Ptitsyn-Eizner λ Parameter for PMMA in Theta Solvents

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SUMMARY

We have calculated the λ parameter from Ptitsyn-Eizner equation for PMMA in several theta solvents (2-heptanone, acetonitrile, n-butyl chloride and nitromethane). We have found an equation that allows us to separate the long- and the short-range contributions to λ parameter.

INTRODUCTION

Starting from the worm-like chain model given by Kratky and Porod (1949), Ptitsyn and Eizner (1962) give an expression which permits to characterize the flexibility of macromolecules and biomolecules in a simple way. To do that they defined the λ parameter, which is proportional to the persistence length, a (λ = a/b, where b is the length of monomeric unit).

In this work, we have studied the behaviour of the Ptitsyn-Eizner's λ parameter for several anionic PMMA fractions, of very narrow distributions, in four solvents near the Flory's theta temperature. Up to now, λ parameter could only be obtained in theta conditions in such a way that it is a measure of the short range interactions. In this paper we have studied the contributions of long range interactions in this parameter obtained when we measure far off Flory's theta temperature. This has permittes us to get an expression that allows to separate both contributions to the Ptitsyn-Eizner's λ parameter.

EXPERIMENTAL PROCEDURES AND RESULTS

PMMA was obtained by anionic polymerization in THF solu
tion initiated with butyllithium (KATIME,RAMIRO VERA
1972). The polymer was reprecipitated from benzene solu
tion with isopropylalcohol. The fractions were obtained
by gradual precipitation of the polymer from the benze-
ne solution with ethanol. Six fractions were selected
for the present physical measurements from a number of
final fractions. Molecular weight determinations by
both light scattering and membrane osmometry on several
fractions showed that $\overline{M}_w/\overline{M}_n < 1.1$.
Solvents used in this study were 2-heptanone, acetoni-
trile, n-butyl chloride and nitromethane.
Light scattering measurements were made over the tempe-
rature range 20 to 70°C using a FICA photometer. Polymer
solutions and solvents on which light scattering measu-
rements were carried out were clarified by centrifuga-
tion for 2 hr. in a Sorvell preparative ultracentrifuge
at 14,000 rpm. Light scattering was performed with light
of wavelength 546 nm. at ten angles between 30-150° for
each of five dilutions. The intrument was calibrated u-
sing benzene for which the Rayleigh ratio was known over
range of temperature. The mean square radius of gyration
$\overline{s}^2$, was calculated using the equation

$$\left(\frac{Kc}{R_\theta}\right)_{\substack{c \to o \\ \theta \to o}} = \frac{1}{M_w} \left| 1 + \frac{16\pi^2 \overline{s}}{\lambda^2} \text{ sen}^2 \frac{\theta}{2} \right| + 2A_2 c$$

In order to evaluate the parameter K it was neccesary to
measure the refractive index increment, dn/dc. A Brice-
Phoenix differential refractometer equipped with a spe-
cial glass cell was used for measurements of refractive
increments at constant solvent composition. Aqueous so-
lutions of KCl at 298 K were used for the calibration of
differential refractometer (KRUISS 1936).
Tables 1-4 shows the mean square radius of gyration as
a function of molecular weight and temperature for the

different solvents used.

TABLE 1. Mean square radius of gyration in function of molecular weight and temperature for PMMA in 2-heptanone

$$\overline{s}^2 . 10^{12} \; cm^2$$

$\overline{M}_w . 10^{-5}$	20	25	30	35	40	45	50
2.9	1.74	1.83	1.88	1.93	2.01	2.09	2.14
5.3	3.22	3.44	3.55	3.76	3.91	4.07	4.17
6.7	4.18	4.39	4.66	4.82	5.03	5.28	5.48
8.6	5.35	5.84	6.05	6.34	6.81	7.10	7.35
10.5	6.67	7.13	7.68	7.92	8.39	8.86	9.26
12.0	7.62	8.24	8.69	9.37	9.81	10.45	10.69

TABLE 2. Mean square radius of gyration in function of molecular weight and temperature for PMMA in acetonitrile

$$\overline{s}^2 . 10^{12} \; cm^2$$

$\overline{M}_w . 10^{-5}$	40	45	50	55	60	65
2.9	1.69	1.75	1.81	1.86	1.92	1.96
5.3	3.15	3.28	3.42	3.55	3.68	3.80
6.7	4.04	4.18	4.36	4.54	4.75	4.94
8.6	5.19	5.53	5.73	6.06	6.24	6.53
10.5	6.44	6.78	7.13	7.42	7.87	8.27
12.0	7.42	7.90	8.33	8.75	9.08	9.56

TABLE 3. Mean square radius of gyration in function of molecular weight and temperature for PMMA in n-butyl chloride

$$\overline{s}^2 . 10^{12} \; cm^2$$

$\overline{M}_w . 10^{-5}$	40	45	50	55	60	65	70
2.9	1.69	1.73	1.80	1.84	1.92	1.96	2.06
5.3	3.15	3.26	3.40	3.53	3.69	3.82	3.94
6.7	3.97	4.15	4.32	4.49	4.72	4.90	5.15
8.6	5.16	5.37	5.64	5.91	6.32	6.55	6.89
10.5	6.42	6.75	7.10	7.45	7.84	8.17	8.69
12.0	7.33	7.68	8.12	8.51	9.05	9.51	9.98

TABLE 4. Mean square radius of gyration in function of molecular weight and temperature for PMMA in nitromethane

$$\overline{s}^2 . 10^{12} \ cm^2$$

$\overline{M}_w . 10^{-5}$	35	40	45	50	55	60	65
2.9	1.69	1.76	1.82	1.87	1.96	2.02	2.08
5.3	3.14	3.28	3.41	3.54	3.72	3.91	4.04
6.7	3.93	4.15	4.34	4.64	4.89	5.05	5.29
8.6	5.16	5.46	5.78	5.98	6.36	6.75	7.10
10.5	6.24	6.64	7.05	7.52	8.07	8.37	8.81
12.0	7.25	7.75	8.15	8.63	9.24	9.73	10.26

DISCUSSION

Ptitsyn and Eizner, starting from the equation of Peter lin (1948, 1950, 1960) and using the worm-like chain mo del, defined the λ parameter which takes into account the short-range interactions, which is characteristic of that kind of polymer. The final expressions they got was

$$\frac{\overline{s}^2}{b^2} - \frac{\lambda N}{3} + \lambda^2 - \frac{2\lambda^4}{N^2}(\frac{N}{\lambda} - 1) = 0 \qquad (1)$$

where $\overline{s}^2$ is the mean square radius of gyration, N the polymerization degree and b the length of the monomeric unit. From this expression it can be calculated, if se veral values of $\overline{s}^2$ are known for different molecular weights, the λ parameter using the method of Newton. The λ values obtained for 2-heptanone, acetonitrile, n-butyl chloride and nitromethane are shown in figures 1-4. As it can be seen λ parameter depends on molecular weight and temperature. However, the λ values extrapola ted to M → 0 converge at the same point.
On the other hand, it is interesting to prove that the slopes of the straight lines obtained decreases as the temperature goes down, tending towards zero when T → Θ. We can prove with experimentally data, that the λ para- meter of Ptitsyn-Eizner, is independent of molecular
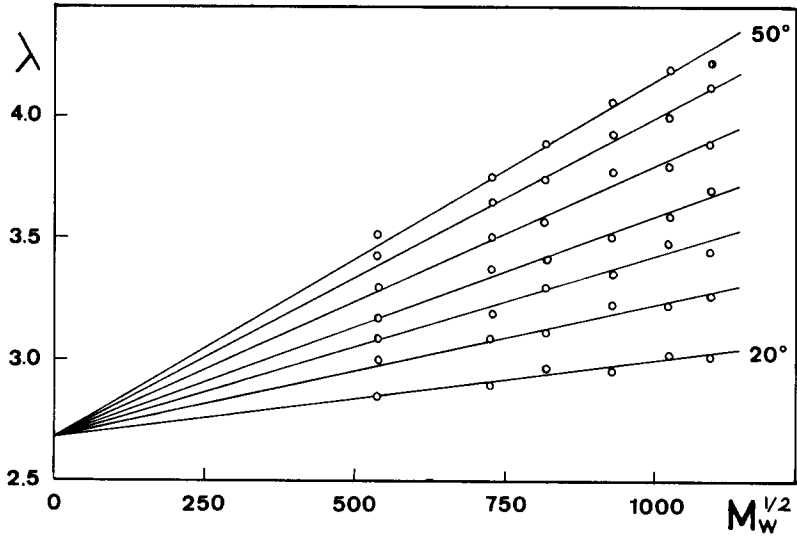
Figure 1. Plot of λ parameter versus $M^{1/2}$ in the temperature range 20-50°C for PMMA in 2-heptanone
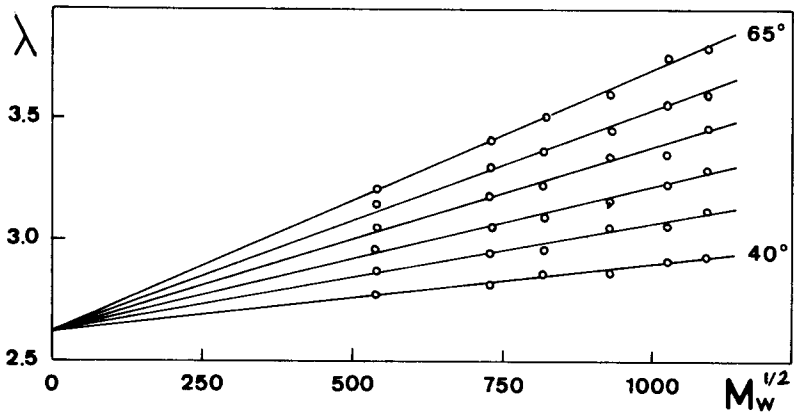

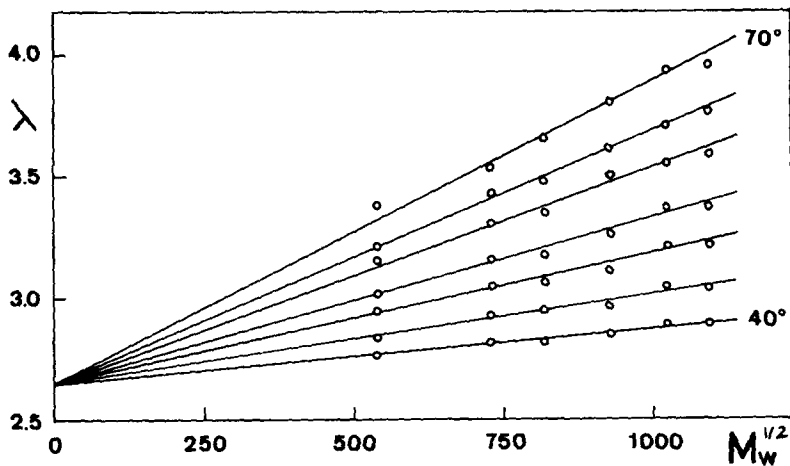Figure 2. Plot of λ parameter versus $M^{1/2}$ in the temperature range 40-65°C for PMMA in acetonitrile

Figure 3. Plot of λ parameter versus $M^{1/2}$ in the temperature range 40-70°C for PMMA in n-butyl chloride
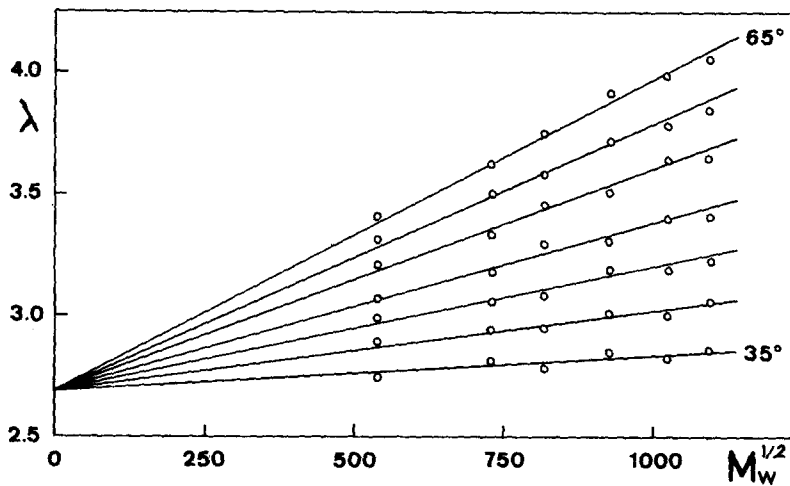

Figure 4. Plot of λ parameter versus $M^{1/2}$ in the temperature range 35-65°C for PMMA in nitromethane

weight in theta conditions.

On the other hand, the extrapolation of the λ parameter for $M^{1/2} \to 0$, gives the same values obtained under ideal conditions $(T = \Theta)$, this make us to think that this extrapolation is equivalent to eliminating the contribution of the excluded volume, that is to say, the long-range interactions, in the λ parameter.

If we compare the extrapolated value of the λ parameter for the different solvents used, we see that λ_Θ values obtained are nearly coincident (Table 5). Small diffe-

TABLE 5. λ_Θ, unperturbed dimensions, theta temperature and c parameter for PMMA in several solvents

solvent	$\lambda_\Theta \pm 0.05$	$\overline{s}_o^2/M.10^{18}$ cm^2	$\Theta/°C$ This work	$\Theta/°C$ Bibl.	$c.10^5$ K^{-1}
2-heptanone	2.68	5.06	11.5	15.0[a]	3.85
acetonitrile	2.62	5.12	30.5	30.0[b]	3.16
n-butyl chloride	2.65	5.04	35.0	37.0[c]	3.45
nitromethane	2.69	5.09	32.0	32.2[a]	3.81

a) KATIME,ROIG 1973; b)COHN-GINSBERG et al.1962; KATIME et al. 1971; c)KATIME,RAMIRO VERA 1972

rences observed are due to the experimental error, made when the mean square radius of gyration is determined.

It all indicates that the variation of this parameter with molecular weight can be described as follows by the relation

$$\lambda = \lambda_\Theta + bM^{1/2} \qquad (2)$$

where b is the parameter that takes into account the long-range interactions. This allows us to calculated the theta temperature for the different systems measured plotting the b parameter as a function of temperature and extrapolating for $b \to 0$. This plot is given in Figure 5 where a linear variation of b with T is observed. If we compare Θ values obtained with the ones in the bibliography, it can be seen that the concordance is good (Table 5). This allows us to write now the eq.(2) in the form

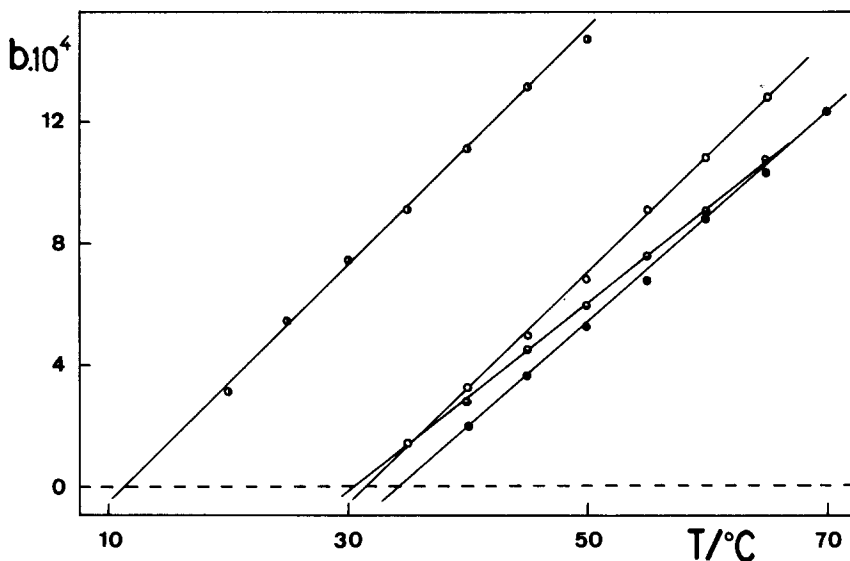$$\lambda = \lambda_\Theta + c(T - \Theta)M^{1/2} \qquad (3)$$

Figure 5. Variation of b parameter as a function of temperature for PMMA in different solvents (● 2-heptanone; ● acetonitrile; ● n-butyl chloride and o nitromethane)

expression that allows us to separate the contributions of short and long-range interactions. c parameter in the Eq.(3) depends on the polymer-solvent system.

REFERENCES

COHN-GINSBERG,E., FOX,T.G. and MARON,H., Polymer, 3, 97 (1962)

KATIME, I., ROIG, A., LEON,L., Anal. Química (Madrid), 67, 811(1971)

KATIME, I. and RAMIRO VERA, C., Anal. Química (Madrid), 68,9(1972)

KATIME, I. and ROIG, A., Anal. Química(Madrid), 69,1217 (1973)

KRATKY, O. and POROD, G., Recueil trav. chim., 68, 1106 (1949)

KRUISS, A., Z. phys. Chem., 834, 13(1936)

PETERLIN, A., International Symp., Paris 1948

PETERLIN, A., J. Polymer Sci., 5, 473(1950)

PETERLIN, A., J. Chem. Phys., 33, 1799(1960)

PTITSYN, O.B. and EIZNER, Y.E., Vysokomol. Soed., 4, 1725(1962)

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