program.[17] One spectrum was computed as a pure $>SF_4$ spectrum (A_2B_2 system), and the other was calculated as a pure $-SF_5$ spectrum (AB_4 system). By joining these two calculated spectra together, a theoretical spectrum for the *cis* form of bis-(pentafluorosulfoxy) sulfur tetrafluoride was constructed that ignored interactions between the fluorine atoms of the different groups. In Fig. 1 it may be seen that good correlation between the centers of extensively split bands of the experimental spectrum and computed lines of the theoretical spectrum was obtained. All bands in the spectrum are explained by this treatment. The *trans* form must be either totally absent in this preparation or present in quite small quantity, because the $-SF_4-$ part of its spectrum would be expected to give an easily observable single band.

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[17] Program furnished by Professor K. B. Wiberg, University of Washington.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

Kinetics and Equilibrium of the System Living α-Methylstyrene Dimer + Monomer ⇄ The Living Trimer. Application of a Stirred-flow Reactor for Studies of Reversible Addition Reactions

BY C. L. LEE, J. SMID AND M. SZWARC

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The kinetic studies of a reversible reaction $A + B \rightleftarrows C$ in a stirred-flow reactor makes it possible to determine simultaneously the rate constants of the forward and backward reactions by plotting $\{[A]_0/([B]_0 - [B]_t) - 1\}[B]_t$ *vs.* $1/t$, where t denotes the residence time. Such a plot produces a straight line with a slope equal to the rate constant of the forward reaction and an intercept giving the equilibrium constant of the process. This technique has been applied to studies of the polymerization of the living α-methylstyrene dimer to the living trimer, *i.e.*

$$^{-}\mathrm{C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)^-} + \mathrm{CH_2{:}C(CH_3)(Ph)} \rightleftarrows {}^{-}\mathrm{C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph)^-}$$

At 25° the rate constant of propagation was found to be 7 times greater than that for a high-molecular weight living poly-α-methylstyrene, whereas the corresponding rate constant of depropagation was lower by about a factor of 100. The equilibrium constant was found to be in fair agreement with the value derived from the equilibrium studies by Vrancken, Smid and Szwarc. The factors affecting the respective rate constants are discussed.

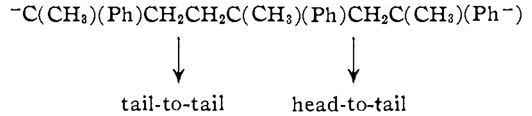
In recent studies, Vrancken, Smid and Szwarc[1] demonstrated that the equilibrium constant of the system α-methylstyrene–living poly-α-methylstyrene depends on the structure of the polymer. For example, the equilibrium constant of the process

$$\text{living }\alpha\text{-methylstyrene dimer} + \text{monomer} \rightleftarrows \text{the living trimer}$$

is substantially larger than that for the growth of an ordinary high molecular weight n-mer. It was shown that the variations in the equilibrium constants arise from differences in the linkages which connect the penultimate unit of the final product with the other segments of the polymer. Thus, the living dimer of α-methylstyrene has the structure[2]

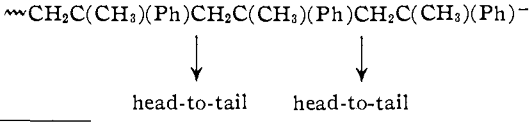
$$^{-}\mathrm{C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)^-}$$

and on addition of the monomer, its terminal unit becomes sandwiched between two α-methylstyrene segments linked in a tail-to-tail and head-to-tail fashion, *i.e.*



$$^{-}\mathrm{C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph^-)} \qquad \underset{\text{tail-to-tail}}{\downarrow} \qquad \underset{\text{head-to-tail}}{\downarrow}$$

On the other hand, in the ordinary head-to-tail polymerization the last unit of a long n-mer becomes flanked by two segments linked in a head-to-tail way when an $n + 1$-mer is formed, namely



$$\sim\mathrm{CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph)^-} \qquad \underset{\text{head-to-tail}}{\downarrow} \qquad \underset{\text{head-to-tail}}{\downarrow}$$

The strain caused by the latter type of linkages is substantially larger than that resulting from the tail-to-tail–head-to-tail array, and this accounts for the reported results. In fact, Vrancken, *et al.*,[1] have shown that the equilibrium constant of the reaction

$$^{-}\mathrm{C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph)^-} + \mathrm{CH_2{=}C(CH_3)(Ph)} \rightleftarrows {}^{-}\mathrm{C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph)CH_2C(CH_3)(Ph)^-}$$

differs insignificantly from that characterizing the high-molecular weight polymerization where head-to-tail linkages are continuously formed. The extent to which these factors affect the equilibrium constants is illustrated by the data collected in Table I.

TABLE I

COMPARISON OF EQUILIBRIUM CONSTANTS IN TETRAHYDROFURAN[a]

$$^{-}(\alpha\mathrm{MeS})_2{}^{-} + \alpha\mathrm{MeS} \rightleftarrows {}^{-}(\alpha\mathrm{MeS})_3{}^{-};\ K_2$$

$$(\alpha\mathrm{MeS})_n{}^{-} + \alpha\mathrm{MeS} \rightleftarrows (\alpha\mathrm{MeS})_{n+1}{}^{-};\ K_\infty \text{ for large } n$$

T, °C.	K_2, l./mole counter-ion K^-	K_∞, l./mole counter-ion Na^-
−15	1750 ± 300	3.3
0	750 ± 100	1.35
+10	450 ± 50	0.9
+25	240 ± 30	0.41

[a] Data taken from ref. 1.

The increase in the equilibrium constant of propagation implies an increase in the propagation rate constant or a decrease in the depropagation rate constant, or both. The work reported in this paper was carried out in order to shed light on these problems and, with this goal in mind, we investigated the kinetics of the reversible reaction

$$\text{living dimer of }\alpha\text{-methylstyrene} + \text{monomer} \rightleftarrows \text{the living trimer}$$

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[1] A. Vrancken, J. Smid and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2036 (1962).

[2] C. E. Frank, *et al.*, *J. Org. Chem.*, **26**, 307 (1961).

This reaction was found to be too fast to be followed by the conventional batch technique, but too slow to be studied by the capillary-flow technique recently developed in this Laboratory.[3]

It was decided, therefore, to adopt the stirred-flow-reactor technique for studying this process. The choice turned out to be most fortunate since this enabled us to determine simultaneously the propagation and depropagation rate constants, as well as the relevant equilibrium constant.

The Theory of Stirred-flow Reactor for a Reversible Addition.—The great simplicity of a stirred-flow reactor arises from the fact that the concentrations of all the reagents and products remain constant in the process.[4] The reagents are fed into the reactor at a constant rate, say, *v* cc./sec., of a solution in which the reagent A is at concentration $C_0{}^A$, the reagent B at $C_0{}^B$, etc. Efficient stirring in the reactor maintains a homogeneous composition of the solution throughout its whole volume *V*, and for a process

$$A + B + \dots \rightleftarrows Q + \dots$$

the respective concentrations in the reactor are $C_t{}^A$, $C_t{}^B \dots C_t{}^Q \dots$, etc. These concentrations are maintained in the liquid which leaves the reactor, and if the reaction in the out-flowing solution is quenched, they can be determined at the end of the experiment.

In our system $A = {}^-\alpha\text{MeS}\alpha\text{MeS}^-$, $B = \alpha\text{MeS}$ and $Q = {}^-\alpha\text{MeS}\alpha\text{MeS}\alpha\text{MeS}^-$, where αMeS denotes the monomer. The reagents are mixed in a specially drilled Teflon three-way stopcock placed just in front of the reactor, and the reacted liquid leaving the reactor flows into wet THF where the process is instantly quenched. The final concentration of the monomer is then determined from the equation

$$v(C_0{}^B - C_t{}^B) = V \times 2k_1C_t{}^A \times C_t{}^B - k_{-1}C_t{}^Q$$

and since

$$2C_0{}^A = [\text{LE}],\ C_0{}^B = [\text{M}]_0,\ 2C_t{}^A = [\text{LE}] - ([\text{M}]_0 - [\text{M}]_t),\ C_t{}^B = [\text{M}]_t$$

and $C_t{}^Q = [\text{M}]_0 - [\text{M}]_t$, the above equation is transformed into

$$1/t = k_1\{[\text{LE}]_0/([\text{M}]_0 - [\text{M}]_t) - 1\}[\text{M}]_t - k_{-1}$$

where $t = V/v$ is the residence time in the reactor and [LE] is the initial concentration of living ends. The factor 2 that appears in the first equation arises from the capacity of each end of the living dimer to react with the monomer. We should stress also that the reactivity of each end is independent of the fate of the other end, *i.e.*, the rate of the reaction

$$^-\text{C(CH}_3\text{)(Ph)CH}_2\text{CH}_2\text{C}^-\text{(CH}_3\text{)(Ph)} + \alpha\text{MeS} \longrightarrow {}^-\text{C(CH}_3\text{)(Ph)CH}_2\text{CH}_2\text{C(CH}_3\text{)(Ph)CH}_2\text{C(CH}_3\text{)(Ph)}^-$$

per reactive end is identical with that of the reaction

$$^-\text{C(CH}_3\text{)(Ph)CH}_2\text{C(CH}_3\text{)(Ph)CH}_2\text{CH}_2\text{C(CH}_3\text{)(Ph)}^- + \alpha\text{MeS} \longrightarrow {}^-\text{C(CH}_3\text{)(Ph)CH}_2\text{C(CH}_3\text{)(Ph)CH}_2\text{CH}_2\text{C(CH}_3\text{)(Ph)CH}_2\text{C(CH}_3\text{)(Ph)}^-$$

On the other hand, the addition to the left end of the trimer shown in the last equation, or the addition to the tetramer, is much slower than the addition to the dimer, and under our experimental conditions this reaction may be neglected. The validity of these statements is justified *a posteriori* by the self-consistency of the results and by the agreement with the previous work[3] (see also the results reported in reference 5). Consequently, if a series of experiments is carried out with different rates of flow, *i.e.*, different *t*, a plot of $1/t$ *vs.* $\{[\text{LE}]_0/([\text{M}]_0 - [\text{M}]_t) - 1\}[\text{M}]_t$ should give a straight line with a slope equal to k_1, an intercept on the *x*-axis equal to the equilibrium constant, and an intercept on the *y*-axis equal to $-k_{-1}$.

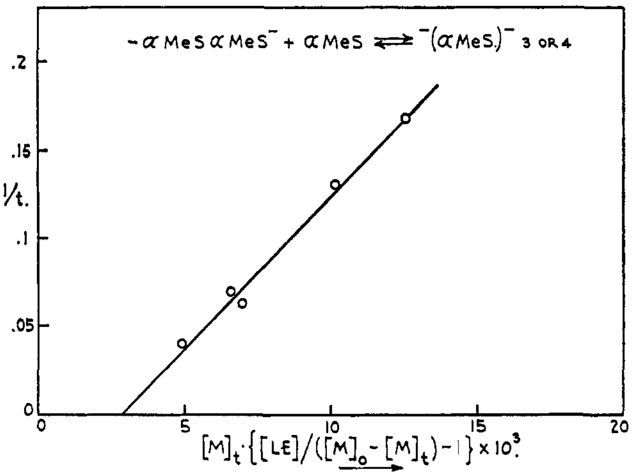

Figure 1.

Results and Discussion

Five series of experiments were carried out at 25° in a stirred-flow reactor of about 8-cc. volume. The conditions maintained in each series and the results of each run are listed in Table II. The procedure described above led to linear plots, one of which is shown in Fig. 1. From such plots the respective rate con-

Table II

Series	$[\text{LE}]_0$, $\times 10^3$ *M*	$[\alpha\text{MeS}]_0$, mole/l. $\times 10^3$	*t*, sec.	$[\alpha\text{MeS}]_t$, mole/l. $\times 10^3$
2	4.41	2.98	21.5	1.87
2	4.46	2.94	13.5	1.98
2	4.39	2.94	9.95	2.08
2	4.39	2.90	7.42	2.17
3	6.31	2.98	26.5	1.41
3	6.48	2.90	14.7	1.65
3	6.47	2.90	10.35	1.765
3	6.48	2.90	7.64	1.85
3	6.48	2.91	5.94	1.95
3	6.57	2.87	4.80	2.02
3	6.18	3.04	47.6	1.255
4	2.92	3.10	24.4	2.20
4	2.97	3.065	14.4	2.30
4	2.98	3.04	7.67	2.46
4	2.96	3.06	5.97	2.56
5	13.8	3.13	18.8	0.974
5	14.1	3.08	12.7	1.195
5	14.2	3.04	9.47	1.370
5	14.2	3.04	7.35	1.485
5	14.4	3.00	5.90	1.542
5	14.5	2.97	4.92	1.757
6[a]	4.38[a]	1.09[a]	24.15[a]	0.718[a]
6[a]	4.38[a]	1.09[a]	24.15[a]	.716[a]
6	4.49	1.07	15.40	.603
6	4.57	1.065	10.74	.670
6[a]	4.55[a]	1.065[a]	8.54[a]	.744[a]
6[a]	4.55[a]	1.065[a]	8.54[a]	.725[a]
6	4.56	1.06	6.59	.778
6	4.48	1.06	5.28	.815

[a] Runs in which consecutive samples were taken from the reactor without interrupting the flow. The constancy of the $[\alpha\text{MeS}]_t$ proves that the reactor attained its stationary state.

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(3) C. Geacintov, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 2508 (1962).

(4) K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944); see also B. Stead, F. M. Page and K. G. Denbigh, *Discussions Faraday Soc.*, **2**, 263 (1947).

(5) D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 533 (1963).

TABLE III

$^-C(CH_3)(Ph)CH_2CH_2C^-(CH_3)(Ph) + \alpha MeS \rightleftarrows$ the living trimer

Solvent, THF; T, 25°; counter-ion, K^+

Series	$[LE]_0$, M $\times 10^3$	$[\alpha MeS]_0$, M $\times 10^3$	$\frac{[\alpha MeS]_0}{[LE]_0}$	k_1, l. mole^{-1} sec.$^{-1}$	k_{-1}, sec.$^{-1}$	K, l./mole
4	3.0	3.0	1.0	17.2	0.050	346
2	4.4	2.9	0.66	17.3	.052	333
3	6.5	2.9	.45	18.9	.062	304
5	14.0	3.0	.21	15.4	.046	333
6	4.5	1.1	.24	16.7	.049	339
			Average	17.1	0.052	331

stants and equilibrium constant were determined, all the results being collected in Table III.

Inspection of Table III shows that the calculated constants are independent of living ends concentration, [LE], which was varied by a factor of about 5, and of monomer concentration which was varied by a factor of 3. Technical difficulties prevented us from further variation of these parameters. The value of the equilibrium constant derived from this work, *i.e.*, 331 l./mole, compares well with that derived from the studies of Vrancken, Smid and Szwarc[1] (240 ± 30 l./mole). The latter was arrived at by a steep extrapolation to zero concentration (see ref. 1), and since the present technique appears to be more reliable, we feel that our recent results are more accurate.

The reliability of our technique and of our assumptions should now be examined: (1) It was proved that the reactor reached its stationary operating conditions since the concentration of the monomer in two consecutively taken samples remained constant (see Table II). (2) It was assumed that the polymerization of trimer to tetramer may be neglected. This is justified by the self consistency of our results and by the agreement with Vrancken's data.[1] Moreover, the rate constant of the first addition was found to be 17 l. mole^{-1} sec.,$^{-1}$ whereas that for the following addition was calculated[6] to be 2.5 l. mole^{-1} sec.$^{-1}$. Finally, no trend in the observed values of k_1 was found when the ratio $[\alpha MeS]_0/[LE]_0$ was varied by a factor of nearly 5. At any rate, it is certain that the continuation of polymerization, if any, could not introduce any substantial error in our data.

We can conclude now that the increase in the equilibrium constant, when the addition to living α-methylstyrene dimer is compared with that to the high-molecular weight polymer, mainly results from a substantial decrease in the rate constant of depropagation. While the rate constant of dissociation of $^-(\alpha MeS)_3^-$ to the dimer is 5×10^{-2} sec.$^{-1}$ at 25°, the calculated value[1,6] for the depropagation rate constant of the high-molecular weight polymer is about 6 sec.$^{-1}$, *i.e.*, higher by two powers of ten. On the other hand, the respective rate constant of propagation increased only by a factor of about 7. This indicates a considerable decrease of steric strain in the transition state when the high-molecular weight polymer degrades.

We emphasized in our discussion the importance of steric factors. The problem arises, however, to what extent the observed changes might be due to electrostatic factors. The repulsion between the two negative charges of the dimer is reduced when the trimer is formed, and this may affect the respective rate constant of propagation and the equilibrium constant. The problem, however, is more complex than stated, since here one deals not with a charge–charge interaction but rather a dipole–dipole interaction of ion-pairs. The latter is substantially weaker than the former and may even lead to an attraction if a favorable orientation of the dipoles is attained. Thus, calculation of the electrostatic energy becomes uncertain.

In order to answer reliably this question, we investigated the rate of addition of α-methylstyrene to cumene potassium. The latter compound may be visualized as "one-meric" living poly-α-methylstyrene. The kinetic studies were carried out in a capillary-flow system[3] since the reaction was found to be very fast. The results are given in Table IV and show that the respective rate constant of propagation is substantially greater than that observed in the process living αMeS dimer → the living αMeS trimer. In fact, these results reflect the pattern observed previously in the system $\alpha MeS^- +$ styrene (see ref. 5). Hence, the steric factors are apparently the important ones in determining the rate and equilibria in polymerizations of different α-methylstyrene polymers and oligomers.

TABLE IV

Cumyl$^-$, $K^+ + \alpha MeS \longrightarrow Ph{\cdot}C(Me)_2{\cdot}CH_2{\cdot}C(Me)(Ph)^-, K^+$

Solvent, THF; T, 25°

$[C_6H_5C(Me)_2^-, K^+]_0$, m./l. $\times 10^3$	$[\alpha MeS]_0$, m./l. $\times 10^3$	Number of points	k_{12},[a] l./m. sec.$^{-1}$
5.0	3.3	4	155
4.8	3.1	4	144

[a] Calculated on the basis of second-order kinetics.

Experimental

The all-glass reactor developed for this study was about 8 cc. in volume. The glass-made stirrer, containing a sealed-in iron bar, was driven magnetically at the rate of about 20 r.p.s. The reagents, the living dimer and the monomer, were stored in calibrated and thermostated reservoirs from which the respective solutions were pressed into a three-way Teflon stopcock sealed to the inlet capillary of the reactor. The outlet capillary was immersed in a beaker containing wet tetrahydrofuran.

The whole apparatus was identical with that described in ref. 3 with the exception that the stirred-flow reactor replaced the capillary tube used as a reactor in the capillary-flow system. The operation was also similar to that outlined in ref. 3, but the reactor had to be run for a time of 3–4t prior to collecting the samples. During this time, the stationary state was established. In calculating the residence time the volumes of the inlet and outlet capillaries were added to the reactor volume, introducing thus a correction of 2% only. It is believed that this gives a slightly more realistic estimate of the residence time.

The solutions of the living α-methylstyrene dipotassium salt and of the monomer were prepared as described in ref. 1 and 3. The reader is referred to those papers for technical details. The concentration of the residual monomer were determined spectrophotometrically (see ref. 3). In series 6, these concentrations were very low and a 10-cm. long optical cell had to be employed. The low optical density introduced some errors in those experiments of this series which corresponded to the highest residence time, *i.e.*, the lowest monomer concentration (see Table II).

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(6) Extrapolated from the data of D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **36**, 1141 (1958). Justification for using the data pertaining to a high-molecular weight polymer for the system trimer → tetramer may be found in ref. 4.