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The Heats of Dilution in Atactic Polymethyl Methacrylate Solutions

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In order to ascertain the dependence of the interaction parameter, χ_H, between the polymer and the solvent molecules on the polymer concentration, the heats of dilution in an atactic polymethyl methacrylate solution have been measured for the polymers with the degrees of polymerization of 3000 and 7800. It was found that the values of χ_H obtained are dependent on the concentration in all the solvents used, as in the solutions of polystyrene and polybutadiene reported as in previous papers. χ_H depends also on the molecular weight, this is in agreement with the suggestion by Huggins (*J. Am. Chem. Soc.*, **86**, 3535 (1964)).

In previous papers,[1,2] we have measured the heats of dilution in atactic polystyrene and *cis*-polybutadiene solutions and have found that the interaction parameter, χ_H, between the polymer and the solvent molecules depends on the polymer concentration.

In order to confirm this fact for other polymer solutions, we measured the heats of dilution of atactic polymethyl methacrylate (PMMA) solutions, using toluene, dioxane and acetone as solvents.

Experimental

Apparatus and Procedure. The calorimeter used in this study is the same as that described in previous papers,[1,2] except for the following improvements. (1) the thirtyjunction copper-constantan thermocouple

1) A. Kagemoto, S. Murakami and R. Fujishiro, This Bulletin, **39**, 15 (1966).
2) A. Kagemoto, S. Murakami and R. Fujishiro, *ibid.*, **39**, 1814 (1966).

TABLE 1. HEATS OF DILUTION ATACTIC POLYMETHYL METHACRYLATE AT 25°C

1. Polymethyl methacrylate-toluene. Endothermic

a) Monomer (methyl-isobutylate)+toluene at 30°C

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
1.00	1.000	2.00	0.500	0.433	0.14
2.00	0.500	3.00	0.333	0.140	0.14
3.00	0.333	4.00	0.250	0.067	0.13
1.00	1.000	2.00	0.500	0.427	0.14
2.00	0.500	3.00	0.333	0.144	0.14
3.00	0.333	4.00	0.250	0.065	0.13

b) $\bar{P}=3000$

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
10	0.141	15	0.094	0.025	0.066
15	0.094	20	0.070	0.012	0.062
10	0.125	20	0.063	0.025	0.056
10	0.176	20	0.088	0.048	0.055
10	0.216	20	0.108	0.077	0.058
20	0.108	30	0.072	0.027	0.060
30	0.072	40	0.054	0.013	0.060
10	0.141	20	0.070	0.036	0.064
10	0.216	30	0.072	0.104	0.058
10	0.216	40	0.054	0.117	0.058
50	0.056	70	0.040	0.016	0.062
30	0.070	50	0.042	0.018	0.054
20	0.083	40	0.042	0.026	0.065
30	0.069	50	0.042	0.020	0.060
40	0.050	60	0.033	0.010	0.052
50	0.043	70	0.030	0.023	0.069
20	0.080	40	0.040	0.015	0.063
30	0.058	50	0.035	0.029	0.065
30	0.070	60	0.035	0.029	0.069

c) $\bar{P}=7800$

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
5	0.253	10	0.127	0.045	0.049
10	0.127	15	0.084	0.016	0.053
10	0.300	20	0.150	0.143	0.056
20	0.150	30	0.100	0.050	0.059
30	0.100	40	0.075	0.022	0.051
10	0.263	20	0.132	0.088	0.044
20	0.132	30	0.088	0.039	0.059
30	0.088	40	0.066	0.017	0.053
5	0.258	15	0.084	0.061	0.034
10	0.300	30	0.100	0.193	0.056
10	0.300	40	0.075	0.215	0.056
10	0.263	30	0.088	0.127	0.048
10	0.263	40	0.066	0.144	0.049
30	0.062	40	0.047	0.011	0.065
40	0.047	50	0.037	0.006	0.058
30	0.062	50	0.037	0.017	0.065
30	0.075	40	0.056	0.013	0.055
40	0.056	50	0.041	0.008	0.060
30	0.075	50	0.041	0.021	0.059
20	0.073	40	0.037	0.018	0.059
30	0.064	50	0.038	0.017	0.061

2. Polymethyl methacrylate-acetone. Endothermic

a) Monomer (methyl-isobutylate+acetone at 25°C)

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
5.00	1.000	10.00	0.500	4.959	0.25
10.00	0.500	15.00	0.333	1.585	0.24
15.00	0.333	20.00	0.250	0.809	0.24
5.00	1.000	10.00	0.500	5.097	0.25
10.00	0.500	15.00	0.333	1.605	0.24
15.00	0.333	20.00	0.250	0.796	0.24

b) $\bar{P}=3000$

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
7.9	0.290	12.9	0.178	0.109	0.055
12.9	0.178	17.9	0.128	0.051	0.058
17.9	0.128	22.9	0.100	0.029	0.059
22.9	0.100	32.9	0.069	0.029	0.055
7.9	0.290	17.9	0.128	0.160	0.056
7.9	0.290	22.9	0.100	0.187	0.056
7.9	0.290	32.9	0.069	0.221	0.059
11.3	0.115	21.3	0.061	0.032	0.059
21.3	0.061	31.3	0.042	0.024	0.060
11.3	0.115	31.3	0.042	0.046	0.062
20.5	0.156	40.5	0.079	0.119	0.056
40.5	0.079	50.5	0.063	0.020	0.052
20.5	0.156	50.5	0.063	0.132	0.057
11.8	0.107	21.8	0.058	0.027	0.056
21.5	0.058	31.5	0.040	0.011	0.058
11.8	0.107	31.5	0.040	0.036	0.054

c) $\bar{P}=7800$

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
20.9	0.126	40.9	0.064	0.057	0.046
40.9	0.064	50.9	0.052	0.013	0.050
20.9	0.126	50.9	0.052	0.068	0.045
12.8	0.191	22.8	0.107	0.070	0.045
22.8	0.107	32.8	0.074	0.029	0.048
32.8	0.074	42.8	0.057	0.016	0.049
12.8	0.191	32.8	0.075	0.099	0.046
12.8	0.191	42.8	0.057	0.103	0.041
7.5	0.237	12.5	0.141	0.058	0.045
12.5	0.142	17.5	0.101	0.028	0.050
17.5	0.101	22.5	0.097	0.018	0.048
22.5	0.097	32.5	0.055	0.019	0.046
7.5	0.237	17.5	0.101	0.086	0.047
7.5	0.237	22.5	0.097	0.104	0.039
7.5	0.237	32.5	0.055	0.123	0.050
22.0	0.094	32.0	0.064	0.019	0.042
32.0	0.064	42.0	0.049	0.011	0.045
22.0	0.094	42.0	0.049	0.029	0.041

3. Polymethyl methacrylate-dioxane. Endothermic

a) Monomer (methyl-isobutylate+dioxane at 25°C)

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$ cal	χ_H
1.00	1.000	2.00	0.500	1.178	0.32
2.00	0.500	3.00	0.333	0.373	0.31

TABLE 1 (Continued)

3.00	0.333	4.00	0.250	0.193	0.32
1.00	1.000	2.00	0.500	0.119	0.31
2.00	0.500	3.00	0.333	0.361	0.30
3.00	0.333	4.00	0.250	0.186	0.31

b) $\bar{P}=3000$

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
10	0.188	20	0.094	0.097	0.080
20	0.094	30	0.063	0.036	0.088
30	0.063	40	0.047	0.020	0.099
10	0.126	20	0.063	0.046	0.089
10	0.210	20	0.105	0.129	0.085
20	0.105	30	0.070	0.045	0.090
30	0.070	40	0.053	0.024	0.093
10	0.163	20	0.082	0.088	0.095
20	0.082	30	0.054	0.029	0.096
30	0.188	40	0.041	0.013	0.088
10	0.188	30	0.063	0.132	0.081
10	0.188	40	0.047	0.151	0.083
10	0.210	30	0.070	0.174	0.086
10	0.210	40	0.053	0.198	0.086
10	0.163	30	0.054	0.118	0.096
10	0.163	40	0.041	0.131	0.095
20	0.076	40	0.038	0.035	0.089
20	0.076	40	0.038	0.038	0.095
40	0.068	70	0.039	0.054	0.099
30	0.045	50	0.027	0.014	0.083
20	0.060	40	0.030	0.022	0.088

c) $\bar{P}=7800$

V, cc	ϕ_2	V', cc	ϕ'_2	$\Delta\bar{H}_d$, cal	χ_H
10	0.188	20	0.093	0.089	0.075
20	0.093	30	0.062	0.033	0.082
10	0.186	30	0.062	0.122	0.077
10	0.292	20	0.146	0.211	0.072
20	0.146	30	0.097	0.077	0.078
30	0.097	40	0.073	0.035	0.070
10	0.292	30	0.097	0.287	0.074
10	0.292	40	0.073	0.318	0.072
10	0.156	20	0.078	0.071	0.085
20	0.078	30	0.052	0.023	0.081
10	0.150	20	0.075	0.069	0.089
20	0.075	30	0.050	0.022	0.086
10	0.150	30	0.050	0.091	0.088
10	0.200	20	0.100	0.117	0.085
20	0.100	30	0.067	0.041	0.090
10	0.200	30	0.067	0.158	0.086
20	0.070	40	0.035	0.030	0.090
30	0.056	50	0.033	0.024	0.095
20	0.063	40	0.032	0.024	0.087
20	0.060	40	0.030	0.025	0.085
30	0.052	50	0.031	0.018	0.083
50	0.042	70	0.030	0.016	0.092

has been replaced by a sixty-junction thermocouple in order to detect smaller temperature changes, and (2) the inner cell containing the solvent before the dilution has been made five or six times larger in volume than the older cell, thus increasing the amount of the heat of dilution by mixing a larger amount of solvent with the solution. The improved cell is shown in Fig. 1.

The procedure is similar to that described in the previous papers,[1,2] except that the cell used as the reference bath for the thermocouple is filled with a solution of the same concentration as that in the dilution cell, instead of being filled with a pure solvent, in order to compensate for the heat of stirring the ingredients with each other.

Materials. Atactic polymethyl methacrylate-(PMMA) samples, the degree of polymerization of which were about 3000 and 7800, were kindly supplied by Dr. Kazuo Nakatsuka of the Mitsubishi Rayon Co., Ltd. These samples were purified by dissolving in toluene, by precipitating them with methanol several times, and by finally drying them under the reduced pressure of 1 mmHg until the solvent has been completely removed.

The solvents used were toluene, dioxane and acetone, they were purified by the ordinary methods described in the literature,[3] and finally distilled by the use of a long column.

Methyl-isobutylate, which is regarded as a monomer of PMMA, was distilled and further fractionally distilled by a long column.

3) A. Weissberger and E. S. Proshauen, "Organic Solvent," Interscience Publishers, New York (1955).

Results and Discussion

The heats of dilution of atactic PMMA solution were measured over the concentration range from 0.3 to 0.04 in the volume fraction of the polymer at 25.00±0.01°C by the successive addition of 5 to 30 ml of a solvent to a solution of a known concentration. The results obtained are shown in Table 1.

All three systems, the solutions of toluene, dioxane and acetone, proved to be endothermic.

As has been shown in previous papers[1,2] the heats of dilution, $\Delta\bar{H}_d$, are related to the initial volume fraction of the polymer, ϕ_2, and the final volume fraction, ϕ_2', as follows:

$$\Delta\bar{H}_d = \boldsymbol{R}T\chi_H\phi_2\phi_2'\Delta n_I \qquad (1)$$

when the interaction parameter, χ_H, is not dependent on the concentration, or

$$\Delta\bar{H}_d/\boldsymbol{R}T\phi_2\phi_2'\Delta n_I = \chi_I + \chi_2(\phi_2+\phi_2')/2 \qquad (2)$$

when χ_H depends linearly on the concentration according to the equation that $\chi_H=\chi_I+\chi_2\phi_2$. In these equations Δn_I is the number of moles of the solvent added.

By using the experimental data listed in Table 1 and Eq. (1), the interaction parameter is obtained for each stage of the dilution process of each system, these values are given in the last column of Table 1. According to Eq. (1), $\Delta\bar{H}_d$ must linearly

vary with $\phi_2\phi_2'\Delta n_1$. However, as Figs. 2 and 3 show, these plots are not linear, indicating that χ_H depends on the concentration. In order to obtain the dependence of the χ_H parameter on the concentration, the least-square analysis of the data was carried out by the use of Eq. (2); this gave the values for χ_1 and χ_2 shown in Table 2.

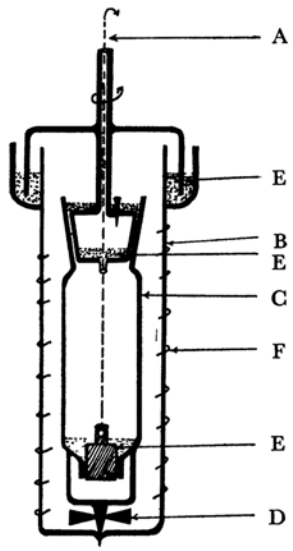

Fig. 1. Mixing cell.
(A) Wire for pulling up the lid
(B) Outer cell
(C) Inner cell
(D) Stirrer
(E) Mercury seal
(F) Heating coil

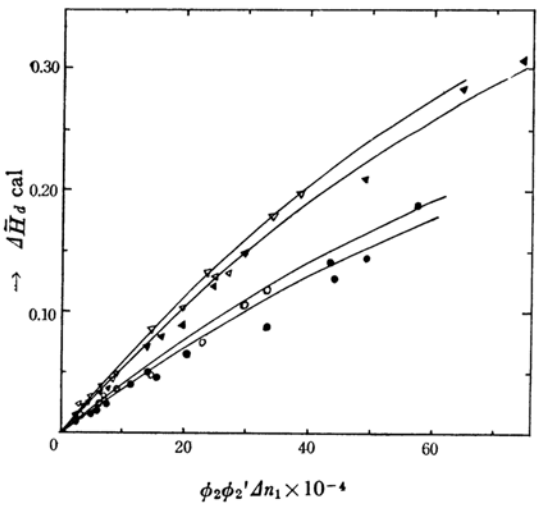

Fig. 2. $\Delta\bar{H}_d$ *vs.* $\phi_2\phi_2'\Delta n_1$ at 25°C for polymethyl methacrylate solution in dioxane -△-, -▲- and in toluene -◑-, -●-.
The curve are drawn according to Eq. (2) with the parameter of Table 2.

PMMA-Dioxane {△ $\bar{P}=3000$; ▲ $\bar{P}=7800$
PMMA-Toluene {◑ $\bar{P}=3000$; ● $\bar{P}=7800$

TABLE 2. VALUES OF INTERACTION PARAMETERS
$\chi_H=\chi_1+\chi_2\phi_2$

	$\bar{P}=3000$		$\bar{P}=7800$	
Solvent	χ_1	χ_2	χ_1	χ_2
Toluene	0.064	−0.039	0.057	−0.026
Dioxane	0.096	−0.065	0.091	−0.087
Acetone	0.057	−0.026	0.047	−0.013

By using the values of χ_1 and χ_2, the $\Delta\bar{H}_d$-$\phi_2\phi_2'\Delta n_1$ curve has been drawn for each system; this curve, which is shown by the full lines in Figs. 2 and 3, is in good agreement with the experimental data for each system.

Huggins[4] has derived the dependence of the interaction parameter χ_H on the concentration by allowing for various factors characteristic of polymers. Our results can not be quantitatively compared with his theory because of the lack of information concerning the chain configuration of the polymer molecules in the solution, but they seem to be qualitatively consistent with his theory.

According to Huggins theory, χ_H must depend not only on the concentration, but also on the molecular weight. As the molecular weight increases, χ_H should decrease, because the interior segments of a convoluted polymer molecule are more shielded from contact with the interior segments of other polymer molecules. This may be very important in dilute solutions, where χ_H is equal to χ_1.

In our experiment, the χ_1 value for the solution of the higher molecular weight is a little smaller than that for the solution of the lower molecular weight for each solvent system.

This suggests that χ_1 depends on the molecular weight, in agreement with the Huggins treatment. In order to make this point clear, the heats of the mixing and dilution of methyl-isobutylate with toluene, dioxane and acetone were also measured. Methyl-isobutylate may be regarded as a stable monomer of PMMA. The results obtained are also shown in Table 1. From these data, χ_H values were calculated by the same procedure as was used for the PMMA solutions, assuming that Eq. (1) can also be used, these values are listed in the last column of Table 1.

In these monomer solutions, χ_H is considered to be hardly dependent on the concentration at all, as is usual in solutions of a low molecular weight; χ_H may be used instead of χ_1, by considering that $\chi_2=0$.

The values of χ_1 for the solutions of the monomer

4) M. L. Huggins, *J. Am. Chem. Soc.*, **86**, 3535 (1964).

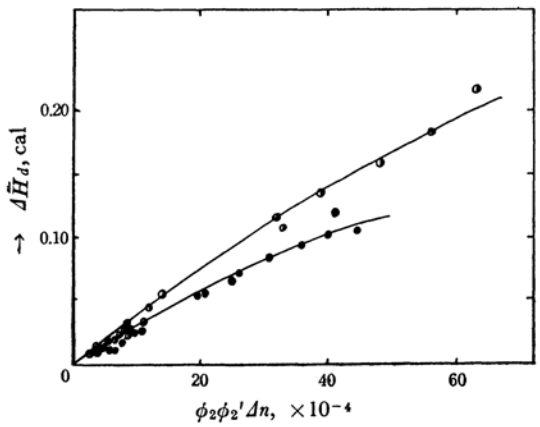

Fig. 3. $\Delta\bar{H}_d$ vs. $\phi_2\phi_2'\Delta n_I$ at 25°C for polymethyl methacrylate solution in acetone -◑-, -●-.
The curve are drawn according to Eq. (2) with the parameters of Table 2.
PMMA - Acetone
◑ $\bar{P}=300$
● $\bar{P}=7800$

TABLE 3. HEAT OF DILUTION PARAMETERS χ_1 FOR POLYMETHYLMETHACRYLATE AT 25°C

Degree of polymerization	Toluene	Dioxane	Acetone
Monomer	0.14	0.31	0.24
3000	0.064	0.096	0.057
7800	0.057	0.091	0.047

and two kinds of polymer in the solvents are tabulated in Table 3. It may be seen that χ_1 depends on the molecular weight, and that it decreases with an increases in the molecular weight.

A more detailed study is necessary for polymer solutions of a variety of molecular weights before any firm conclusion can be drawn.

TABLE 4. VALUES OF THE INTERACTION PARAMETER OBTAINED BY VARIOUS AUTHORS

Solvent	χ_1*1	χ_1*2	χ_1*3	χ_1*4
Toluene	0.020	0.076	0.064	0.057
Dioxane	0.030	—	0.096	0.091
Acetone	0.029	0.050	0.059	0.047

*1 See Ref. 5, osmotic pressure
*2 See Ref. 6, viscosity
*3 This paper, $\bar{P}=3000$
*4 This paper, $\bar{P}=7800$

The interaction parameter χ_I in the dilute solutions has been studied by various authors,[5,6] using such indirect methods as the temperature-dependence of the osmotic pressure. The values of χ_I obtained by these various methods are listed in Table 4, together with our data. The agreement between our values and those obtained by other authors is fairly good.

The authors wish to thank Dr. Kazuo Nakatsuka of the Mitsubishi Rayon Co., Ltd. for supplying the sample to them.

5) G. V. Shulz and H. Doll, *Z. Elektrochem.*, **57**, 841 (1953).
6) T. G. Fox, *Polymer*, **3**, 111 (1962).