Light scattering study of stereocomplex behaviour in solutions of poly(methyl methacrylate)

Issa Katime†, José R. Quintana, Rosa Valenciano
Grupo de Propiedades Termodinamicas de Macromoléculas en Disolución, Departamento de Química Fisica, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao, Spain

and Claude Strazielle
Institute Charles Sadron (CRM–EAHP), 6, Rue Boussingault, 67083 Strasbourg Cedex, France

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The behaviour of mixtures of iso- and syndiotactic poly(methyl methacrylate) (PMMA) as a function of time and polymer whole concentration in several solvents has been studied by light scattering and laser light scattering. The different solvents investigated in this study are acetonitrile, ethyl acetate, dimethylformamide (DMF), tetrahydrofuran (THF) and 1,4-dioxane. We have found that the last one behaves as a weakly complexing solvent, while the others show a complexing power decreasing from acetonitrile to THF.

An increase in polymer whole concentration induces a higher aggregation of the macromolecular coil, while the compaction process of stereocomplex particles is not strongly influenced. The influence of time in stereocomplex behaviour depends on the nature of the solvent employed. In strongly complexing solvents there is initially a strong increase in the aggregation process and a decrease in compaction. However, in weakly complexing solvents these kinetic processes are less important.

(Keywords: laser light scattering; complexing solvent; aggregation process; stereocomplex; syndiotactic length sequence; second virial coefficient; radius of gyration)

INTRODUCTION

The mixing of solutions of isotactic and syndiotactic poly(methyl methacrylate) (it- and st-PMMA) in suitable solvents leads to the formation of a stereocomplex by intermolecular association of isotactic and syndiotactic sequences. The study of the PMMA stereocomplex has aroused increasing interest in the last couple of decades[1–32], but the stereoassociation still remains an unexplained phenomenon.

This behaviour occurs in most solvents, but to a different extent. The solvents can be classified into three groups according to their behaviour: the strongly complexing, the weakly complexing and the non-complexing.

Up to now, the study of this phenomenon has been investigated by various physical methods: viscometry[1–5], light scattering[6,7] and turbidimetry[8], sedimentation analysis[9], osmometry[10], high-resolution and broad-line n.m.r. spectroscopy[11–13], infra-red spectroscopy[14], flow birefringence[15], thin-layer chromatography[16,17], X-ray diffraction[18,19], thermal analysis[20–24], dielectric measurements[25], and dynamic mechanical measurements[22]. Recently, Belnikevitch *et al.*[32], using light scattering, have studied the ratio of stereopolymers and the stereocomplex formation as a function of total concentration of polymer, and of time. It was found that the increase in molecular weight during growth of stereocomplexes is accompanied by a macromolecular coil contraction.

One of the principal characteristics of the phenomena is their kinetic character. Accordingly, we have studied this phenomenon by laser light scattering in several pure liquids (THF, DMF, acetonitrile, ethyl acetate and 1,4-dioxane) as a function of steric content of the syndiotactic PMMA, polymer whole concentration and time.

We have employed in all experiments the ratio between both stereopolymers as 1:2 (it:st). In the literature some authors have reported different values of this optimum ratio, ranging between 1:1 and 1:2.

EXPERIMENTAL

Isotactic PMMA was prepared by anionic polymerization in toluene at low temperature (195 K) with phenylmagnesium bromide as initiator[33]. Several samples of syndiotactic PMMA were prepared by free radical polymerization using different solvents and temperatures, and 1,2-azobisobutyronitrile as initiator. All samples were fractionated by solubility (benzene/methanol) and divided into eleven fractions. Polydispersity, as determined by g.p.c., lay between 1.2 and 1.5.

The weight average molecular weight, $\bar{M}_w$, measured by light scattering has been determined in ethyl acetate and acetone solutions at 298 K. The g.p.c. measurements have been made in THF, at 298 K, with two μ-Shodec columns (A 80M) calibrated with polystyrene standards. The tacticities of the two PMMA samples were determined in

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solution in chloroform at 318 K by a 200 MHz ^{1}H n.m.r. spectrometer. Molecular and structural parameters of the fractions employed in this paper are given in *Table 1*.

Solvents used in this study were dimethylformamide (DMF), tetrahydrofuran (THF), acetonitrile (ACN), ethyl acetate and 1,4-dioxane; they were purified by standard procedures and freshly distilled before use. Solutions of the individual stereoisomers were optically purified by centrifugation at 15 000 rev/min for 2 h. After centrifugation both solutions were mixed directly into the light scattering cells to obtain different concentrations of both polymers.

Light scattering measurements were made at eleven angles between 30° and 150° for each solution, at 298 K. Two light scattering photometers have been used. The first was a modified Fica 4200 light scattering photometer. Both light source and optical block of the incident beam were replaced by a He–Ne laser (Spectra Physics model 157), which emits at 633 nm with a power of 3 mW. The photo-goniodiffusometer was calibrated with pure benzene by using natural light and taking the Rayleigh ratio as $R_B = 8.96 \times 10^{-6}\,\mathrm{cm}^{-1}$.[34] A Fica 50 light scattering photometer was also employed. The apparatus was calibrated with pure benzene by using vertically polarized light of wavelength 546 nm and taking the Rayleigh ratio at right-angles to the incident beam as $22.53 \times 10^{-6}\,\mathrm{cm}^{-1}$.

The angular dependence technique or Zimm plot was employed for determination of $\bar{M}_w^*$ and R_G^{*2}:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w}\left(1 + \frac{16\pi^2 R_G^2}{3\lambda^2}\sin^2\frac{\theta}{2}\right) + 2A_2c$$

Apparent molecular weight, $\bar{M}_w^*$, is the molecular weight calculated from experimental data at finite concentrations using the equation valid for infinite dilution only

$$\frac{1}{M_w^*} = \frac{1}{M_w} + 2A_2c$$

By extrapolating towards zero angle in the light scattering general expression, we obtain the apparent molecular weight

$$M_w^* = \left(\frac{R_\theta}{Kc}\right)_{\theta \to 0}$$

To evaluate the K parameter, it was necessary to measure the specific refractive index increment, dn/dc. A Brice–Phoenix differential refractometer equipped with a special glass cell was used for measurements of refractive increments at 298 K and $\lambda = 546$ nm. Aqueous solutions of KCl at 298 K were used for calibration of the differential refractometer[35]. For the dn/dc measurements at $\lambda = 633$ nm it was necessary to calibrate the differential refractometer employing the literature data[36] (*Table 2*). The light source used was a He–Ne laser (Spectra Physics model 156), which emits at 633 nm with a power of 1 mW.

Table 1 Molecular and structural parameters of the fractions used in this work

	I	H	S	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
OC5	2	24	74	2.65	1.25
PO3	5	40	55	1.50	1.52
I1003	99	1	0	4.18	1.24
FB2	99	1	0	6.20	1.25
FB3	99	1	0	4.68	1.25
FB4	99	1	0	3.11	1.26
FB5	99	1	0	2.12	1.25
FB6	99	1	0	1.37	1.23

Table 2 Refractive index, n, and refractive index increments, dn/dc, for PS and PMMA in various solvents at $\lambda = 633$ nm

Polymer	Solvent	n_{633}	dn/dc (ml g^{-1})	Reference
PS	Benzene	1.4947	0.1047	36
	Toluene	1.4905	0.106	36
	1,4-dioxane	1.4185	0.166	36
	THF	1.4037	0.186	36
	Ethyl acetate	1.3686	0.2158	36
PMMA	1,4-dioxane	1.4185	0.068	36
	THF	1.4037	0.087	36
	Ethyl acetate	1.3686	0.118	36
	DMF	1.4268	0.060	This work
	Acetonitrile	1.3383	0.140	This work

RESULTS AND DISCUSSION

In *Table 3* we can see that the ethyl acetate and acetonitrile are strongly complex-forming liquids. Likewise, the DMF and THF are considered to be liquids that are highly complexing. However, in this Table a great difference in the complexing power of these liquids can be seen, depending on the polymer considered, i.e. if we choose PMMA OC5 we observe a large increase of apparent molecular weight at initial time. But for PMMA PO3 the results obtained are very different, as can be seen in *Table 2*. This is due to the different steric distribution of syndiotactic triads of both polymers (*Table 1* and *Figures 1* and *2*).

Spevacek and Schneider[11] have shown that a threshold value of syndiotactic length sequence is necessary for the appearance of polymer complexing effects. Sequence length distributions for both polymers can be taken from *Figures 1* and *2*, as calculated by Johnsen[37] using first-order Markow statistics. In these figures we can see for PMMA OC5 that the sequence length of highest statistical weight is for six monomeric units, while, for PMMA PO3, it is for three. Likewise, in PMMA PO3 we can observe that the statistical weight decreases more quickly with the increase of sequence length than in PMMA OC5. This means that the association in the PMMA OC5 is more favoured than in the other polymer. This explains the behaviour of this polymer in THF and DMF.

From the Zimm plot we have obtained the second virial coefficients for the different systems studied (*Table 4*). These values are not absolute because of the fact that stereocomplex formation depends on concentration, as can be seen in *Figure 3*. As the virial second coefficient is related to the intermolecular interactions of the system, and taking into account that the stereocomplex formation is a kinetic process that depends on the polymer concentration, it is necessary to know the size distribution and its dependence on concentration to determine the absolute values of the second virial coefficient.

It should be taken into account that the stereocomplex formation is a kinetic process that depends on the whole polymer concentration; at constant time, as polymer concentration increases, the size of the stereocomplex also

Table 3 Molecular weight of the mixture of both polymers, $\bar{M}_w$, and apparent molecular weights, $\bar{M}_w^*$, after 4 h at $c_{mix} = 1.20 \times 10^{-3}$ g ml^{-1} polymer whole concentration

PMMA		$\bar{M}_w \times 10^{-5}$	$\bar{M}_w^* \times 10^{-5}$ (Stereocomplex)				
Syn.	Iso.	mixture	dioxane	DMF	Ethyl acetate	THF	ACN
OC5	FB4	2.80	3.06	73.0	170	–	–
PO3	I1003	2.40				4.00	–
PO3	FB2	3.07			27.0	3.65	23.6
PO3	FB3	2.56	–	11.5	–	–	–
PO3	FB5	1.71	–	5.25	–	1.80	–
PO3	FB6	1.45	–	4.00	–	–	–

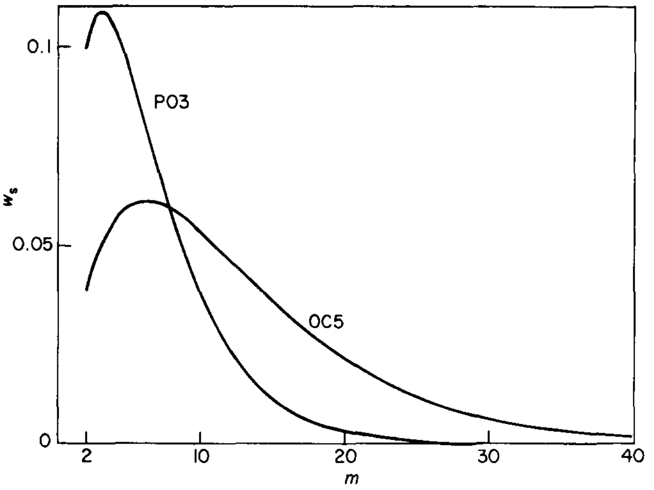

Figure 1 Differential weight distribution, w_s, of syndiotactic sequences of length m monomeric units in st-PMMA samples

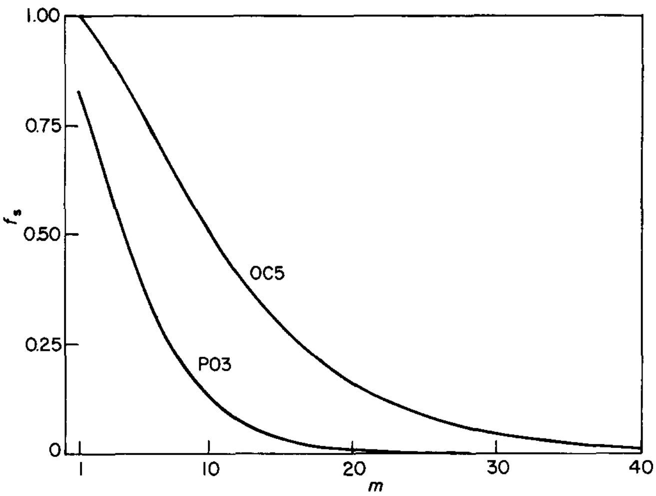

Figure 2 Weight fraction, f_s, of syndiotactic sequences longer than m units as a function of m in st-PMMA samples

Table 4 Apparent second virial coefficients for the different systems measured in several solvents

Polymers	$A_2^* \times 10^4$ (cm mol g^{-2})	Solvents
PO3/I1003	1.96	THF
PO3/FB2	2.22	
PO3/FB5	3.37	
PO3/FB5	−2.00	DMF
PO3/FB6	−2.80	
PO3/FB2	−0.34	Ethyl acetate
PO3/FB2	0.52	Acetonitrile

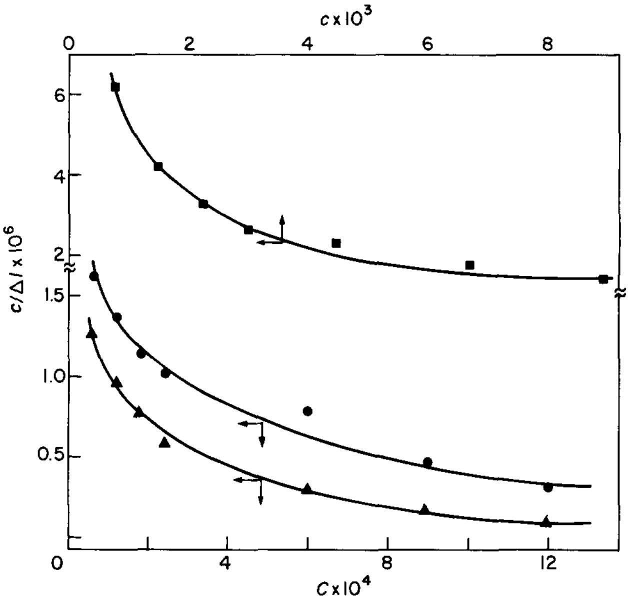

Figure 3 Variation of $(c/\Delta I)$ as a function of concentration for DMF measured at 3 h after mixing (■) and ethyl acetate measured at 3 h (●) and 20 h (▲) after mixing, at 298 K. $\Delta I = (I - I_0)$, where I and I_0 are the scattered intensity of the solutions and solvents, respectively

increases. So the influence of concentration on apparent molecular weight is effected by the absolute molecular weight and second virial coefficient. For this reason the A_2 values that we have calculated are A_2^*, and so we cannot give a definitive physical meaning to these values.

A_2^* values are shown in *Table 4*. As can be seen, there are three kinds of values: positive for THF, negative for DMF and practically zero for ethyl acetate and acetonitrile. These values can be explained by taking into account the above discussion and the different complexing character of liquids.

THF is the weakest complexing solvent among all that we have studied. However, in the literature this liquid is classified as a strongly complexing solvent. This can be explained is we consider the low syndiotactic triads of the PMMA used in this paper (*ca.* 55%). For this polymer the complexing phenomenon goes slowly. At $t = 4$ h, the stereocomplex formation is still small, as can be seen in *Table 2*. This behaviour can explain the positive values of A_2^*.

The negative values of A_2 for DMF can be explained by taking into account its highly complexing character. Considering that the stereocomplex particle size depends on concentration, the more concentrated solutions show

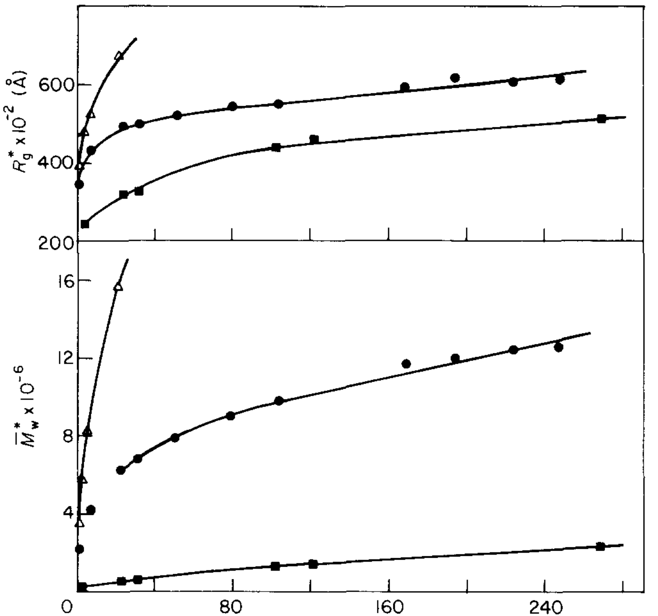

Figure 4 Variation of apparent molecular weight, $\bar{M}_w^*$, and radius of gyration, R_G^*, as a function of time for ethyl acetate (▲), DMF (●) and 1,4-dioxane (■), at 298 K (concentration = 0.60×10^{-3} g ml^{-1})

higher $\bar{M}_w^*$ values at the measuring time. Owing to this, $1/\bar{M}_w^*$ has a smaller value and the variation with concentration is negative.

For ethyl acetate and acetonitrile, the observed small values for A_2^* can be explained by considering their very highly complexing character (for acetonitrile the minimum sequence length necessary for stereocomplex formation is of the order 3)[11]. This produces a very fast complexation, which indicates that the whole polymer is associated at the measuring time (*Table 3*). So the concentration dependence of the complexing kinetics is not considered.

The influence of time on molecular parameters ($\bar{M}_w^*$ and R_G^*) has also been studied as a function of the complexing character of the liquids and polymer whole concentration. *Figure 4* shows the $\bar{M}_w^*$ and R_G^* variation against time for 1,4-dioxane, DMF and ethyl acetate at a polymer whole concentration of 0.60×10^{-3} g ml^{-1}, at 298 K. As can be seen in this Figure, ethyl acetate is the stronger complexing solvent and 1,4-dioxane is the weakest. Ethyl acetate complexing character is so strong that the polymer gel formation can be observed 30 h after mixing the iso- and syndio-PMMA solutions.

As can be seen, $\bar{M}_w^*$ and R_G^* tend to a limiting value for these liquids. For strong complexing solvents, $\bar{M}_w^*$ and R_G^* experience a fast increase during the first moments, tending soon towards their limiting values. However, for weak complexing solvents, this increase is slower and the limiting value is reached very late. Likewise, we find for strong complexing solvents a great increase of $\bar{M}_w^*$ compared with the smaller increase of R_G^*. This behaviour gives us an idea of the great compaction of the stereocomplex particles.

Figure 5 represents the variation of $\bar{M}_w^*$ and R_G^* with time as a function of the whole polymer concentration in ethyl acetate solutions. We can observe how the stereocomplexation is faster at increasing concentration. This is because the probability of intermolecular contacts increases with the latter. Similarly, the limiting values of $\bar{M}_w^*$ and R_G^* also increase with concentration, as is clearly evident in *Figure 5*.

As interesting as working with these apparent magnitudes is using a ratio that represents an absolute property. Considering the Zimm plot shown in *Figure 6*, the weight average molecular weights are calculated by using the expressions

$$\frac{1}{\bar{M}_w} = \text{ordinate P}$$

and

$$\left(\frac{1}{\bar{M}_w^*}\right)_{c_1} = \frac{1}{\bar{M}_w} + 2A_2c = \text{ordinate Q}$$

The values of R_G and R_G^* are given by the expressions

$$R_G^2 = 3\left(\frac{\lambda_0}{4\pi n_0}\right)^2 \frac{\text{slope PA}}{\text{ordinate P}}$$

$$R_G^{*2} = 3\left(\frac{\lambda_0}{4\pi n_0}\right)^2 \frac{\text{slope QB}}{\text{ordinate Q}}$$

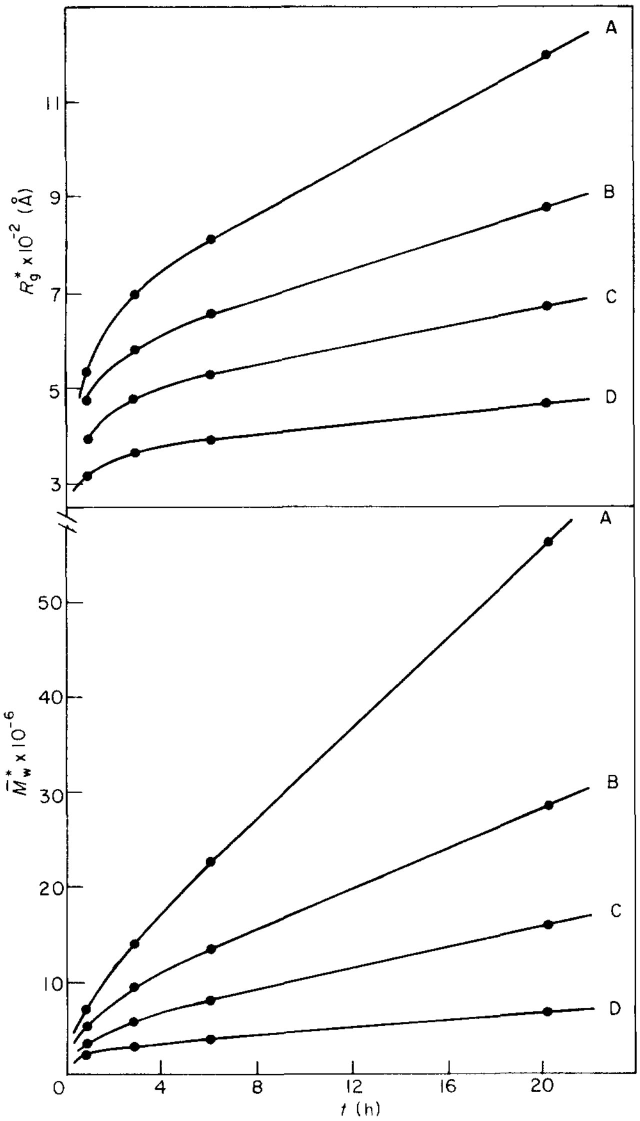

Figure 5 Variation of apparent molecular weight, $\bar{M}_w^*$, and radius of gyration, R_G^*, as a function of time for ethyl acetate at four concentrations, at 298 K: A, 1.21; B, 0.90; C, 0.60; and D, 0.31×10^{-3} g ml^{-1}

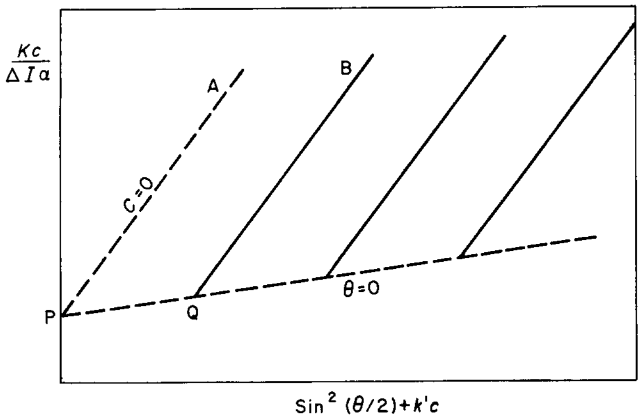

Figure 6 A Zimm plot model. $\Delta I=(I-I_0)$ and $\alpha=\sin\theta/(1+\cos\theta)$

Table 5 $(R_G^2/\bar{M}_w)\times 10^2$ values for the system PMMA (FB4/OC5) in 1,4-dioxane, at different polymer concentrations and time. R_G values are expressed in ångstroms

	$c\times 10^3$ (g ml^{-1})			
t(h)	0.31	0.60	0.90	1.21
7.8	20.1	19.7	22.5	22.8
101.0	15.4	14.3	14.4	14.2
268.5	12.3	11.5	11.8	12.2

Taking into account that slope PA = slope QB, then

$$\frac{R_G^{*2}}{R_G^2}=\frac{\bar{M}_w^*}{\bar{M}_w}$$

From this expression we can obtain the relation between both radii of gyration

$$R_G^{*2}=\frac{R_G^2}{1+2A_2c\bar{M}_w}$$

In *Tables 5–7* the $(R_G^2/\bar{M}_w)$ values for the systems studied and their variation with time and polymer whole concentration are presented. As can be seen, the values decrease with time and tend to a limiting value. Likewise, strong complexing solvents (DMF, ethyl acetate) tend approximately to the same limiting value, while weak ones (1,4-dioxane) yield a value that is markedly different and bigger.

What is the physical sense of this magnitude? It is related to the stereocomplex segment density. This means that stereocomplexes obtained in liquids with high complexing power present a strong interpenetration of the coils. This leads to a greater segment density of the stereocomplex particles compared with that observed in the original polymers.

In weak complexing solvents we can observe that the values of $R_G/\bar{M}_w$ are much higher than those corresponding to DMF and ethyl acetate. This fact can be explained by considering that intermolecular interactions between isotactic and syndiotactic chains occur near the molecular surface.

Table 6 $(R_G^2/\bar{M}_w)\times 10^2$ values for the system PMMA (FB4/OC5) in ethyl acetate, at different polymer concentrations and time. R_G values are expressed in ångstroms

	$c\times 10^4$ (g ml^{-1})			
t(h)	0.62	1.20	1.79	2.42
1.4	6.9	4.9	5.8	3.9
9.0	4.5	3.4	4.3	3.4
195.3	4.0	3.2	3.1	2.9

Table 7 $(R_G^2/\bar{M}_w)\times 10^2$ values for the system PMMA (FB4/OC5) in dimethylformamide, at different polymer concentrations and time. R_G values are expressed in ångstroms

	$c\times 10^4$ (g ml^{-1})			
t(h)	0.31	0.60	0.90	1.21
3.8	4.5	4.6	4.5	4.6
51.3	3.8	3.4	3.3	3.2
222.8	3.4	3.0	2.8	2.8

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