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Kinetics of Radical Polymerization. XXXIII. Solvent Effect in the System Styrene/Carbon Tetrachloride

T. Földes-Berezsnich^a; M. Szesztay^a; E. Boros Gyevi^a; F. Tüdös^b

^a Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

^b Department of Chemical, Technology Eötvös Lorand University, Budapest, Hungary

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**Kinetics of Radical Polymerization. XXXIII.
Solvent Effect in the System
Styrene/Carbon Tetrachloride**

T. FÖLDES-BEREZSNICH, M. SZESZTAY, and E. BOROS GYÉVI

Central Research Institute for Chemistry of the Hungarian Academy
of Sciences
H-1025 Budapest, Hungary

and

F. TÜDÖS

Department of Chemical Technology
Eötvös Lorand University, H-1088
Budapest, Hungary
Central Research Institute for Chemistry of the Hungarian Academy
of Sciences
H-1025 Budapest, Hungary

ABSTRACT

A study was made of the polymerization of styrene initiated by azo-bis-isobutyronitrile in carbon tetrachloride solution. The overall and initiation rate as well as the degree of polymerization were found to decrease greatly with increasing dilution. Furthermore, it is pointed out that the "constant" of the chain transfer process occurring in the styrene/ CCl_4 system depends on the monomer and solvent concentrations. The solvent dependence of the chain transfer and chain propagation process is described by the hot radical theory.

INTRODUCTION

In our previous paper a kinetic analysis of the polymerization of styrene in benzene [1] and in dimethylformamide [1, 2] was given. It was shown that, contrary to literature data [3, 4], measurable chain transfer does not take place in these systems and the dependence of the degree and rate of polymerization on the concentrations of solvent and monomer is a consequence of the solvent effect on chain propagation and initiation processes.

Our present work deals with the investigation of radical polymerization of styrene in carbon tetrachloride and tries to find an explanation of the phenomenon observed by several authors (e.g., Refs. 5 and 6) that the "constant" of chain transfer with the solvent is dependent on the concentrations of monomer and solvent in this system. Therefore, a detailed investigation was carried out regarding the effect of the reaction medium on the overall and initiation rate, and the degree of polymerization.

EXPERIMENTAL

Purifications of styrene (St), carbon tetrachloride, and azo-bis-isobutyronitrile were carried out as described earlier [7, 8].

Polymerization kinetic measurements were performed dilatometrically at 50°C. Deoxygenation of the mixtures to be polymerized was done by the usual freezing and thawing method. Polymerizations were carried out in scaled dilatometers up to 10% conversion, then, after sudden cooling and opening the dilatometers, the polymerizing mixtures were poured into flasks containing inhibitor.

The overall rate of polymerization (W_{St}) was determined by the graphic differentiation of $\log m_0/m = f(t)$ curves. The rate of initiation was measured by the inhibition method, using the Banfield radical [7, 9]. Molecular weights of the polymers formed were determined by gel permeation chromatography in a Waters ALC/GPC type, high-pressure equipment at room temperature, using tetrahydrofuran (THF) as solvent.

As is known, a considerable chain transfer process takes place in the styrene/ CCl_4 system. Consequently, mainly at high solvent concentrations, polymers with very low molecular weights can be formed, which may be lost if the usual precipitation technique is applied. In order to avoid this loss, the polymerization mixtures were directly used for the GPC measurements as follows.

Knowing the initial monomer concentrations and conversions of the polymerizing mixtures, samples containing exactly 10 mg polymer were taken from each mixture. A considerable portion of the monomer and the solvent was evaporated, then 2 mL THF freshly distilled from Cu_2Cl_2 and from KOH were added. These solutions were filtered and 80 μ L aliquots were chromatographed in a series of μ -styrogel

TABLE 1. Dependence of the Rate of Polymerization on the Initiator Concentration, System St/AIBN/CCl₄/50°

m_0 (mol/dm ³)	$x_0 \times 10^2$ mol/dm ³)	$W_{st} \times 10^5$ (mol/dm ³ /min)
8.45	0.201	3.760
	0.750	7.26
	1.860	11.43
	2.921	14.32
	5.878	20.25
	12.300	29.40
1.75	0.289	2.63
	0.419	3.21
	0.645	3.86
	3.976	9.78
	6.390	12.40
	10.260	15.71

GPC columns ($10^6 + 10^5 + 10^4 + 10^3 + 500 + 100 \text{ \AA}$). The calculation of the molecular weight will be presented in another publication.

EXPERIMENTAL RESULTS AND THEIR EVALUATION

The dependence of the rate of polymerization on the initiator concentration was studied at two styrene concentrations. The rate of polymerization data and the initial concentrations of monomer (m_0) and of initiator (x_0) are listed in Table 1.

It can be seen from the $\log W_{st} - \log x_0$ dependences shown in Fig. 1 that the rate of polymerization is proportional to (initiator concentration)^{1/2} both in bulk and in great dilution. The order of reaction related to the initiator calculated by the least-squares method was 0.499 ($m_0 = 8.45 \text{ mol/L}$) and 0.501 ($m_0 = 1.75 \text{ mol/L}$).

The dependences of the rate ($W_1 = 2k_1fx_0$) and the rate constant ($2k_1f$) of initiation on the concentrations of monomer and of solvent were studied by the inhibition method at 50°C. The $2k_1f$ values determined at different initial monomer and solvent concentrations and at

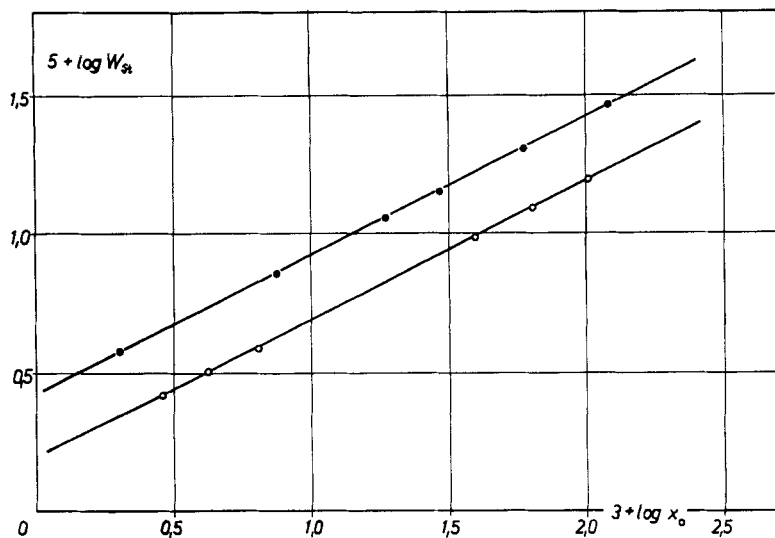


FIG. 1. Dependence of the rate of polymerization on the initiator concentration (●, $m_0 = 8.45 \text{ mol/L}$; ○, $m_0 = 1.75 \text{ mol/L}$).

TABLE 2. Dependence of the Rate Constant of Initiation ($2k_{if}$) on the Solvent Concentration, System St/AIBN/ $\text{CCl}_4/50^\circ$

χ_{CCl_4}	$2k_{if} \times 10^4$ (min^{-1})
0	1.75
0.150	1.66
0.380	1.51
0.536	1.40
0.764	1.28
0.803	1.14

constant initiator concentration ($x_0 = 2.5 \times 10^{-2} \text{ mole/L}$) are listed at Table 2 (where χ_{CCl_4} denotes the mole fraction of carbon tetrachloride).

The $2k_{if}$ values obtained, as can be seen from the data, are highly dependent on the dilution and can be given within the limits of experimental error ($\pm 5\%$) by the following linear equation:

$$10^4 \times 2k_{if} = 1.764 - 0.700 \chi_{\text{CCl}_4} \text{ min}^{-1} \quad (1)$$

The dependences of the rate of polymerization and of the overall rate constant (K) of styrene on the reaction medium were investigated at the initial concentrations of monomer (m), solvent (s), and initiator (x_0) listed in Table 3.

From the rate of polymerization measured dilatometrically, the value of K was calculated by

$$\frac{d}{dt} \log \frac{m_0}{m} = \frac{K\sqrt{x_0}}{2,303} \quad (2)$$

These data are also given in Table 3, together with the number-average molecular weights (\bar{M}_n) of the polymers (with the experimental limits of error), as well as the data of reciprocal values of the degree of polymerization (\bar{P}_n) calculated from \bar{M}_n .

The K and $1/\bar{P}_n$ values of Table 3 show that both the overall rate constant and the degree of polymerization considerably depend on the dilution. As is known, the overall rate constant includes the rate constants of the three elementary steps [chain propagation (k_2), chain termination (k_4), and initiation ($2k_{if}$):

$$K = \frac{\tilde{k}_2}{\sqrt{k_4}} \sqrt{2k_{if}} \quad (3)$$

In the knowledge of the solvent dependence of $2k_{if}$ (see Eq. 1 and Table 2), $k_2/\sqrt{k_4}$ was calculated from the experimental values of K . The $k_2/\sqrt{k_4}$ values also show (see Table 3) a considerable dependence on the monomer and solvent concentration.

In the polymerization of styrene, chain termination takes place by the recombination of the polymer radicals [10] and there is no chain transfer with the monomer [1, 2], thus the equation of the degree of polymerization is given by the following simple relation [1]:

$$\frac{1}{\bar{P}_n} = \frac{1}{2} \frac{\sqrt{W_1 k_4}}{\tilde{k}_2 m} + \tilde{C}_s s/m \quad (4)$$

where \tilde{C}_s is the constant of chain transfer to the solvent.

Upon the considerations published in Ref. 11, Eq. (4) can be transformed into the following, computationally "improved" linear equation:

TABLE 3. Kinetic Data of the System St/AIBN/CCl₄/50°

No.	<i>m</i> (mol/dm ³)	<i>s</i> (mol/dm ³)	<i>x</i> ₀ × 10 ² (mol/dm ³)	<i>K</i> × 10 ³ (dm ³ /2/mol ^{1/2} /min)	$\tilde{k}_2/\sqrt{k_4} \times 10^2$ (dm ³ /2/mol ^{1/2} /min ^{1/2})	\bar{M}_n	$\frac{1}{\bar{P}_n} \times 10^3$
1	0.815	9.00	3.386	1.03	9.55	-	-
2	1.35	8.40	3.009	1.08	10.00	2610 ± 190	39.90
3	1.79	7.84	2.632	1.17	10.55	-	-
4	2.01	7.62	2.956	1.18	10.71	3490 ± 120	29.84
5	2.52	6.99	2.547	1.25	11.20	-	-
6	2.66	6.84	2.861	1.31	11.65	4420 ± 200	23.56
7	3.33	6.05	2.953	1.35	11.80	5730 ± 260	18.18
8	3.55	5.80	2.691	1.39	11.98	-	-
9	3.98	5.29	2.899	1.44	12.32	7190 ± 150	14.48
10	4.65	4.50	2.946	1.49	12.51	9650 ± 550	10.79
11	4.97	4.09	2.687	1.56	12.92	-	-
12	5.31	3.71	2.877	1.61	13.26	11940 ± 490	8.722
13	6.14	2.72	2.761	1.66	13.49	-	-
14	6.68	2.10	2.890	1.74	13.79	21890 ± 810	4.757
15	7.29	1.37	2.998	1.79	13.92	32340 ± 870	3.220
16	8.07	0.456	2.871	1.90	14.46	61990 ± 2050	1.680
17	8.45	0	2.879	1.93	14.530	113480 ± 2800	0.918

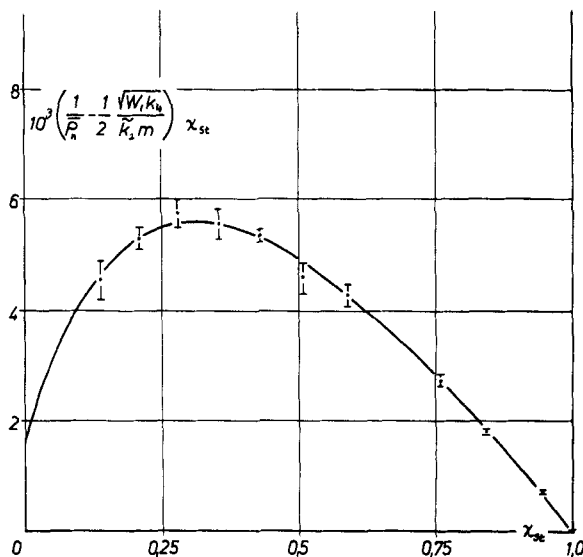


FIG. 2. Experimental data of the system St/AIBN/CCl₄/50° plotted according to Eq. (5).

$$\chi_M \left[\frac{1}{\bar{P}} - \frac{1}{2} \frac{\sqrt{W_1 k_4}}{\tilde{k}_2 m} \right] = \tilde{C}_S (1 - \chi_M) \quad (5)$$

where χ_M is the molar fraction of the monomer. This equation, in contrast with Eq. (4), sets the experimental data in the 0-1 interval (instead of 0- ∞) and, if the supposed mechanism is valid, makes the precise determination of \tilde{C}_S possible.

Figure 2 shows the plot of experimental data of the polymerization system studied (see Tables 2 and 3) according to Eq. (5), together with the experimental limits of error.

It is obvious from Fig. 2 that the data of the system studied do not show such a linear dependence which should be observed according to Eq. (5) if the basic assumptions of the classical treatment ($k_2 = \text{const}$ and $\tilde{C}_S = \text{const}$) were valid. The significant nonlinear dependence obtained can be interpreted only by the assumption that \tilde{k}_2 (and $\tilde{C}_S = k_3/\tilde{k}_2$) is not constant but depends on the dilution. Such deviations have also been found by other authors, even if in not such an explicit form (see, e.g., Refs. 5 and 6). In the investigation of the terpolymerization of styrene (measuring only the degree of polymerization), Olaj [6] found from the $1/\bar{P} = f(s/m)$ dependence a variation of \tilde{C}_S

with the variation of the initial concentrations of the monomer and solvent. To interpret this phenomenon, Olaj assumed the formation of an EDA complex between styrene and carbon tetrachloride and the participation of this complex in the chain transfer. It must be noted, however, that he could not detect directly the assumed EDA complex.

In the polymerization of styrene, Burnett et al. [12] investigated the effects of different solvents on the absolute values of rate constants of chain propagation and termination steps. They pointed out the decrease of k_2 with the increase in solvent concentration. According to the diffusion theory, the variation of k_4 is determined by the viscosity of the monomer-solvent mixture. In a system such as St/ CCl_4 , however, where the viscosities of the components very slightly differ from each other (styrene, $\eta = 0.552$ cP (50°C) [13]; CCl_4 , $\eta = 0.652$ cP (50°C) [8]), the solvent dependence of $k_2/\sqrt{k_4}$ can be attributed to the chain propagation process. In the literature there are two theories attempting to interpret the latter process, the so-called EDA complex theory [14, 15] and the theory of hot radicals [1]. Let us investigate which of the two theories can describe the dependences of $k_2/\sqrt{k_4}$ values of the polymerization system St/AIBN/ $\text{CCl}_4/50^\circ$ on the dilution.

The EDA complex theory [14, 15] states that in the polymerization in solution, electron-donor-acceptor complexes are formed by the interaction of the polymer radical with the monomer (m) and with the solvent (s). In the chain propagation, however, only the complexes formed between the polymer radical and the monomer have a role, thus the rate of polymerization depends on the concentration of the monomer and of the solvent. The extent of the interaction is considered by the τ lifetime of EDA complexes.

According to the theory, the τ_s/τ_m ratio is a constant characteristic of the given monomer/solvent system and independent of the dilution. It can be determined by the following linear equation [16]:

$$\chi_M \frac{m_b}{\Phi^b m} = \left(1 - \frac{\tau_s}{\tau_m}\right) M + \frac{\tau_s}{\tau_m} \quad (6)$$

where

$$\Phi^b = \frac{(k_2/\sqrt{k_4})}{(\tilde{k}_2/\sqrt{\tilde{k}_4})_b} \quad (7)$$

and the subscript b refers to bulk polymerization. We note that Eq. (6) is a computationally improved variation of the authors equation [14, 15]; for more details see Ref. 16.

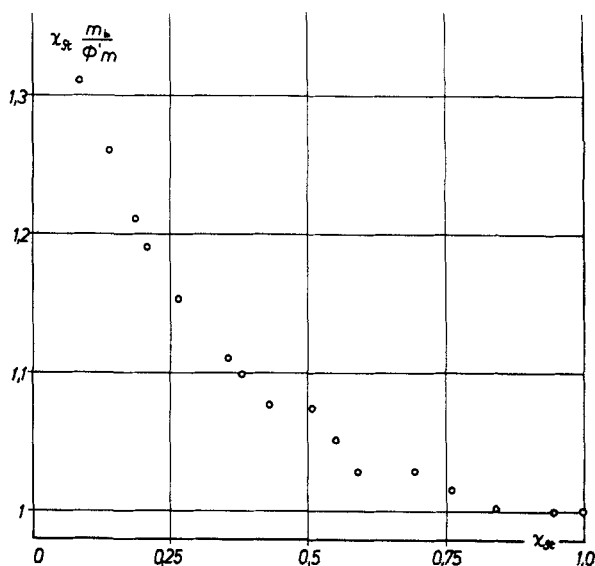


FIG. 3. Experimental data of the system St/AIBN/CCl₄/50° plotted according to Eq. (6).

Figure 3 shows the plot of experimental data of the systems St/AIBN/CCl₄/50° (see Table 3) according to Eq. (6).

As can be seen from Fig. 3, the experimental data do not exhibit any linearity, therefore the solvent effect observed cannot be described by the EDA complex theory. It must be mentioned that this theory was not suitable for the description of solvent effects in several other systems either (see, e.g., Refs. 16 and 17).

The theory of hot radicals [1] is based on the fact that the propagating radical contains, in the moment of its formation, the reaction heat and activation energy of the exothermal elementary process of chain propagation in the form of excitation energy of the inner (mainly vibrational) degrees of freedom.

The vibrationally excited hot radical (R*) formed in the



chain propagation step can be deactivated in collisions with the components of the reaction mixture (monomer and solvent):



The theory of hot radicals assumes that a portion of the active centers having a high excess energy (in the case of styrene polymerization: $E^* = E_2 + \Delta H_{\text{pol}} = 25 \text{ kcal/mol}$) can react with the monomer before deactivation:



The activation energy demand of this chain propagation reaction is covered by the excess energy of the hot radical, thus the process does not need any activation from outside.

As is known, carbon tetrachloride readily reacts with the radical localized on the C atom. Such a reaction also takes place very likely with the hot C radicals. Subsequently, trichloromethyl radicals formed in the chain transfer reaction can easily react with the monomer, resulting in the formation of the R^* radical.

Thus, assuming the participation of hot radicals in addition to ordinary ones in the chain transfer process to the solvent, two reactions are to be considered instead of the usual one elementary step:



If the rates of initiation and of bimolecular termination are considered in the usual way [4] and the Bodenstein principle is applied to both kinds of radicals, the differential equation system of the process is

$$-dm/dt = k_2 r m + k_2^* r^* m \quad (14)$$

$$dr^*/dt = k_2 r m - k_7 r^* m - k_7' r^* s - k_3^* r^* s \simeq 0 \quad (15)$$

$$dr/dt = W_1 - k_2 r m + k_7 r^* m + k_7' r^* s + k_3^* r^* s - k_4 r^2 \simeq 0 \quad (16)$$

From (15), the concentration of hot radicals

$$r^* = \frac{k_2 r}{k_7 + (k_7' + k_3^*)s/m} \quad (17)$$

is proportional to the concentration of the cold radicals, but it depends on the dilution. The usual expression is given from (16) for the concentration of cold radicals:

$$r = \sqrt{W_1/k_4} \quad (18)$$

The rate of polymerization with Eqs. (17) and (18) is

$$-\frac{dm}{dt} = k_2 \sqrt{\frac{W_1}{k_4}} m \left[1 + \frac{1}{\gamma + (\gamma' + C_S^*)s/m} \right] = \tilde{k}_2 \sqrt{\frac{W_1}{k_4}} m \quad (19)$$

where

$$\gamma = k_7/k_2^* \quad (20)$$

and

$$\gamma' = k_7'/k_2^* \quad (21)$$

finally

$$C_S^* = k_3^*/k_2^* \quad (22)$$

According to the theory of hot radicals, the "effective" chain propagation constant (k_2) has two limiting cases:

(a) Bulk polymerization

$$\lim_{s/m \rightarrow 0} \tilde{k}_2 = (1 + \frac{1}{\gamma}) \quad (23)$$

(b) Infinite dilution

$$\lim_{s/m \rightarrow \infty} \tilde{k}_2 = k_2 \quad (24)$$

In terms of the theory, in the case of one individual monomer and temperature, the value of k_2 always approaches the same limiting value at infinite dilution regardless of the nature of the solvent applied. The cooling (deactivation) parameters (γ and γ') are, however, independent of the reaction temperature, whereas γ' depends on the nature of the solvent.

Applying the classical equation of the rate of polymerization

$$-dm/dt = K\sqrt{x_0}m \quad (25)$$

the overall rate constant (K) of the polymerization can be expressed as

$$K = \frac{\tilde{k}_2}{\sqrt{k_4}} \sqrt{2k_1f} = \left[\frac{k_2}{\sqrt{k_4}} \sqrt{2k_1f} \right] (1 + D) \quad (26)$$

where

$$D = \frac{1}{\gamma + (\gamma' + C_s^*)s/m} \quad (27)$$

is the so-called dilution factor.

The degree of polymerization (which, by definition, is the quotient of the rate of chain propagation and of the rate of formation of polymer molecules) can be expressed in terms of the above reaction scheme as follows:

$$\bar{P}_n = \frac{k_2rm + k_2^*r^*m}{\frac{1}{2}(1 + \lambda)k_4r^2 + k_3rs + k_3^*r^*s} \quad (28)$$

Equation (28) can be transformed, using (17), (18), (27), and $\lambda = 0$ [10], into

$$\frac{1}{\bar{P}_n} = \frac{1}{2} \frac{\sqrt{W_1k_4}}{k_2(1 + D)m} + \frac{(C_s + C_s^*D)}{(1 + D)} s/m \quad (29)$$

and

$$\frac{1 + D}{\bar{P}_n} = \frac{1}{2} \frac{\sqrt{W_1k_4}}{k_2m} + (C_s + C_s^*D)s/m \quad (30)$$

where

$$C_s = k_3/k_2 \quad (31)$$

is the constant of chain transfer with the cold radicals.

Thus the expression derivable in terms of the hot radical theory differs from the generally used equation of the degree of polymerization

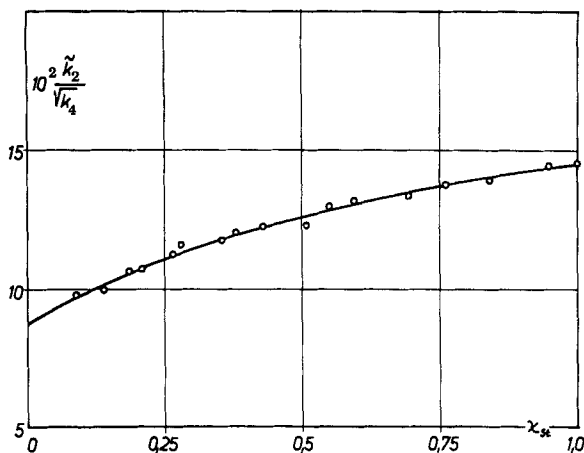


FIG. 4. Dependence of the parameter $\tilde{k}_t/\sqrt{k_4}$ on the dilution, system St/AIBN/CCl₄/50°.

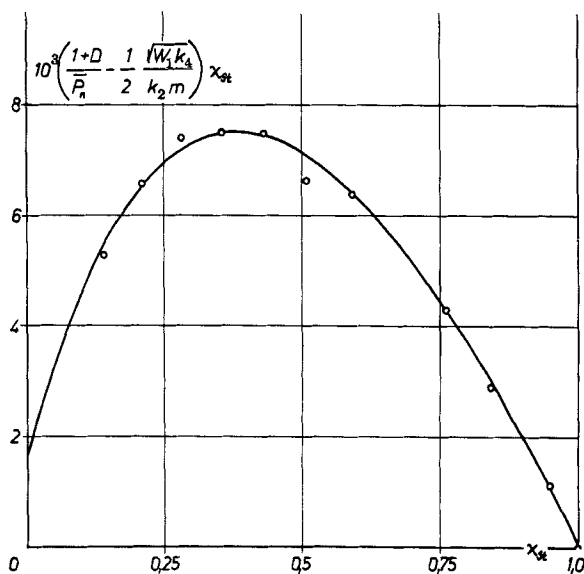


FIG. 5. Experimental data of the system St/AIBN/CCl₄/50° plotted according to Eq. (32).

TABLE 4

System	$(k_2/\sqrt{k_4}) \times 10^2$	γ	γ'
St/AIBN/CCl ₄ /50°	8.75	1.505	0.716
St/AIBN/Bz/50°	8.63	1.478	0.521
St/AIBN/DMF/50°	8.78	1.510	0.678

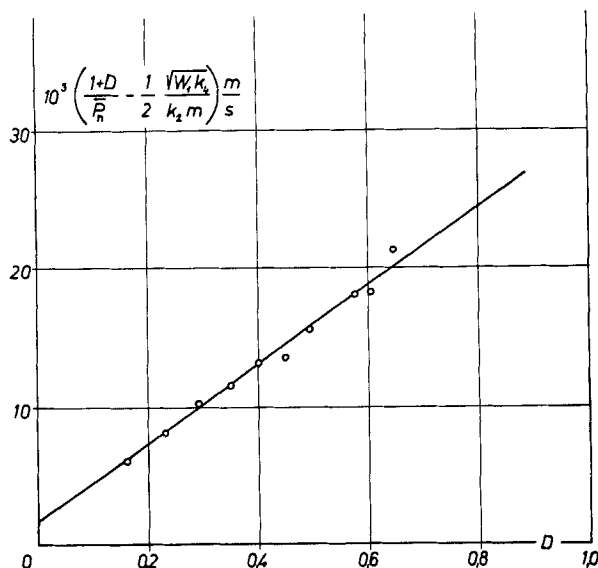


FIG. 6. Experimental data of the system St/AIBN/CCl₄/50° plotted according to Eq. (33).

not only because it contains the constant (C_s^*) of chain transfer process taking place between the hot radical and the solvent, but also it takes into account the dependence of the degree of polymerization on the dilution, which can exist even when there is no chain transfer in the system, since k_2 itself depends on the dilution.

Because of the computationally uncomfortable properties of s/m , for numerical calculations it is better to use the molar fraction (χ_M) of the monomer as an independent variable. The improved form of Eq. (30) is

$$\left\{ \frac{1 + D}{\bar{P}_n} - \frac{1}{2} \frac{\sqrt{W_1 k_4}}{k_2 m} \right\} \chi_M = (C_S + C_S^* D)(1 - \chi_M) \quad (32)$$

To illustrate the preciseness with which the hot radical theory describes the St/AIBN/CCl₄/50° system investigated, the $k_2/\sqrt{k_4}$ data (see Table 3) in the function of the mole fraction of styrene are shown in Fig. 4.

The solid line curve was calculated by Eq. (26). The optimal parameters of the equation were determined with iteration by the simplex method. The values of the parameters obtained, together with the analogously determined parameters of the systems St/AIBN/Bz/50° and St/AIBN/DMF/50°, are listed in Table 4.

The data of Table 4 support the basic assumption of the hot radical theory which states that, in the case of one individual monomer, the parameters $k_2/\sqrt{k_4}$ and γ must be independent of the nature of the solvent applied [1].

Having the data (γ, γ') necessary for the calculation of the dilution factor, the constants of chain transfer processes between the cold radical and the solvent as well as the hot one and the solvent were calculated from the experimental data given in Tables 2 and 3 by Eq. (30).

The values of C_S and C_S^* , which were calculated by a computer using the least-squares method, are the following:

$$C_S = 1.70 \times 10^{-3}$$

$$C_S^* = 2.84 \times 10^{-2}$$

The solid line curves of Figs. 2 and 5 were calculated by these constants.

Equation (30) can be given as a relationship linear for D:

$$\left(\frac{1 + D}{\bar{P}_n} - \frac{1}{2} \frac{\sqrt{W_1 k_4}}{k_2 m} \right) \frac{m}{s} = C_S + C_S^* D \quad (33)$$

The experimental data of the system St/AIBN/CCl₄/50° plotted according to Eq. (33) are shown in Fig. 6.

The linear relationship of Fig. 6 is also evidence for the validity of equations derived in terms of the hot radical theory.

REFERENCES

- [1] F. Tüdös, *Acta Chim. Acad. Sci. Hung.*, **43**, 397 (1965); **44**, 403 (1965).

- [2] T. Földes-Bereznich, M. Szesztay, E. Boros Gyevi, and F. Tüdös, J. Polym. Sci., Polym. Chem. Ed., **18**, 1223 (1980).
- [3] M. H. George, J. Polym. Sci., **A2**, 3169 (1964).
- [4] G. E. Ham (ed.), Vinyl Polymerization, Vol. 1, Dekker, New York, 1967.
- [5] M. H. George and P. F. Onyon, Trans. Faraday Soc., **59**, 1390 (1963).
- [6] O. F. Olaj, Makromol. Chem., **136**, 255 (1970).
- [7] F. Tüdös, T. Földes-Bereznich, and M. Azori, Acta Chim. Acad. Sci. Hung., **24**, 91 (1960).
- [8] A. Weissberger and E. S. Proskauer, Organic Solvents, Interscience, New York, 1955.
- [9] F. H. Banfield and I. Kenyon, J. Chem. Soc., p. 1612 (1926).
- [10] J. Bevington, H. Melville, and R. Taylor, J. Polym. Sci., **12**, 449 (1952); **14**, 643 (1954).
- [11] T. Kelen and F. Tüdös, J. Macromol. Sci.-Chem., **A9**, 1 (1975).
- [12] G. M. Burnett, G. G. Cameron, and S. N. Joiner, J. Chem. Soc., Faraday Trans. 1, 69 322 (1973).
- [13] R. H. Boundy and R. F. Boyer (eds.), Styrene, Reinhold, New York, 1952.
- [14] G. H. Olivé and S. Olivé, Z. Phys. Chem., **47**, 286 (1965); **48**, 35 (1966).
- [15] G. H. Olivé and S. Olivé, Makromol. Chem., **96**, 211 (1966).
- [16] A. Fehérvári, T. Földes-Bereznich, and F. Tüdös, Magy. Kém. Foly., Eur. Polym. J., **16**, 185 (1980).
- [17] L. Czajlik, T. Földes-Bereznich, F. Tüdös, and S. Szakács, Eur. Polym. J., **14**, 1059 (1978).

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