess of the azo sulfone over monomer concentration; reaction of PPAS with styrene gave a hydrazone type product, $C_6H_5SO_2CH_2C(C_6H_5){=}N{-}NHC_6H_5$, suggesting that chain-transfer reaction to PPAS with the polystyryl radical could occur to give a hydrazone-type end group *via* hydrogen transfer from azo-type ending. On the other hand, the azo-type product, $CH_3SO_2CH_2CH(C_6H_5){-}N{=}NC_6H_5$, was obtained from the reaction of MPAS with styrene. The implications with respect to the reaction mechanism of azo sulfone with monomers are discussed on the basis of the results of the polymerization and telomerization.

In the course of a study of the radical copolymerization of sulfur dioxide and styrene,[1,2] it seemed interesting to investigate the induced formation of sulfonyl radicals from the reaction of sulfonyl compounds with polystyryl and other carbon radicals. It is well known that sulfonyl radicals can be generated easily from the homolytic scission of azo sulfones. The thermal decomposition of azo sulfones in solvents was extensively studied by Overberger,[3,4] Kice,[5,6] and Kojima,[7] and their collaborators. They determined the rate constants for unimolecular decomposition of azo sulfones and identified the decomposition products. We have used azo sulfones ($R{-}SO_2{-}N{=}N{-}C_6H_5$, containing R = CH_3, $C_6H_5CH_2$, C_6H_5, and p-X$-C_6H_4$) to homolytically decompose to yield both sulfonyl and phenyl radicals and nitrogen. Benzylsulfonyl radical which

$$R{-}SO_2N_2C_6H_5 \longrightarrow R{-}SO_2\cdot + C_6H_5\cdot + N_2 \tag{1}$$

may result from the homolysis of benzyl phenylazo sulfone, $C_6H_5CH_2SO_2N_2C_6H_5$, further decomposes to benzyl radical and sulfur dioxide.[6] Overberger and Rosenthal[3,4]

$$C_6H_5CH_2SO_2\cdot \longrightarrow C_6H_5CH_2\cdot + SO_2 \tag{2}$$

also studied the polymerization of styrene initiated by phenyl phenylazo sulfone and they confirmed the incorporation of both phenylsulfonyl ($C_6H_5SO_2$–) and phenylazo ($C_6H_5{-}N{=}N$–) groups at the polystyrene endings. Ueha-

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Table I
Chain-Transfer Constants (C_{tr}) to Azo Sulfones with Polystyryl Radical (70°)

Azo Sulfone ($R—SO_2N_2C_6H_5$)	$p-CH_3OC_6H_4-$	$p-CH_3C_6H_4-$	C_6H_5-	$p-ClC_6H_4-$	CH_3-	$C_6H_5CH_2-$
C_{tr}	9.7	11.3	13.0	18.7	23.4	13.1

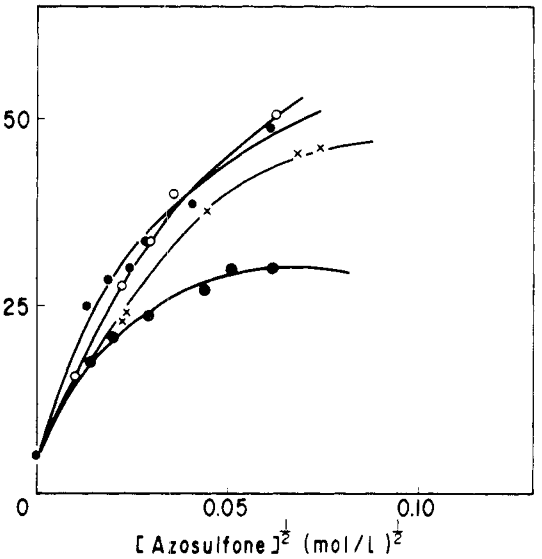

Figure 1. Relationship between overall rates of polymerization (R_p) of styrene and square root of concentrations of azo sulfones at 70°. The concentration of styrene is kept constant at 8.73 mol/l. (bulk polymerization): azo sulfones are $p-CH_3C_6H_4SO_2N_2C_6H_5$ (●), $C_6H_5SO_2N_2C_6H_5$ (○), $p-ClC_6H_4SO_2N_2C_6H_5$ (⊙), and $p-CH_3OC_6H_4SO_2N_2C_6H_5$ (×).

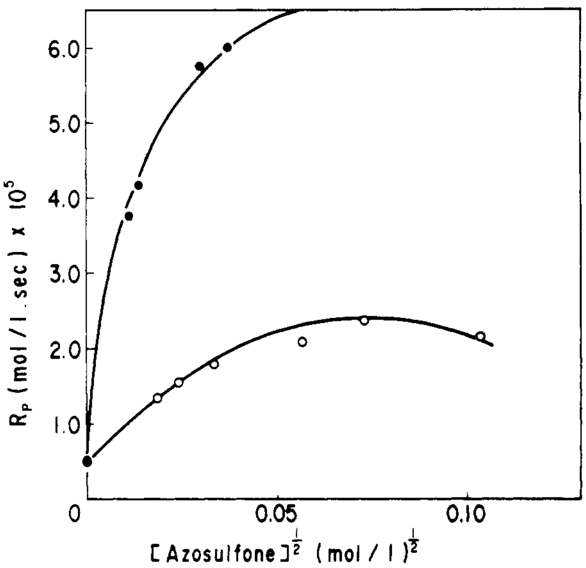

Figure 2. Relationship between R_p's and $[I]^{1/2}$ of azo sulfones at 70°. The concentration of styrene is kept constant at 8.73 mol/l. (bulk polymerization): azo sulfones are $CH_3SO_2N_2C_6H_5$ (○) and $C_6H_5CH_2SO_2N_2C_6H_5$ (●).

ra[8] studied the kinetics of polymerization of methyl methacrylate (MMA) initiated by *p*-tolyl phenylazo sulfone with and without dimethylaniline. However, it may be said without much exaggeration that quantitative study on the induced decomposition of azo sulfones, especially that with polymer radicals, has not been reported. The present paper is concerned with the determination of relative rate constants for induced decomposition of some azo sulfones with polymer radicals which can be evaluated from the measurement of chain-transfer constants. We found that azo sulfones were effective chain-transfer agents for styrene polymerization owing to the ease of the addition reaction of the styryl radical to a -N=N- double bond of azo sulfone (eq 8) and to the ease of the release of the sulfonyl radical from such an addition intermediate (eq 9). These reactions were confirmed through the study of telomerization of styrene with azo sulfones.

Experimental Section

Purification of Solvents and Monomers. Benzene, pyridine, toluene, triethylamine, ethyl acetate, and isooctane were purified by the usual methods. Styrene and MMA were washed three times with a 10% aqueous solution of sodium hydroxide and with water, respectively, dehydrated with calcium chloride (for styrene) and with anhydrous sodium sulfate (for MMA), and then distilled twice under a reduced pressure in nitrogen atomosphere.

Preparation and Purification of Azo Sulfones. Aryl phenylazo sulfones, $p-X—C_6H_4SO_2N_2C_6H_5$ (X = CH_3O, CH_3, H, and Cl), were prepared according to the method of Hantzsch and Singer[9,10] by allowing benzenediazonium chloride to react with the sodium salt of substituted benzenesulfinic acid. Methyl phenylazo sulfone was prepared by allowing benzenediazonium fluoroborate to react with sodium methanesulfinate. Benzyl phenylazo sulfone was prepared from benzenediazonium chloride and sodium phenylmethanesulfinate. All azo sulfones were recrystallized two or three times from ethanol or a *n*-hexane-benzene solution.

Polymerization was conducted essentially according to the method previously reported.[2] Polymerization proceeded in a homogeneous system. In a region of low conversion, the time-conversion curves obtained in the polymerization experiments were fairly straight lines through an origin. Polymerizations were stopped at conversions of no more than 10 wt %. The molecular weight of polymers was evaluated from the measurements of intrinsic viscosities. The intrinsic viscosities, $[\eta]$, of the polymers which were purified prior to measurements by reprecipitation from a methanol-benzene solvent system were measured using Ubbelohde-type viscometer. The number-average degrees of polymerization of polystyrene and poly(MMA) were evaluated from eq 3 and 4, respectively.

$$\text{polystyrene } \overline{M}_n = 1.67 \times 10^5[\eta]^{1.37} \text{ (in benzene, 30°)} \quad (3)^{11}$$

$$\text{poly(MMA) } [\eta] = 2.45 \times 10^{-5}\overline{M}_n^{0.8} \text{ (in acetone, 25°)} \quad (4)^{12}$$

Telomerization. A. Reaction of Phenyl Phenylazo Sulfone and Styrene. A mixture of phenyl phenylazo sulfone (5 g, 20 mmol) and styrene (1.0 g, 10 mmol) was placed in a reaction vessel, degassed three times by the freeze-thaw method, and allowed to react in a water bath kept at 70° for 10 hr. A reaction mixture was added to a large amount of *n*-hexane. The precipitate deposited was then dried and recrystallized twice from a ethanol-chloroform mixture. $C_6H_5SO_2CH_2C(C_6H_5)=N—NH—C_6H_5$ (yield 0.48 g, 0.28 mol/mol of styrene) was obtained: yellow crystal, mp 166-167° dec, lit.[13] mp 165.5-167°; ir (KBr) (in cm^{-1}) 3350 (-N(H)-); nmr (60 MHz) (δ in ppm) δ 6.8-7.9 (multiplet, C_6H_5- and -N(H)-), 4.6 (singlet, $-CH_2-$). *Anal.* Calcd for $C_{20}H_{18}N_2O_2S$: C, 68.57; H, 5.17; N, 8.00; S, 9.14. Found: C, 68.41; H, 5.17; N, 8,00; S, 9.32.

B. Reaction of Phenyl Phenylazo Sulfone and MMA. A mix-

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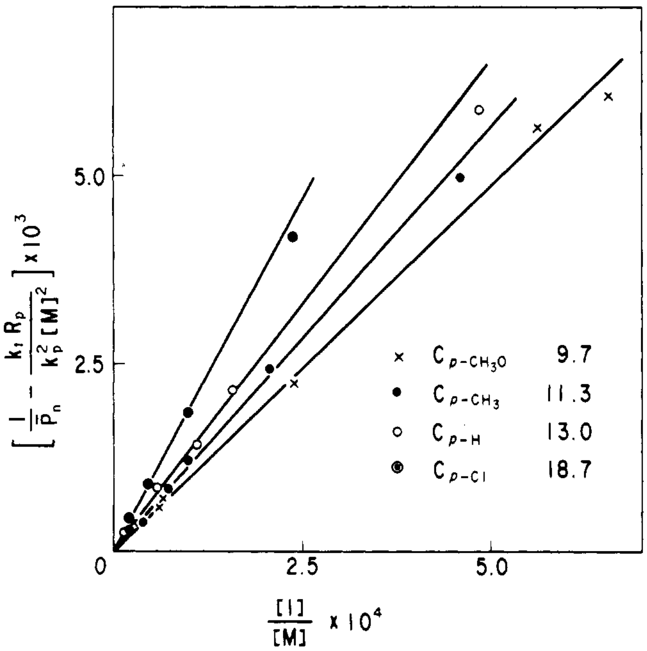

Figure 3. Plots of $\bar{P}_n - (k_t/k_p^2)R_p/[M]^2$ *vs.* [I]/[M]. C_x's represent chain-transfer constants of para-substituted aryl phenylazo sulfones.

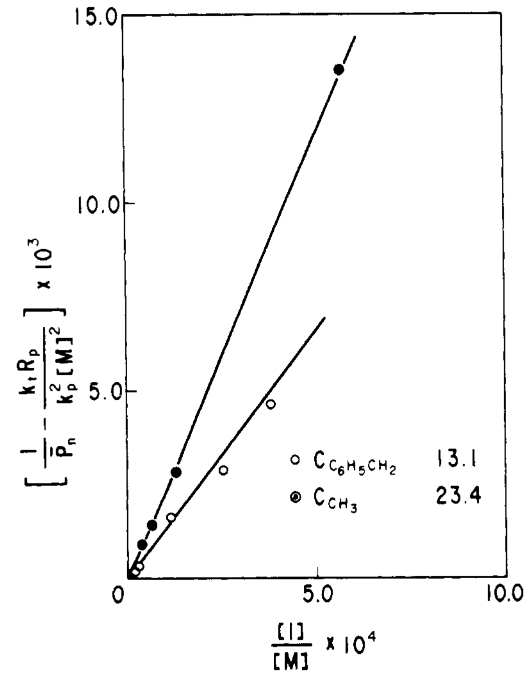

Figure 4. Plots of $\bar{P}_n - (k_t/k_p^2)R_p/[M]^2$ *vs.* [I]/[M]. C_x's represent chain-transfer constants of $CH_3SO_2N_2C_6H_5$ (⊙) and $C_6H_5CH_2SO_2N_2C_6H_5$ (○).

ture of phenyl phenylazo sulfone (5 g, 20 mmol) and MMA (1.0 g, 10 mmol) was allowed to react at 70° for 8 hr. The ir spectrum of the precipitate obtained coincided well in positions with those of poly(MMA) except for end groups incorporated. The molecular weight of the poly(MMA) which was purified by reprecipitation from a benzene-petroleum ether (bp 30-70°) mixture was about 3350 with vapor pressure osmometry. *Anal.* Found: C, 61.16; H, 7.92; S, 1.44; N, 0.00.

C. Reaction of Phenyl Phenylazo Sulfone and 1-Hexene. A mixture of phenyl phenylazo sulfone (5 g, 20 mmol) and 1-hexene (3.3 g, 40 mmol) was allowed to react for 11 hr at 70°. After the precipitation with *n*-hexane, *n*-hexane was decanted and residual *n*-hexane was evaporated under a reduced pressure; residue was recrystallized twice from ethanol. $C_6H_5SO_2CH_2CH(n\text{-}C_4H_9)\text{—N=N—}C_6H_5$ (0.05 g, 0.08 mol/mol of azo sulfone) was obtained: pale yellow crystal, mp 67-68°; ir 1140 and 1280 ($\text{-}SO_2\text{-}$); nmr 7.5-8.0 (multiplet, $C_6H_5\text{-}$), 3.2-4.1 (multiplet, $CH_2\text{-}CH\text{-}$), 0.6-1.6 (multiplet, $C_4H_9\text{-}$); uv λ_{max} (in nm) 403 ($\epsilon \simeq$ 190, -N=N-). *Anal.* Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.46; H, 6.67; N, 8.49. Found: C, 65.13; H, 6.80; N, 8.41.

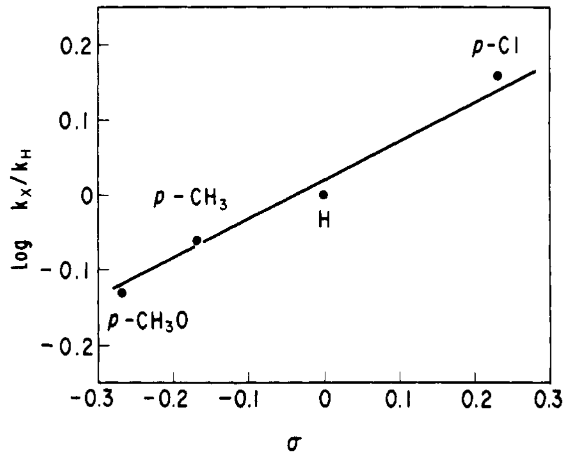

Figure 5. The Hammett plot for chain-transfer constants of para-substituted aryl phenylazo sulfones.

Table II
Solvent Effect on Polymerization Rate of Styrene Initiated by *p*-Tolyl Phenylazo Sulfone at 70°[a]

Solvent	Vol %	Styrene (mol/l.)	$R_p \times 10^5$ (mol/l.·sec)
Benzene	75	2.07	1.66
Pyridine	75	2.07	1.34
Triethylamine	75	2.07	0.53
Ethyl acetate	75	2.07	1.49
Diphenylmethane	50	4.14	1.91
Isooctane	50	4.14	1.57
Toluene	50	4.14	1.94
Triethylamine	50	4.14	0.95

[a] [*p*-Tolyl phenylazo sulfone] was being kept constant at 3.83×10^{-3} mol/l.

D. Reaction of Methyl Phenylazo Sulfone and Styrene. A mixture of methyl phenylazo sulfone (1.98 g, 20 mmol) and styrene (1.0 g, 10 mmol) was allowed to react at 70° for 10 hr. After the precipitation with *n*-hexane and recrystallization from ethanol, $CH_3SO_2CH_2CH(C_6H_5)\text{—N=N—}C_6H_5$ (1.15 g, 0.4 mol/mol of styrene) was obtained: pale yellow crystal, mp 103.5-104.5°; ir (KBr) 1300 and 1140 ($\text{-}SO_2\text{-}$); nmr 5.8 (triplet, -CH-), 3.6-4.6 (multiplet, $\text{-}CH_2\text{-}$), 2.8 (singlet, $CH_3\text{-}$); uv λ_{max} 400 ($\epsilon \simeq$ 210, -N—N-). *Anal.* Calcd for $C_{15}H_{18}N_2O_2S$: 62.58; H, 5.56; N, 9.72. Found: C, 62.48; H, 5.59; N, 9.88.

Results

Polymerization of Styrene with Some Azo Sulfones. In the radical polymerization initiated with the usual type of thermal initiators, the rate of polymerization, R_p (in our polymerization it was evaluated by the weight of methanol-insoluble polymer), would be proportional to the square root of the initiator concentration, $[I]^{1/2}$, that is, $R_p = k_p(fk_d/k_t)^{1/2}[I]^{1/2}[M]$.

The relationship between R_p for the polymerization initiated by para-substituted aryl phenylazo sulfones ($p\text{-}X\text{—}C_6H_4SO_2N_2C_6H_5$) and $[I]^{1/2}$ is shown in Figure 1, for both methyl phenylazo sulfone and benzyl phenylazo sulfone, see Figure 2; R_p's are not proportional to $[I]^{1/2}$. Furthermore, the polymerization rate tends to decrease through a maximum with significantly increasing initiator concentration; in agreement with this phenomenon a large quantity of methanol-soluble polymer was obtained. For example, the weight of methanol-soluble polymer is up to about 60 wt % of that of methanol-insoluble polymer

Table III
Telomerizations of Monomers with Azo Sulfones at 70° in Benzene

Monomer	Azo Sulfone	Reaction Time (hr)	Product
Styrene	$C_6H_5SO_2N_2C_6H_5$	10	$C_6H_5SO_2CH_2C(C_6H_5){=}N{-}NHC_6H_5$
Styrene	$CH_3SO_2N_2C_6H_5$	10	$CH_3SO_2CH_2C(C_6H_5)H{-}N{=}N{-}C_6H_5$
1-Hexene	$C_6H_5SO_2N_2C_6H_5$	11	$C_6H_5SO_2CH_2CH(n\text{-}C_4H_9){-}N{=}N{-}C_6H_5$
MMA	$C_6H_5SO_2N_2C_6H_5$	8	Poly(MMA)

Table IV
Chain-Transfer Constants (C_{tr}) to Some Initiators and Transfer Agents with Polystyryl and Poly(MMA) Radicals Reported in the Literatures (60°)[a]

C_{tr} with	AIBN	BPO	CCl_4	CBr_4	n-C_4H_9SH	Azo Sulfones[b]
Polystyryl radical	0.0–0.02	0.05	0.01[5]	1.8	22	9.7–23.4
Poly(MMA) radical	0.0	0.02	1–5 × 10^{-5}	0.27	0.67	0

[a] Data from J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," Interscience Publishers, New York, N. Y., 1965, pp II-87 to 109 and II-127 to 129. [b] From Table I in this paper (70°).

when the concentrations of initiator (p-$CH_3C_6H_4SO_2N_2C_6H_5$) and styrene are 0.019 and 4.36 mol per l., respectively.

These results suggest that when the initiator concentration is high the molecular weight of the polymer obtained is so low that the polymer is soluble in methanol. This lowering of the molecular weight may be explained by the chain-transfer reaction to initiator; this is confirmed from telomerization of styrene with azo sulfones as is described later. Therefore, all polymerizations have been carried out with a negligible amount of methanol-soluble polymer as compared to the methanol-insoluble polymer. Chain-transfer constants to azo sulfones have been determined by using a well-known R_p-$\bar{P}_n$ relationship (eq 5), in which

$$1/\bar{P}_n = C_m + C_s[S]/[M] + C_i[I]/[M] + (k_t/k_p^2)R_p/[M]^2 \qquad (5)$$

$C_m = k_{trm}/k_p$, $C_s = k_{trs}/k_p$, and $C_i = k_{tri}/k_p$ are chain-transfer constants to monomer, solvent, and initiator, respectively, and k_p, k_t, [M], [S], and [I] denote propagation and termination rate constant and concentrations of monomer, solvent, and initiator, respectively.

In the bulk polymerization as in our case, $C_s = 0$. Therefore, if $1/\bar{P}_n - (k_t/k_p^2)R_p/[M]^2$ was plotted *vs.* [I]/[M], the line slope and the intercept should be C_i and C_m, respectively. In the case of the substituted p-X—aryl phenylazo sulfones (X = CH_3O, CH_3, H, and Cl), the above relation is shown in Figure 3; as shown in this figure good straight lines are obtained and C_m was practically zero. This agrees essentially with the literature value ($C_m = 6 \times 10^{-5}$ at 70°),[14] showing that the treatment used herein suffices to determine the relative rate constants for induced decomposition of azo sulfones. For both methyl phenylazo sulfone and benzyl phenylazo sulfone the results are shown in Figure 4. The chain-transfer constants to azo sulfones evaluated from the slope of these lines by using a literature value[15] of 494 at 70° (l./mol·sec)$^{-1}$ for k_t/k_p^2 are summarized in Table I.

The Hammett plot for relative rate constants evaluated from chain-transfer constants of para-substituted aryl phenylazo sulfones, p-X—$C_6H_4SO_2N_2C_6H_5$ (X = CH_3O, CH_3, H, and Cl), is shown in Figure 5; it is clear from this plot that electron-withdrawing substituents accelerate the chain-transfer reaction and -donating groups retard the reaction.

The solvent effect on the polymerization rate of styrene initiated by p-tolyl phenylazo sulfone is shown in Table II; the basic solvent (triethylamine) retards the polymerization compared to benzene and toluene.

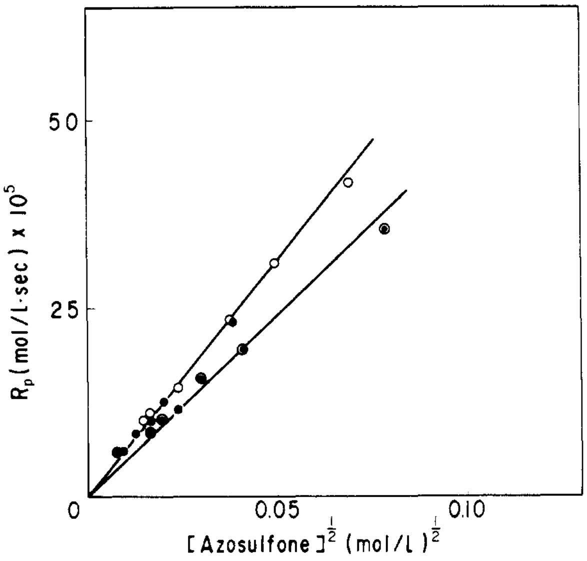

Figure 6. Relationship between R_p's and $[I]^{1/2}$ of azo sulfones. The concentration of MMA is kept constant at 9.41 mol/l. (bulk polymerization). Azo sulfones are p-$CH_3C_6H_4SO_2N_2C_6H_5$ (●), $C_6H_5SO_2N_2C_6H_5$ (○), and p-$ClC_6H_4SO_2N_2C_6H_5$ (⊙).

Polymerization of Methyl Methacrylate with Some Azo Sulfones. MMA was polymerized with para-substituted aryl phenylazo sulfones. From the relationship between R_p and $[I]^{1/2}$ (Figure 6), it is clear that R_p is proportional to $[I]^{1/2}$; a polymerization condition similar to styrene, that is, bulk polymerization, was used. It was revealed from both Figure 6 and the relationship between $1/\bar{P}_n$ and R_p, that for MMA polymerization, unlike the case of styrene, C_i in eq 5 is approximately zero, showing that the chain-transfer reaction to azo sulfones with poly(MMA) radical (induced decomposition of azo sulfones with poly(MMA) radical) has not occurred. From the intercept and line slope in the figure plotted as $1/\bar{P}_n$ *vs.* R_p, the C_m and k_t/k_p^2 were found to be 1.8–2.4 × 10^{-5} (lit. value,[15] 4.5 × 10^{-5}) and 33.6–63.0 (lit. value,[16] 44 (l./mol·sec)$^{-1}$), respectively.

Telomerization of Some Monomers with Azo Sulfones. The results of telomerizations of styrene and of 1-

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hexene with some azo sulfones in high concentrations of azo sulfone have been described in the Experimental Section and are summarized in Table III; as shown in the table, in the case of MMA monomer only, poly(MMA) was obtained instead of telomers.

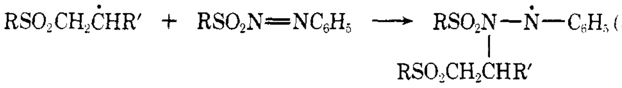
Discussion

The literature values of chain-transfer constants both to some initiators and transfer agents with polystyryl radical are summarized in Table IV. It can be seen from Tables I and IV that chain-transfer constants to azo sulfones are enormously large as compared with those to thermal initiators and are comparable to those of mercaptans.

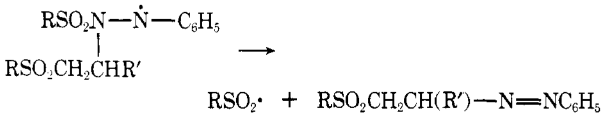
The telomers obtained from telomerization of monomers with azo sulfones would be formed by a following sequence.

$$RSO_2N{=}NC_6H_5 \longrightarrow RSO_2\cdot + N_2 + \cdot C_6H_5 \qquad (6)$$

$$RSO_2\cdot + CH_2{=}CHR' \longrightarrow RSO_2CH_2\dot{C}HR' \qquad (7)$$

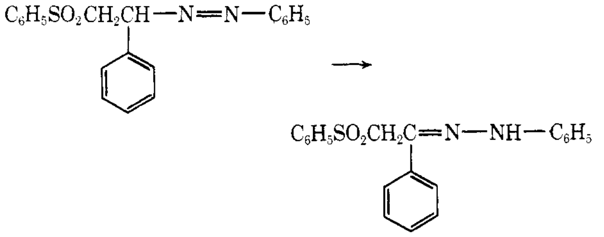


$$RSO_2CH_2\dot{C}HR' + RSO_2N{=}NC_6H_5 \longrightarrow \underset{RSO_2CH_2CHR'}{RSO_2N}{-}\dot{N}{-}C_6H_5 \qquad (8)$$



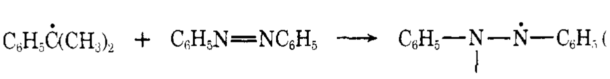
$$\underset{RSO_2CH_2CHR'}{RSO_2N}{-}\dot{N}{-}C_6H_5 \longrightarrow RSO_2\cdot + RSO_2CH_2CH(R'){-}N{=}NC_6H_5 \qquad (9)$$

In the case of telomerization of styrene ($R' = C_6H_5$) with phenyl phenylazo sulfone ($R = C_6H_5$), the following tautomerization may occur.



(10)

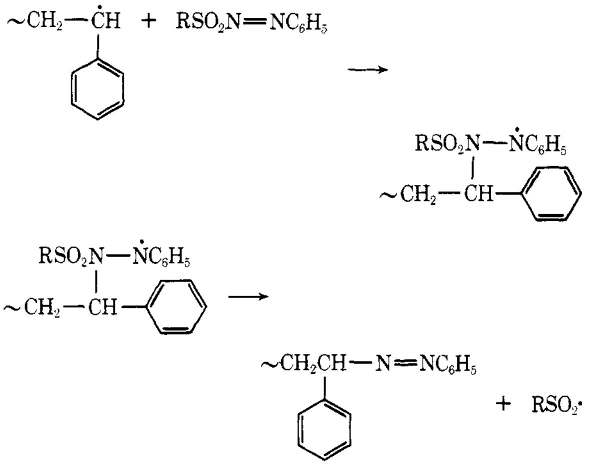
A few examples of the addition reaction of a free radical to a N=N double bond have been demonstrated by Dacey,[17] Batt,[18] and other investigators; Batt reported that displacement reaction of methyl radical *via* the addition of $CH_3\cdot$ across the N=N double bond of $CF_3N_2CF_3$ in the gas phase followed by the elimination of $CF_3\cdot$. And *N*,*N*′-diphenyl-*N*-(1-methyl-1-phenylethyl)hydrazil has been detected by esr.[19] On the other hand, β scission of



$$C_6H_5\dot{C}(CH_3)_2 + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5{-}\underset{C_6H_5C(CH_3)_2}{N}{-}\dot{N}{-}C_6H_5 \qquad (11)$$

the hydrazo radical (elimination of a sulfonyl radical) (eq 9) has not been proved, but in the addition reaction of sulfonyl radical to olefin the elimation reaction of sulfonyl radical, the reverse reaction of addition, has often been assumed.[20] And, elimination reaction of a thiyl radical, which is attached at the β position of the carbon radical, has been studied as extensively as the reverse reaction, the addition of thiyl radical to olefin. Therefore, it would be reasonable to propose the sequence shown in eq 6–10. It is most likely that reactions 8 and 9 are not a stepwise reaction as shown but rather simultaneous reactions.

From the results described a mechanism for chain-transfer reaction to azo sulfones with polystyryl radicals may be considered (eq 12 and 13). From the result of Figure 4 it is clear that the rate of these reactions (eq 12 and 13) increases by electron-withdrawing substituent in azo sulfones. This may be explained by the donor character (or nucleophilicity) of the polystyryl radical as demonstrated in the alternating radical copolymerization of styrene and maleic anhydride; *i.e.*, alternating copolymer is attributable to the much higher reactivity of polystyryl radical toward maleic anhydride monomer than styrene monomer.



(12)

(13)

Figures 5 and 6 reveal that chain-transfer constant to azo sulfones with poly(MMA) radical is practically zero and results on the telomerization would support this behavior, suggesting that the addition reaction to a N=N double bond in azo sulfone (eq 12) may not occur; it is most likely due to the polar effect owing to electrophilic radical and probably also due to steric hindrance of the α-methyl group.

Finally, we will discuss Table II showing the solvent effect on the polymerization of styrene initiated by *p*-tolyl phenylazo sulfone. By parity of reasoning with Uehara's result[8] a redox-type decomposition of *p*-tolyl phenylazo sulfone with triethylamine (and probably also with pyridine) would occur, but the donor solvent (triethylamine) retarded the polymerization compared with those in benzene and other solvents. The reason for this retardation is not completely clear at the present time. Presumably the reactivity of a complexed sulfonyl radical formed between the sulfonyl radical and triethylamine due to a charge-transfer-type interaction is less than that of an uncomplexed sulfonyl radical. Therefore in the donor solvent the addition reaction of sulfonyl radical to styrene monomer would be suppressed. This type of retardation was encountered in the copolymerization of sulfur dioxide and styrene in the presence of pyridine;[21] by the addition of pyridine the overall rate of polymerization was suppressed probably due to a similar reason.

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