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Determination of Chain Transfer Constant for Solvent When the Viscosity of the Polymerizing System Is Considered Important

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ABSTRACT

The chain transfer constant of the polymethyl methacrylate radical for N,N-dimethylaniline was determined in two solvents, benzene and dimethyl phthalate. Plots were made using

$$1/P_n = k_t^\circ R_p/k_p^2[M]^2\eta + C_{S_1}[S_1]/[M] + C_{S_2}[S_2]/[M] + C_M$$

where η = viscosity of monomer-solvents mixture, k_t° = rate coefficient of termination when η = 1 cP, S_1 = benzene or dimethyl phthalate, S_2 = N,N-dimethylaniline, and other symbols have their usual meanings. The plots agreed well for the two solvents. If the plots were made without considering the viscosity term, two separate lines resulted for the two solvents. Thus it is essential to consider the viscosity of the polymerizing system in the analysis of chain transfer reactions when the termination reaction is diffusion-controlled and the viscosities of the monomer and solvent differ markedly.

INTRODUCTION

In our previous paper [1] it was shown that the conventional rate equation

$$R_p = k_p(k_d f/k_t)^{1/2}[M][I]^{1/2} \tag{1}$$

where R_p = initial rate of polymerization; k_p, k_d, and k_t = rate coefficients of propagation, initiator decomposition, and termination, respectively; f = initiator efficiency; [M] and [I] = concentrations of monomer and initiator, respectively; did not hold with respect to the monomer kinetic order for the radical polymerization of methyl methacrylate (MMA) in solvents having different viscosities from that of the monomer. Alternatively, Eq. (2), derived from Eq. (1) by substituting Eq. (3) according to the diffusion-controlled termination theory [2], successfully held in any such solvent:

$$R_p = k_p(k_d f/k_t^{\circ})^{1/2}[M][I]^{1/2}\eta^{1/2} \tag{2}$$

$$k_t = k_t^{\circ}/\eta \tag{3}$$

where η = viscosity of monomer-solvent mixture, and k_t° = rate coefficient of termination when η = 1 cP.

In the present paper it will be demonstrated that consideration of the viscosity of a polymerizing system is also essential in the analysis of chain transfer reactions.

THEORY

The number-average degree of polymerization, P_n, is given by

$$1/P_n = k_t R_p/k_p^2[M]^2 + C_S[S]/[M] + C_M \tag{4}$$

where C_S and C_M = chain transfer constant for solvent and monomer, respectively, [S] = concentration of solvent, and C_S can be determined by plotting $1/P_n - k_t R_p/k_p^2[M]^2$ vs [S]/[M].

However, when the rate of termination is diffusion-controlled and when the monomer and the solvent differ in their viscosities, k_t can no longer be assumed constant in the whole range of [S]/[M]. In such circumstances, Eq. (4) should be transformed into Eq. (5) by using Eq. (3) as above:

$$1/P_n = k_t{}^{\circ}R_p/k_p{}^2[M]^2\eta + C_S[S]/[M] + C_M \qquad (5)$$

The following experiments have been performed to test this equation. MMA was polymerized with azobisisobutyronitrile (AIBN) in two solvent mixtures, benzene-N,N-dimethylaniline and dimethyl phthalate-N,N-dimethylaniline. C_S values for N,N-dimethylaniline, calculated using Eqs. (4) and (5), were compared.

EXPERIMENTAL

MMA was washed successively with saturated sodium hydrogen bisulfite, 5% sodium hydroxide, 20% sodium chloride, and distilled water; dried over anhydrous sodium sulfate; and distilled at reduced pressure under nitrogen. Distillation was repeated after a partial polymerization just before use. Benzene was washed with concd sulfuric acid and water, dried over calcium chloride and sodium, and distilled under nitrogen. N,N-Dimethylaniline was treated with p-toluenesulfonyl chloride-sodium hydroxide, steam-distilled, dried over anhydrous sodium sulfate, and distilled at reduced pressure under nitrogen. AIBN was recrystallized twice from ethanol.

The initial rate of polymerization was determined dilatometrically in a 10-ml ampoule at 30.0 ± 0.01°C. Polymerization was continued to 5-8% conversion, then the polymer was precipitated into methanol, reprecipitated thrice from benzene solution into methanol, and freeze-dried to constant weight.

The intrinsic viscosity of polymer sample was measured with an Ubbelohde viscometer in benzene at 30°C. The degree of polymerization was calculated according to the following equation [3]:

$$[\eta] = 8.69 \times 10^{-5} M_n{}^{0.76}$$

The viscosity of monomer-solvent mixture was measured with an Ostwald viscometer at 30°C.

TABLE 1. Determination of k_t°/k_p^2 [a]

AIBN ($\times 10^3$ mole/l)	R_p ($\times 10^5$ mole/l-sec)	$[\eta]$ (dl/g)	$1/P_n$ ($\times 10^5$)
10.4	1.58	4.45	6.37
12.1	1.72	4.17	7.05
13.1	1.75	4.27	6.71
3.38	0.906	6.02	4.46
4.53	1.03	5.68	4.61

[a] Methyl methacrylate, bulk, 30°C.

RESULTS AND DISCUSSIONS

Determination of k_t°/k_p^2

Bulk polymerization experiments were conducted with various amounts of AIBN, and $1/P_n$ vs R_p (Table 1) are plotted in Fig. 1 according to

$$1/P_n = k_t R_p/k_p^2[M]^2 + C_M = k_t^\circ R_p/k_p^2[M]^2\eta_0 + C_M \tag{6}$$

The slope of this plot gives $k_t/k_p^2[M]^2 = 3.15$ and the intercept gives

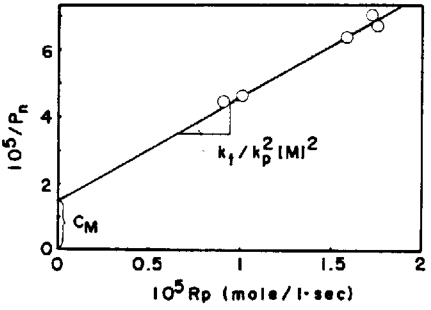

FIG. 1. Determination of k_t°/k_p^2, MMA, bulk, 30°C

$C_M = 1.5 \times 10^{-5}$ (lit. [4], 1.17×10^{-5}; lit. [5], 2.60×10^{-5}). Substituting [M] = 9.30 mole/l and η_0 (viscosity of pure monomer) = 0.516 cP [6], we obtain $k_t/k_p^2 = 3.15 \times (9.30)^2 = 2.72 \times 10^2$ mole-sec/l and $k_t^\circ/k_p^2 = 2.72 \times 10^2 \times 0.516 = 1.40 \times 10^2$ mole-sec/l-cP. Because the termination mode of the polymerization of MMA consists of 48% disproportionation and 52% recombination at 30°C [12], the above obtained "k_t/k_p^2" is really $(1 + \lambda)k_t/2k_p^2$, where λ = fraction of disproportionation in total termination. Therefore, the real $k_t/k_p^2 = 2 \times 2.72 \times 10^2/(1 + 0.48) = 3.68 \times 10^2$, which lies among the literature values obtained kinetically, 5.96×10^2 [5], 5.95×10^2 [6], and 2.32×10^2 [12].

Determination of C_S for Benzene, Dimethyl Phthalate, and N,N-Dimethylaniline

From the data of the previous paper [1], (calculation of C_S in the previous paper [1] was in error), C_S values are determined in Table 2 and Fig. 2 using Eq. (4) for benzene and Eq. (5) for dimethyl phthalate and N,N-dimethylaniline. Because MMA and benzene have almost equal viscosity, the use of Eq. (5) is not necessary. Although the difference between the plots using Eq. (4) (not shown in Fig. 2) and Eq. (5) for N,N-dimethylaniline is small, it can not be overlooked for dimethyl phthalate. In Fig. 3, the application of Eq. (4) for dimethyl phthalate gives a negative slope, which has no chemical meaning.

The plots for benzene and dimethyl phthalate are rather scattered when compared to the plots for N,N-dimethylaniline. Certainly, however, C_S values for these solvents are very small, and hereafter we use C_S for benzene = 1×10^{-6} (lit. [7], 3.6×10^{-6} at 50°C; lit. [8], 2.7×10^{-6} at 52°C and 4.0×10^{-6} at 60°C) and C_S for dimethyl phthalate = 2×10^{-5}. These values have little effect on the conclusion. C_S for N,N-dimethylaniline is given as 24.5×10^{-5} in Fig. 2 (lit. [9], 304×10^{-5} at 50°C; lit [10], 4300×10^{-5} at 50°C; lit. [11], 108×10^{-5} at 70°C).

Determination of C_S for N,N-Dimethylaniline in Benzene and Dimethyl Phthalate

Polymerization data of MMA in benzene—N,N-dimethylaniline and in dimethyl phthalate—N,N-dimethylaniline are shown in Table 3 where

TABLE 2. Determination of C_S for Benzene, Dimethyl Phthalate, and N,N-Dimethylaniline[a]

[M] (mole/l)	R_p ($\times 10^5$ mole/l-sec)	[η] (dl/g)	$1/P_n$ ($\times 10^4$)	[S]/[M]	$1/P_n - k_t R_p/k_p^2[M]^2$[b] ($\times 10^4$)	η[c] (cP)	$1/P_n - k_t^\circ R_p/k_p^2[M]^2\eta$[d] ($\times 10^4$)
				Benzene			
8.65	1.215	3.70	0.81	0.143	0.37		
6.74	0.779	3.69	0.82	0.512	0.35		
6.71	0.935	3.70	0.81	0.526	0.25		
4.83	0.735	3.30	0.94	1.188	0.09		
4.79	0.686	3.31	0.94	1.251	0.13		
2.95	0.397	2.40	1.44	2.728	0.19		
				Dimethyl Phthalate			
8.68	1.229	4.10	0.71	0.073	0.26	0.563	0.30
6.76	1.176	3.45	0.84	0.277	0.14	0.886	0.43
4.90	1.131	4.34	0.66	0.632	-0.44	1.428	0.20
3.02	0.893	3.25	0.96	1.416	-1.70	2.540	0.42
4.78	1.112	3.36	0.92	0.664	-0.40	1.472	0.46

			N,N-Dimethylaniline				
8.74	1.206	3.61	0.84	0.091	0.41	0.516	0.41
6.73	1.140	2.41	1.43	0.358	0.74	0.604	0.84
5.06	0.780	1.46	2.76	0.794	1.93	0.687	2.13
2.99	0.521	0.82	5.88	1.855	4.30	0.839	4.91
4.89	0.756	1.46	2.76	0.817	1.90	0.698	2.12
5.67	0.878	1.81	2.08	0.572	1.33	0.653	1.49
6.86	0.968	2.17	1.64	0.349	1.08	0.598	1.16
3.00	0.521	0.82	5.88	1.836	4.31	0.839	4.92

[a] Methyl methacrylate in each solvent, AIBN 6.1 × 10^{-3} mole/l, 30°C.

[b] $k_t/k_p^2 = 2.72 \times 10^2$ mole-sec/l.

[c] Viscosity of methyl methacrylate-solvent mixture.

[d] $k_t^\circ/k_p^2 = 1.40 \times 10^2$ mole-sec/l-cP.

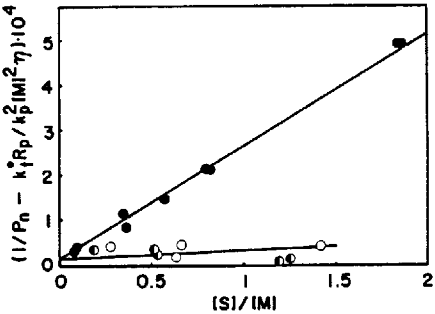

FIG. 2. Determination of C_S for benzene (◐), dimethyl phthalate (○), and N,N-dimethylaniline (●).

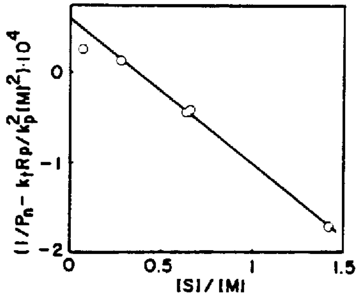

FIG. 3. Determination of C_S for dimethyl phthalate using Eq. (4).

S_1 = benzene or dimethyl phthalate and S_2 = N,N-dimethylaniline. Benzene and dimethyl phthalate act as inert solvents because C_S values for these solvents are very small as described above, but act so as to make the viscosities of the two experimental series different. Dimethyl phthalate was chosen because it is a viscous solvent (η = 10.21 cP [1]).

The chain transfer constant for N,N-dimethylaniline C_{S_2} is given as a slope by plotting

$$1/P_n - k_tR_p/k_p^2[M]^2 - C_{S_1}[S_1]/[M] \text{ vs } [S_2]/[M]$$

corresponding to Eq. (4) (conventional) or by plotting

TABLE 3. Determination of C_S for N,N-Dimethylaniline in Benzene and Dimethyl Phthalate[a]

[M] (mole/l)	R_p ($\times 10^5$ mole/l-sec)	[η] (dl/g)	$1/P_n$ ($\times 10^4$)	$[S_1]/[M]$[b]	$[S_2]/[M]$[c]	$(1/P_n - k_tR_p/k_p^2[M]^2 - C_{S_1}[S_1]/[M])$[d] ($\times 10^4$)	η (cP)	$(1/P_n - k_t^\circ R_p/k_p^2[M]^2\eta - C_{S_1}[S_1]/[M])$[e] ($\times 10^4$)
In Benzene								
4.15	0.645	2.14	1.66	1.19	0.274	0.63	0.653	0.85
4.35	0.750	1.73	2.20	0.671	0.482	1.12	0.672	1.37
6.22	0.850	2.72	1.22	0.298	0.205	0.62	0.751	0.81
6.81	0.934	3.47	8.85	0.296	0.098	0.33	0.569	0.39
3.40	0.575	1.32	3.16	0.899	0.821	1.80	0.602	2.00
In Dimethyl Phthalate								
5.96	1.024	3.76	0.79	0.286	0.101	-0.05	1.06	0.27
3.83	0.686	1.51	2.64	0.280	0.835	1.31	1.19	1.95
5.02	0.792	2.32	1.50	0.253	0.390	0.59	0.982	0.93
5.96	0.988	2.91	1.11	0.201	0.211	0.31	0.948	0.60
4.75	0.797	2.00	1.82	0.206	0.538	0.82	0.961	1.20

[a] Methyl methacrylate in two solvents, AIBN 6.1×10^{-3} mole/l, 30° C.

[b] S_1 = benzene or dimethyl phthalate.

[c] S_2 = N,N-dimethylaniline.

[d] $k_t/k_p^2 = 2.72 \times 10^2$ mole-sec/l.

[e] $k_t^\circ/k_p^2 = 1.40 \times 10^2$ mole-sec/l-cP.

$$1/P_n - k_t^\circ R_p/k_p^2[M]^2\eta - C_{S_1}[S_1]/[M] \text{ vs } [S_2]/[M]$$

corresponding to Eq. (5) (considering the viscosity term).

The former plots in Fig. 4 result in two separate lines. The benzene series gives a slope (C_{S_2}) of 20 × 10^{-5} and an intercept (C_M)

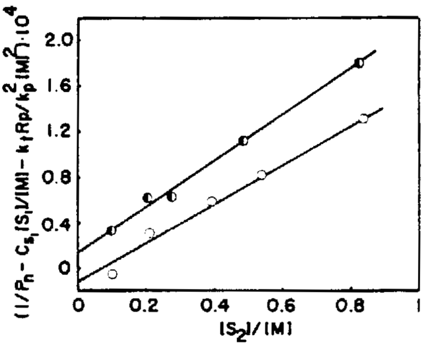

FIG. 4. Determination of C_S for N,N-dimethylaniline in benzene (◐) and dimethyl phthalate (○) using Eq. (4).

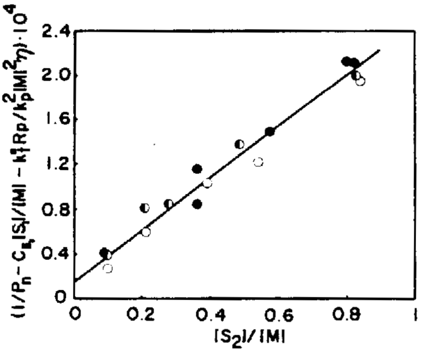

FIG. 5. Determination of C_S for N,N-dimethylaniline (●) in benzene (◐) and dimethyl phthalate (○) using Eq. (5).

of 1.5×10^{-5}. The dimethyl phthalate series, on the other hand, lies below the benzene series and gives a slope of 17×10^{-5} and an intercept of -1.4×10^{-5}. However, on the latter plots in Fig. 5 the benzene series and the dimethyl phthalate series both result in a single line giving a slope of 23×10^{-5} and an intercept of 1.5×10^{-5}. The MMA—N,N-dimethylaniline data in Table 2 also fall on this line.

In conclusion, although the agreement of the three series is not very good, it is enough to emphasize the importance of the viscosity of a polymerizing system in the analysis of chain transfer reactions.

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