Study of Polymer Complexes by Size Exclusion Chromatography Coupled with Light Scattering in Combination with Fluorescence Spectroscopy

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SUMMARY: Poly(methyl methacrylate) stereocomplexes prepared at different concentration in dilute tetrahydrofuran solutions were studied by size exclusion chromatography coupled with refractive and light scattering detectors in combination with fluorescence spectroscopy. A considerable increase in segment density due to complexation compared with free poly(methyl methacrylate) chain was only slightly affected by the polymer concentration in solution where stereocomplexes were formed. At polymer concentrations up to 3×10^{-3} g cm^{-3}, an increase in non-uniformity of polymer complex molecular weight and size and a shift to higher values of both were observed. In semidilute solutions (at $c > 3\times10^{-3}$ g cm^{-3}) stereocomplexes virtually did not become heavier and larger.

Introduction

The phenomenon of stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate)s (i- and s-PMMA) in solution has been much investigated[1]. The concentration of polymer in solution as one of the variables of stereocomplex formation was first evidenced experimentally by Vorenkamp and Challa[2]. In order to get a more precise idea of the effect of that variable on the stereocomplex nature, we used computerized high-resolution chromatographic technique and fluorescence spectroscopy. The results obtained are presented here.

Experimental

Polymers. Data on PMMA polymers used are listed in Table 1. Unlabeled[3] polymers (i-PMMA, s-PMMA, atactic at-PMMA) and polymers labeled[4] with anthracene (i-PMMA$_A$, at-PMMA$_A$) and carbazole (s-PMMA$_C$, at-PMMA$_C$) polymers were prepared and characterized as described elsewhere[3,4].

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Table 1. Molecular and structural characteristics of PMMA samples

Polymer	Label content (mol %)	$\langle M\rangle_w \times 10^{-4}$ g mol^{-1}	$\langle M\rangle_w/\langle M\rangle_n$	Tacticity (%)		
				i	h	s
at-PMMA	0	29	2.1	5	32	63
i-PMMA	0	7	3.2	83	12	5
s-PMMA	0	29	1.7	3	10	87
at-PMMA$_A$	1.09	14	2.4	5	34	61
at-PMMA$_C$	1.12	12	2.4	4	32	64
i-PMMA$_A$	0.69	10	1.8	84	12	4
s-PMMA$_C$	1.75	57	9.5	2	11	87

Polymer complexes were prepared in tetrahydrofuran (THF) solutions of different concentrations using stereoregular PMMA pairs mixed very slowly at an i/s ratio at which the intensity of complexation was the highest. The maximum ratio of anthracene and carbazole emission intensities[3], I_A/I_C , was found at i:s = 1:2. The same i/s ratio was confirmed by a maximum absolute increase in apparent weight-average polymer complex molecular weight as compared with the hypothetic additive value of the uncomplexed mixture of stereoisomers used, $\langle M\rangle_{w,app} / \langle M\rangle_{w,add}$ (Fig. 1).

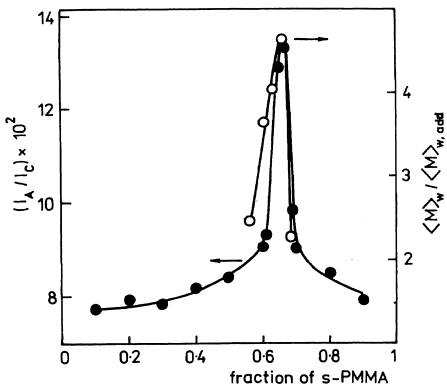

Fig. 1: Dependence of I_A/I_C [(●), c = 1.5×10^{-2} g cm^{-3}, concentration of fluorophores c_F = 10^{-7} mol cm^{-3}] and $\langle M\rangle_w/\langle M\rangle_{w,add}$ [(○), $c = 2\times5.10^{-4}$ g.cm^{-3}] on weight fraction of s-PMMA 24 h after mixing solutions of i- and s-PMMA

Measurements

Static light scattering (LS) measurements were performed with a photo-gonio-diffusometer Fica, model 42.000 (Sofica,France) in vertically polarized light, wavelength 546 nm, angular range 30-150°. Sample concentration was 2.5×10^{-4} g cm^{-3}.

Fluorescence spectroscopy. Reflectance fluorescence spectra were measured on a Hitachi Perkin-Elmer MPF-2A apparatus (USA). The donor (carbazole) was excited at 292 nm, and the energy transfer efficiency was characterized by the ratio of emission intensity of the acceptor (anthracene) at 411 nm and the donor at 345 nm.

Size exclusion chromatography (SEC). The chromatographic equipment (Laboratory Instruments, Prague, Czech Republic) consisted of a pump HPP 5001, an injection valve LC-30 with a 100-μl loop, a RIDK-102 differential refractometer and a low-angle laser light scattering (LALLS) detector (KMX-6, Chromatix, USA), both detectors being connected through an A/D converter 2308 (Black*Star Ltd., England) to a computer with a printout facility. The software (M. Netopilík, this Institute) allows on-line data accummulation as well as calculation of molecular weight- (***M***- D) or size-distribution ($\boldsymbol{R}_{\eta}$-D) and ***M***- or ***R***-averages. A commercial stainless steel column HP (7.5/600 mm) packed with PLGel 10 μm MIX (Polymer Laboratories, Inc., Shropshire, England) was used with THF as eluent; sample concentration was about 1×10^{-3} g cm^{-3}. Refractive index increment of PMMA in THF, $d\boldsymbol{n}/d\boldsymbol{c}$ = 0.087 g cm^{-3}, was found independent of tacticity or association. Under experimental conditions of SEC separation, the axial dispersion was negligible.

Results

Molecular weight distribution of stereocomplexes formed at different polymer concentrations in solution

Using the concentration and LS signals, the molecular weight distribution (***M***-D) of stereocomplex systems was estimated and confronted with ***M***-D of a hypothetical mixture of non-interacting stereoisomers as the sum of appropriate reduced ***M***-D of i- and s-PMMA (Fig. 2).

The hydrodynamic particle volume control SEC separation proportionally to the product $\boldsymbol{M}[\eta]$ ($\boldsymbol{M}$ is the molecular weight and $[\eta]$ is the intrinsic viscosity). Due to topological non-uniformity in stereocomplex systems, the weight fraction having a given $\boldsymbol{M}[\eta]$ and separating at an elution volume $\boldsymbol{V}_e$ should be expected to have different particle weight. Hence, in spite of using LS detection, the evaluation of SEC data provided rather an apparent ***M***-D.

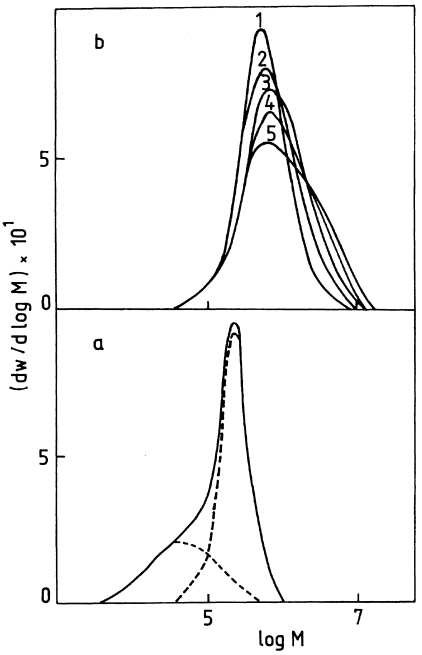

Fig. 2: Molecular weight distribution of (a) constituent stereoregular component (- - -) and their hypothetical uncomplexed mixture (—), (b) stereocomplexes formed at polymer concentrations 1 1.10^{-3}, 2 $1.8.10^{-3}$, 3 $2.5.10^{-3}$, 4 3.10^{-3}, 5 $5.5.10^{-3}$ g cm^{-3}

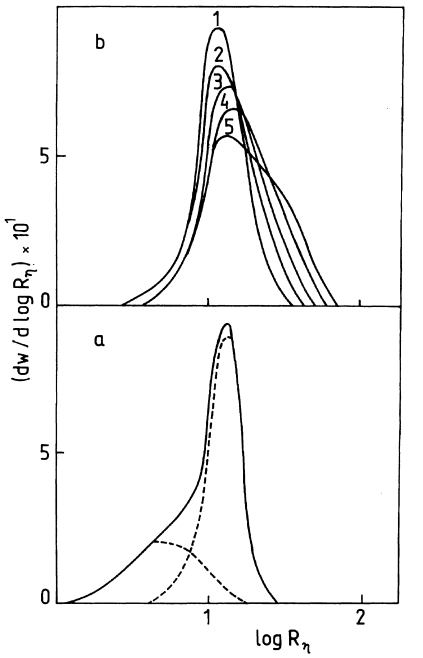

Fig. 3: Size distribution of (a) constituent stereoregular component (- - -) and their hypothetical uncomplexed mixture (—), (b) stereocomplexes formed at polymer concentrations 1 1×10^{-3}, 2 1.8×10^{-3}, 3 2.5×10^{-3}, 4 3×10^{-3}, 5 5.5×10^{-3} g cm^{-3}

Size distribution of stereocomplexes formed at different polymer concentrations in solution

If the existing universal calibration of a SEC system (dependence of $M[\eta]$ on V_e) is transformed to the R_η calibration using the Einstein relation[5,6] ($R_\eta=(3[\eta]M/(10\pi N_A))^{1/3}$, N_A is Avogadro´s number), the real weight distribution of radii of the "viscosity" hydrodynamic sphere of stereocomplexes, R_η-D, can be calculated from the concentration profile (Fig. 3).

Dependence of the stereocomplex size on the molecular/particle weight obtained by SEC coupling with LALLS

In SEC separation, the directly measured molecular weights, M, of free PMMA chain and stereocomplexes formed in solutions at different polymer concentrations are confronted with their calculated R_η values in Fig. 4. Shrinking of the PMMA free chain by complexation was

higher than that observed when PMMA chain is transferred from a very good to Θ-solvent. At the same time, only slight dependence on polymer concentration in the range used was found. Compactness of stereocomplexes followed simply from relation between M and $[\eta]$ calculated using SEC data (Fig. 5).

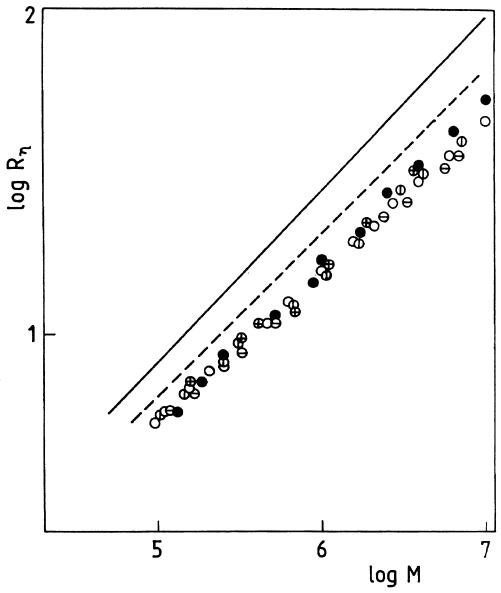

Fig. 4: Dependence of R_η on M of a separated fraction of linear atactic PMMA in THF (—), in Θ-solvent (- - -) and of stereocomplexes formed at polymer concentrations O 1×10^{-3}, ⊖ 1.8×10^{-3}, ⊕ 2.5×10^{-3}, ⊕ 3×10^{-3}, ● 5.5×10^{-3} g cm^{-3}

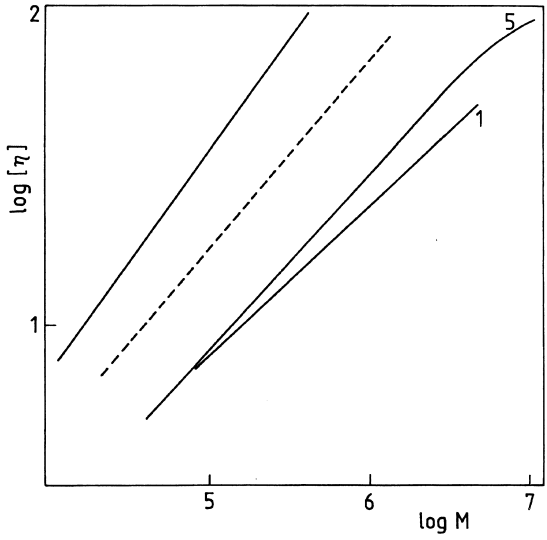

Fig. 5: Dependence of $[\eta]$ on M of a separated fraction of linear atactic PMMA in THF (—), in Θ-solvent (- - -) and of stereocomplexes formed at polymer concentrations 1 1×10^{-3}, 5 5.5×10^{-3} g cm^{-3}

Effect of polymer concentration on complexation process

Knowing the M-D and R_η-D, we could calculate real weight-average molecular weight, $\langle M \rangle_w$, and weight-average "viscosity" radius, $\langle R_\eta \rangle_w$, of individual stereocomplex systems. These parameters together with fluorescence spectroscopic data enabled an insight into polymer solution under complexation.

Up to polymer concentration $c = 3\times10^{-3}$ g cm^{-3}, $\langle M \rangle_w$ and $\langle R_\eta \rangle_w$ values increased markedly while the ratio of the emission intensities of the acceptor and donor, I_A/I_C, remained constant (Fig. 6). Consequently, the average distance between the acceptor and donor on PMMA chains, mostly inside the stereocomplex particle, did not change. This is consistent with finding a slight dependence of stereocomplex compactness on the polymer concentration at their formation. At $c > 3\times10^{-3}$ g cm^{-3}, the increase in $\langle M \rangle_w$ and $\langle R_\eta \rangle_w$ values nearly stopped, i.e., the number of stereocomplex particles should be increased. At the same time, the I_A/I_C ratio increased, since interparticle energy transfer became stronger. This idea is supported by the similarity of the trend of I_A/I_C values for labeled atactic free PMMA chains (Fig.6b,c). Here, in the whole polymer concentration range used, only intermolecular energy transfer controlled by continuous decrease in an average distance between acceptor and donor should be operative.

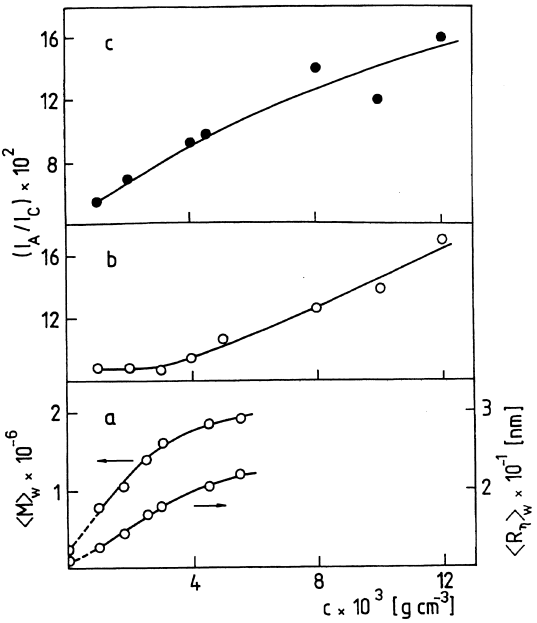

Fig. 6: Dependence of (a) $\langle M \rangle_w$ and $\langle R_\eta \rangle_w$, (b) I_A/I_C of stereocomplexes, (c) I_A/I_C of atactic polymer on polymer concentration

Conclusion

The nature of PMMA stereocomplexation was investigated in dependence on the polymer concentration in solution where stereocomplexes were formed.

The experimental technique used gave "viscosity"size/ intrinsic viscosity as a function of molecular/particle weight and thus revealed a considerable increase in segment density due to complexation as compared with a free PMMA chain. At the same time, the sterecomplex compactness was only slightly affected by the polymer concentration in solution (Fig. 4).

With increasing concentration (up to 3×10^{-3} g cm^{-3}), an increase in non-uniformity of particle weight and size as well as a shift to higher values of both were observed (Figs 2 and 3). Regarding the $\langle M\rangle_{w,add}$ and $\langle R_\eta\rangle_{w,add}$ values, the average parameters $\langle M\rangle_w$ and $\langle R_\eta\rangle_w$ increased approximately eight times and twice, respectively.

In semidilute solutions (at $c > 3\times10^{-3}$ g cm^{-3}), stereocomplex particles virtually did not become heavier and larger but their number probably increased as followed from a combination of SEC and fluorescence measurements (Fig. 6).

The hydrodynamic behaviour and structure of stereocomplexes with regard to the polymer concentration were investigated using much shorter isotactic than syndiotactic chains. It should be stressed that the role of polymer concentration in the stereocomplexation process may be affected by the molecular weight of constituent stereoregular polymers. This aspect has not been examined here.

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