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Study of Poly(methyl methacrylate) Stereocomplexes by Size Exclusion Chromatography and Dynamic Light Scattering

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ABSTRACT: Poly(methyl methacrylate) stereocomplexes prepared in dilute tetrahydrofuran solutions were studied by size exclusion chromatography coupled with refractive index and light scattering detectors in combination with dynamic light scattering. In addition to the molecular/particle weight of the separated fraction and distribution of radius of the “viscosity” hydrodynamic sphere, the distribution of hydrodynamic radii was obtained as well. By mixing of iso- and syndiotactic polymers, a considerable increase in polymer particle mass was observed, while particle size varied much less. Consequently, an appreciable increase in the segment density of the particles was proved to be the result of stereocomplexation. This phenomenon was quantified by variation of the hydrodynamic shrinking factor (ratio of the “viscosity” radius of the complex particle and free poly(methyl methacrylate) molecule) during the separation. The results obtained support the picture of the stereocomplex particle as a structure with associated segments of different stereoregularity which should form branched, multifunctional points.

Introduction

The phenomenon of stereocomplex formation of isotactic and syndiotactic poly(methyl methacrylate) (i- and s-PMMA) was much investigated in the past,[1] and a pseudostar[2] or multistar[3] macrostructure was proposed for these stereocomplexes. A careful combination of precise data for hydrodynamic extension and polymer segment density in relation to molecular weight could further substantiate these proposals. Hence, molecular weight, size distribution, and particle density analysis by size exclusion chromatography with refractive index and low-angle light scattering detection (SEC/LALLS) as well as dynamic light scattering (DLS) were chosen for this purpose.

The hydrodynamic coil volume controls the SEC separation proportionally to the product $M[\eta]$, where M is the molecular/particle weight and $[\eta]$ is the intrinsic viscosity. $M[\eta]$ is known as a universal calibration parameter which is valid irrespective of topological structure of the polymer molecules/aggregates.[4] If the existing universal calibration of a SEC system (dependence of $M[\eta]$ on elution volume) is transformed to the R_η calibration via the Einstein relation,[5,6] the weight distribution of radii of the “viscosity” hydrodynamic sphere of stereocomplexes, R_η, can be calculated. The use of low-angle laser light scattering (LALLS) detection on line with refractometric (RI) detection makes possible an “intensity weighting” of SEC data and a comparison of results coming from SEC/LALLS and DLS measurements.

DLS has become a routine technique[7] often used to determine hydrodynamic size distribution of polymers and dispersions. A translational diffusion coefficient, D, is measured by DLS, and the hydrodynamic radius of the coil, R_h (i.e., the radius of an equivalent sphere having the same D), is inversely proportional to D through the Stokes−Einstein formula. The scattered light intensity from a very dilute solution of macromolecular particles of the R_h radius is proportional to the number of these particles per unit volume and to the square of their molecular weight, M, if the Mie effect is neglected. In a polydisperse system, every particle size contributes by its z-fraction to the total measured intensity of scattered light. A z-average diffusion coefficient[8] results in this case, and the intensity-defined distribution of D as well as the corresponding distribution of R_h (cf. ref 9) is obtained from the multiexponential autocorrelation function by the inverse Laplace transformation.[10] Hence, the inverse z-average is obtained from DLS data.

The objective of this paper is (a) determination of the average molecular/particle weights, (b) comparison of the weight-defined R_η distributions of aggregated and hypothetical nonaggregated systems, and (c) comparison of intensity-defined R_η and R_h distributions. The hydrodynamic shrinking factor (ratio of the “viscosity” radius of the complex particle and free poly(methyl methacrylate) molecule having the same molecular weight) calculated on the basis of reliable relations between R_η and particle weight obtained from an SEC/LALLS experiment will be presented as a “measure of complex compactness” as well.

Experimental Section

Polymers. Conventional atactic PMMA was prepared in toluene solution by radical polymerization initiated with 2,2′-azobis(isobutyronitrile) at 45 °C. Isotactic i-PMMA was prepared in benzene solution by anionic polymerization initiated with lithium *tert*-butoxide at 20 °C. Syndiotactic s-PMMA was prepared in toluene solution by coordination polymerization catalyzed with titanium(IV) chloride and triethylaluminum at

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Table 1. Molecular and Structural Characteristics[a] of PMMA Samples

PMMA	$\langle M\rangle_w \times 10^{-5}$	$\langle M\rangle_w/\langle M\rangle_n$	triads (%)		
			syndio	hetero	iso
atactic	2.9	2.1	63	32	5
isotactic 1 (i1)	0.7	3.2	5	12	83
isotactic 2 (i2)	6.6	3.8	11	17	72
syndiotactic 1 (s1)	2.9	1.7	87	10	3
syndiotactic 2 (s2)	2.6	1.9	92	8	0
syndiotactic 3 (s3)	4.5	1.8	91	8	1

[a] $\langle M\rangle_w$ and $\langle M\rangle_w/\langle M\rangle_n$ by SEC/LALLS; tacticity was determined from ^{1}H NMR spectra in a mixture of 1,2-dichlorobenzene and tetrachloroethene at −140 °C.

Table 2. Average Parameters of Stereocomplex Systems

sample PMMA	1 (atactic)	2 (i1+s1)	3 (i1+s3)	4 (i2+s3)	5 (i2+s2)
$\langle M\rangle_w \times 10^{-5}$	2.9	7.8	9.2	35.7	46.0
$\langle M\rangle_n \times 10^{-5}$	1.2	2.2	1.8	7.4	2.3
$\langle X\rangle_w{}^a$		3.6	3.0	6.6	11.2
$\langle X\rangle_n{}^a$		4.9	3.8	3.5	1.5
$\langle 1/R_\eta\rangle_z{}^{-1}$ [nm]	17.5	14.7	19.2	35.4	29.8
$\langle 1/R_h\rangle_z{}^{-1}$	16.5	16.0	19.7	37.0	33.5

[a] $\langle X\rangle_x = \langle M\rangle_x/\langle M\rangle_{x,o}$, where $\langle M\rangle_{x,o}$ is hypothetic average molecular weight of a mixture of uncomplexed stereoregular components.

−78 °C. All PMMAs have unimodal molecular weight distribution as found by SEC/LALLS. Their molecular and structural parameters obtained are given in Table 1.

Complexes. Strong complexation took place in dilute tetrahydrofuran solutions (1×10^{-3} g cm^{-3}) using PMMA stereoisomers.[12] These were very slowly mixed in the weight ratio i:s = 1:2 at which the extent of complexation should be the highest.[13] After equilibration (∼20 h), the aggregated systems (samples 2−5, see Table 2) were investigated by SEC with RI and LALLS detection as well as by DLS. No gelation or macroscopic polymer separation was observed.

Size Exclusion Chromatography. The chromatographic equipment used (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 LALLS detector (KMX-6, Chromatix, Sunnyvale, CA), both detectors being connected through an A/D converter 2308 (Black*Star Ltd., St. Ives, Huntingdon, England) to an IBM-compatible computer with a printout facility. The software (M. Netopilík, this institute) allows an on-line data accumulation as well as calculation of M or R_g distribution and M or R_g 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; the sample concentration was 1×10^{-3} g cm^{-3}. Refractive index increment of PMMA in THF, dn/dc = 0.087, was found independent of tacticity or association. To calculate universal calibration dependence,[4] the Mark−Houwink−Sakurada equation for linear PMMA in THF (cf. ref 14) was used. Under given experimental conditions of SEC separation, the axial dispersion was negligible.

Dynamic Light Scattering. An Inova 70 series 4 W argon ion laser (Coherent Laser Division, Palo Alto, CA) tuned to 514.5 nm was focused on a precision scattering cell (Hellma GmbH, Mullheim Baden, Germany). The optical components were mounted on a massive steel bench (Newport Research Corporation, Fountain Valley, CA). The scattered photon flow was monitored at an angle of 90° using a commercially available Brookhaven photomultiplier unit and a 128-channel BI-8000 digital correlator (Brookhaven Instruments Corp., Holtsville, NY). The Brookhaven particle distribution software package[15] contains five of the most common size analysis procedures; the Brookhaven CONTIN version 3.0 (including Mie correction) procedure was used here.

Results and Discussion

Using the concentration and light-scattering signals, the weight-average molecular/particle weight of separated fractions, $M_{(w)}$, and dependence of the log $M_{(w)}$ on elution volume V_e of individual stereocomplex systems were calculated. The SEC technique separates macromolecular particles according to their hydrodynamic volumes ($[\eta]M$); i.e., polymer complexes having a given hydrodynamic volume must be expected to have different molecular/particle weights. Then the weight-average molecular weight, $M_{(w)}$, for a definite stereocomplex size at a given $V_{e,i}$ is obtained from RI/LALLS detection. In such a case, there is no correct way to transform SEC data to a true molecular weight distribution (MWD) because the mass fraction of aggregates with a specific value of M is not unambiguously given here. Consequently, in contrast to real weight-average molecular/particle weight, $\langle M\rangle_w$, measured directly, an apparent number-average molecular/particle weight of samples, $\langle M\rangle_n$, could be estimated using the corresponding experimentally determined dependence log $M_{(w)}$ vs V_e. In Table 2 are given the molecular weight averages and parameters $\langle X\rangle_w$ and $\langle X\rangle_n$, which are defined as $\langle X\rangle_x = \langle M\rangle_x/\langle M\rangle_{x,o}$, with $M_{x,o}$ characterizing a mixture of uncomplexed stereoregular components, calculated using data from Table 1. In addition to an increase in $\langle M\rangle_w$ providing clear evidence for the formation of associated species, the parameters $\langle X\rangle_w$ and $\langle X\rangle_n$ compare nonuniformity in M of stereocomplexes and hypothetic uncomplexed mixture.

On the other hand, the SEC separation mechanism can provide a real size distribution.[5] Using very broad linear PMMA, the universal calibration ($[\eta]M$ vs V_e) was established from a SEC/LALLS experiment and then transformed to the corresponding universal calibration in terms of radii of the "viscosity" hydrodynamic sphere by means of relation

$$R_\eta = (3[\eta]M/10\pi N_0)^{1/3} \qquad (1)$$

where N_0 is Avogadro's number. Assuming this calibration (R_η vs V_e) to be universally valid (see below), weight-defined R_η distributions of stereocomplex systems were estimated from the corresponding concentration profiles (full lines) and confronted with R_η distributions for hypothetical mixtures (dashed lines) of noninteracting stereoisomers, which are the sums of appropriate reduced weight-defined distributions of i- and s-PMMA (dotted lines) as shown in Figure 1. In the case of stereoregular pairs with shorter isotactic chains (i1 in samples 2 and 3), we observed a significant decrease in the size nonuniformity but very low shift to higher sizes. At the same time, the particle weight increased several times, and its nonuniformity relative to the uncomplexed mixture decreased as follows from $\langle X\rangle_w < \langle X\rangle_n$ (cf. Table 2). Stereocomplex particle weights corresponding to free PMMA chains, separated according to coil sizes in THF (line 1) and in the Θ-solvent (line 1′), as well as those of the stereocomplex samples mentioned (line 3 and 2, 4) are presented in Figure 2. Shrinking of particle size by complexation is seen to be higher than that observed when the PMMA chain is transferred from THF to the Θ-solvent. (Dependence 1′ in Figure 2 was calculated using literature data.[16]) Hence, such decrease in R_η at the same molecular/particle weight could take place if definite, but limited, amounts of stereoisomer sequences are packed close

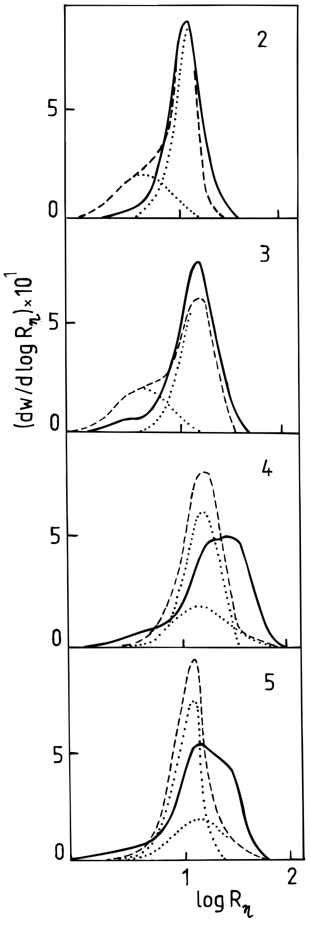

Figure 1. Weight-defined size distribution: (···) of individual stereoregular components, (- - -) of the hypothetical mixture of uncomplexed stereoregular components, (—) of the stereocomplex denoted by the number of sample.

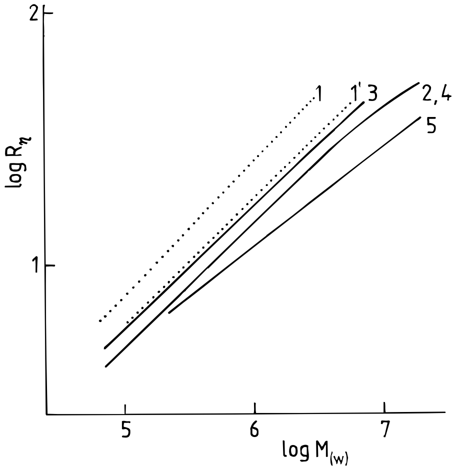

Figure 2. Dependence of R_η on $M_{(w)}$ of separated fractions of linear atactic PMMA (···), 1 in THF, 1′ in Θ-solvent; of stereocomplex system (—); 3, sample 3; 2,4, sample 2 and 4; 5, sample 5.

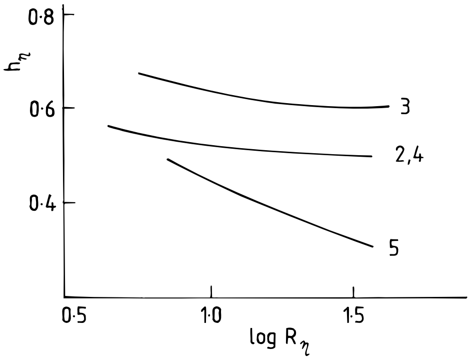

Figure 3. Shrinking factor, $R_\eta/R_{\eta,o} = h_\eta$, of separated fractions of stereocomplex system as a function log R_η; curves denoted by the sample number.

together; in other words, they might be attached to one junction point. A number of such pseudostar structures and number of chain sequences participating in each of them should then determine the stereocomplex particle size.[2,3]

Differences in chain length of stereoregular components and their tacticity rank among factors[1] important in the complexation process. When a shorter isotactic chain was used, the power-law exponent in the relation between R_η and $M_{(w)}$ (line 3 and low-molecular-weight part of line 2, 4 in Figure 2) differed very slightly from that of the linear PMMA chain even in the case[17] when a 5-fold concentration of sample 2 was used. On the other hand, the use of a 10 times longer isotactic chain having lower tacticity (i2 in samples 4 and 5) resulted in the increase in size (cf. curves 4 and 5 in Figure 1) and considerable increase in molecular/particle weight (Table 2). Probably, parts of a long, already associated isotactic chain that are protruding into the solution can continue in an interparticular association as indicated especially by the increase in size and mass of the complex and, at the same time, by the increase in their nonuniformity relative to uncomplexed mixture as follows from $\langle X\rangle_w > \langle X\rangle_n$ (cf. Figure 1 and Table 2). Then, cross-linked structures, separated according to hydrodynamic volumes, were approaching dense spherical particles swollen more (high-molecular-weight part of dependence 2, 4) or less (dependence 5 in Figure 2) by the solvent. Regarding the role of syndiotactic chain used, stereocomplexes with the shorter one were shown to be more compact (samples 2 and 5). To quantify the phenomenon discussed above, we used the ratio of the "viscosity" radius of a nonlinear, R_η, and a linear macromolecule, $R_{\eta,0}$, of the same molecular weight M, i.e., third root of the viscosity shrinking factor $(g')^{1/3} = R_\eta/R_{\eta,0} = h_\eta$ as follows from eq 1. Strictly speaking, the value of M of topologically nonuniform (nonlinear) species of stereocomplexes was a presumable weight-average value, $M_{(w)}$, despite their elution at definite V_{ei}. The SEC/LALLS experiment made possible to approximate this factor as a function of log R_η and allowed us to reveal its size dependence (Figure 3). For instance, molecular-weight-independent hydrodynamic shrinking factors of random stars having f nonuniform arms, predicted[11] to be $h_{star} = 16[(f+1)/\pi]^{1/2}/[3(f+3)]$, cover the same range of experimental h_η values given in Figure 3 for f starting from 13 up to 80, i.e., indicating a very high density.

Using the calibration R_η vs V_e assumed to be universally valid,[5] z-defined R_η distributions of stereocomplex systems were further calculated from the corresponding concentration and molecular/particle weight profiles, the z-fraction being defined as $z_i = (w_iM_i)/\sum w_iM_i$. To compare z-distributions from SEC/LALLS and DLS data, the R_η distributions were transformed to the same scale as obtained from CONTIN (the maximum ordinate is unity). For a linear polymer chain it was experimentally shown that $R_h < R_\eta$; due to higher compactness of

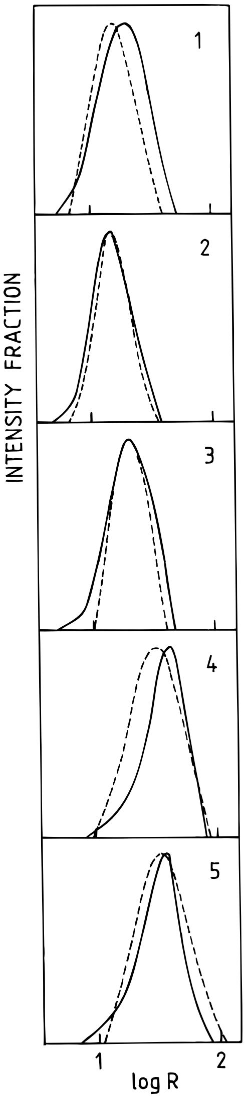

Figure 4. Intensity-defined "viscosity" (—) and hydrodynamic (- - -) size distribution denoted by the number of sample.

stereocomplexes, their R_h and R_η are much closer to each other than those for an atactic linear chain (Figure 4).

Having access to the R_η distributions using eq 1, we could compare the identical size averages coming from SEC and DLS experiments. The R_η value analogous to the DLS average hydrodynamic radius, defined[18,19] as the inverse z-average

$$\left(\sum w_i M_i / R_{h,i}\right) / \sum w_i M_i = \langle 1/R_h \rangle_z \qquad (2)$$

was evaluated replacing R_h by R_η in the preceding equation.

According to Yamakawa,[21] all current theoretical predictions for linear random-flight chain in good solvent resulted in $R_\eta/R_h > 1.2$. Recent experimental data[6] concerning the equivalent spheres applicable to viscosity and diffusion measurements did not contradict the theoretical expectation. For an atactic PMMA (sample 1) $\langle 1/R_\eta \rangle_z^{-1} > \langle 1/R_h \rangle_z^{-1}$ was found, and their ratio 1.05 was shown to be rather low (cf. Figure 4 and Table 2). At the same time, all complex systems under study showed $\langle 1/R_\eta \rangle_z^{-1} < \langle 1/R_h \rangle_z^{-1}$ (Table 2). Due to the compactness of stereocomplex particles (Figure 2), a relative increase in the hydrodynamic size, compared with the "viscosity" size, might decrease the difference between them until they merge (identity). This is the limit situation of hard spheres. Low and unrealistic differences between $\langle 1/R_\eta \rangle_z^{-1}$ and $\langle 1/R_h \rangle_z^{-1}$ for linear PMMA and stereocomplexes, respectively, appear when comparing the results coming from the technique used and could be explained by systematic accompanying phenomenon (e.g., overestimation of R_h to some extent[20]).

Conclusion

To our knowledge, it is the first time the "viscosity" size distributions of polymer complexes (weight and intensity (z) defined) obtained by a separation technique are presented (Figures 1 and 4). The experimental technique used also gave "viscosity" size as a function of molecular/particle weight. Depending on the stereoregular pairs used, a different character of complex particles followed from the relation between R_η and $M_{(w)}$ (cf. Figure 2). A considerable increase in segment density due to stereocomplexation as compared with a free PMMA chain was quantified by the shrinking factor[11] (cf. Figure 3) as a function of the stereocomplex size. Examining Figure 4, one finds a satisfactory relation between intensity-defined (z-defined) size (Stokes) distributions mathematically mediated using DLS data and that evaluated from SEC/LALLS experiments.

Concerning the macrostructure of the stereocomplexes described in this work, it appears that the structures formed might contain multifunctional branch points due to the association of syndiotactic and isotactic sequences as predicted by Vorenkamp and Challa.[3]

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