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Study of Macromolecular Chain Dynamics in Polymer Complexes by Time-Resolved Fluorescence Spectroscopy

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Poly(methyl methacrylate)s labeled with the anthracene fluorophore were prepared by free radical, anionic, and coordination polymerization yielding atactic and syndiotactic polymers. Unlabeled isotactic poly(methyl methacrylate) was prepared by anionic polymerization. Time-resolved fluorescence spectroscopy was used to study polymer association in solution. The time-dependent decays of fluorescence anisotropy show that stereocomplexation causes an increase in rotational correlation times of anthracene fluorophores both embedded in the polymer backbone and attached at the end of the side chain of polymer molecules. The rotational correlation time of anthracene fluorophore in dimethylformamide as a part of stereocomplex is 11.9 and 30 ns in the side chain and embedded in the polymer backbone, respectively, and shorter than 3 ns in noncomplexing solvent.

KEY WORDS: Syndiotactic and isotactic poly(methyl methacrylate)s; stereocomplex formation; anthracene-labeled polymers; rotational correlation time; limiting fluorescence anisotropy.

INTRODUCTION

Isotactic and syndiotactic poly(methyl methacrylate)s (i-PMMA and s-PMMA) associate in some solvents and form so-called stereocomplexes [1]. It was proved that PMMA stereoassociation takes place as a results of interaction of i-PMMA ester groups and the α-CH_3 groups of the syndiotactic component [2]. The formation and structure of PMMA stereocomplex in solutions depend on a number of factors, e.g., on the ratio i-PMMA/s-PMMA in the mixture, the degree of stereoregularity of the components, the temperature, the time, the thermal history, and the solvent [1]. All these factors act together, which may cause some difficulties in separating their effects. The stereocomplex of i-PMMA and s-PMMA has a double-stranded helical structure consisting of an isotactic helix surrounded by a syndiotactic one [3].

In general, the fluorescence depolarization measurement provides information on local mobility, and this method is expected to be fairly sensitive to the complexation phenomenon, which is associated with changes in the local environment.

In the present work, we investigated the stereocomplex of i-and s-PMMA in dimethylformamide (strongly complexing solvent) by the fluorescence depolarization method in the nanosecond time region. For this purpose, two syndiotactic materials labeled with the anthracene group in the middle of the chain and at the end of side chains were prepared. These polymers were mixed with unlabeled i-PMMA in dimethylformamide to form the anthracene-labeled stereocomplex. Local conformational motions of polymer segments in the stereocomplex were compared with those found for polymers in noncomplexing solvent (chloroform) or with those found for labeled syndiotactic polymers. The fluorescence

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method was utilized to investigate the formation of polymer complexes.

EXPERIMENTAL

Polymer Synthesis

Unlabeled Polymers

Atactic poly(methyl methacrylate) (a-PMMA) was prepared by free radical polymerization of methyl methacrylate (MMA) in toluene at 60°C using 2,2′-azobis(2,2′-dimethylpropionitrile) initiator.

Isotactic PMMA (i-PMMA) was prepared by anionic polymerization of MMA in toluene at −78°C using t-butylmagnesium bromide initiator [4].

Polymers with Anthracene in the Side Chain

Fluorescent label was introduced into PMMA by copolymerization of MMA with (9-anthryl)methyl methacrylate (AMMA). Anthracene-labeled a-PMMA (a-PMMA-A) was prepared by copolymerization of MMA with AMMA in the same way as unlabeled a-PMMA.

Syndiotactic PMMA labeled with anthracene in the side chain (s-PMMA-A) was prepared by copolymerization of MMA with AMMA initiated by the $TiCl_4$–Et_3Al system at −78°C in toluene [5].

Polymers with Anthracene in the Backbone

Syndiotactic PMMA labeled with the anthracene fluorophore in the middle of the polymer chain (s-PMMA-9,10-A) was prepared by anionic polymerization of MMA using 1,1-diphenylhexyllithium initiator at −78°C in tetrahydrofurane [6]. The living ends were deactivated at −78°C by a bifunctional terminator, 9,10-bis(bromomethyl)anthracene [7]. This raw polymer (s-PMMA-9,10-A) was further purified by GPC to eliminate the end-labeled fraction.

Polymer Characterization

The molecular weights of prepared polymers were determinated by GPC in tetrahydrofurane using a Hewlett–Packard 1090 apparatus controlled by a HP 85B computer as shown in Table I. PL gel, 10-μm MIXED, or PL gel, 10-μm 500 (Polymer Laboratories Ltd., Shropshire, UK), columns were used for analysis. The apparatus was calibrated using atactic PMMA ($M_w/M_n < 1.05$; Polymer Standard Service, Mainz, FRG). The triad tacticity was determined [8] by ^1H NMR spectroscopy from integrated intensities of the α-CH_3 signals at 0.80 ppm (rr), 1.00 ppm (mr), and 1.15 ppm (mm) in deuterium chloroform at 60°C. ^1H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz using hexamethyldisiloxane as an inner standard. The content of anthracene fluorophore in copolymers was evaluated by UV–vis spectrometry in dioxane. UV–vis spectra were taken on a Hewlett–Packard 8451A spectrophotometer. The molar absorption coefficient of AMMA ($\varepsilon = 8460$ l mol^{-1} cm^{-1} at 366 nm) was used for calculation (Table I).

Time-Resolved Fluorescence Measurements

Time-dependent decays of fluorescence anisotropy were obtained using a time-resolved fluorimeter, FL 900 CDT (Edinburgh Analytical Instruments, UK). This apparatus uses the time-correlated single-photon counting method. The time-resolved intensity decay of the parallel [$R_{VV}(t)$] and the perpendicular [$R_{VH}(t)$] components of the emission were measured in L-format and the time-resolved anisotropy $r(t)$ was calculated point by point using Eq. (1).

$$r(t) = \frac{GR_{VV}(t) - R_{VH}(t)}{GR_{VV}(t) + 2R_{VH}(t)} \tag{1}$$

where $G = \sum_t R_{HH}(t)/\sum_t R_{HV}(t)$.

The emission anisotropy $r(t)$ was analyzed using the experimental function Eq. (2) without deconvolution [9]:

$$r(t) = r_\infty + \sum_i B_i \exp(-t/\phi_i) \tag{2}$$

where ϕ_i is the rotational correlation time of the fluorophore and r_∞ is the limiting emission anisotropy.

Samples for fluorescence measurements were prepared as follows. The polymer in dimethylformamide was heated at 90°C until the solution was completely homogeneous and then cooled to room temperature (zero time). Fluorescence measurements were performed 6 days later. Polymers in chloroform were prepared at room temperature. The reflectance fluorescence spectra were taken from a triangular cell. The anthracene fluorophore was excited at 398 nm and its emission was recorded at 427 nm.

Table I. Polymer Microstructure Characterization (Triad Tacticities I, H, S), Content of Anthracene Fluorophores (ψ), and Average Molar Weights of Polymers (M_n, M_w)

Sample	ψ (mol %)	I (%)	H (%)	S (%)	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$
a-PMMA	—	3.9	34.1	62.0	84	45
a-PMMA-A	1.09	4.6	34.7	60.7	136	57
i-PMMA	—	95.0	3.0	2.0	19	16
s-PMMA-A	1.86	3.5	13.8	82.7	433	40
s-PMMA-9,10-A	0.21	0.0	14.0	86.0	52	47

RESULTS AND DISCUSSION

A fluorophore bound to polymer molecule has an orientational freedom which depends on its placement in the macromolecule. Figure 1 shows the placement of the anthracene label both in the side chain of copolymer s-PMMA-A and in the polymer backbone of s-PMMA-9,10-A. It is apparent that motion of the label independent of the macromolecule is possible for polymer s-PMMA-9,10-A but should not produce depolarization additional to that due to chain motions. In s-PMMA-9,10-A polymer the absorption and emission transition dipoles are in the plane of the ring and lay along the 9,10 axis of the anthracene moiety [10]. For excitation of anthracene fluorophore at the longest wavelength of the absorption spectrum (375–400 nm), the absorption and emission transition dipoles are parallel [11]. Therefore, depolarization of the emitted radiation is caused by relaxation of backbone segments of poly(methyl methacrylate) only. Knowledge of the rotational correlation time of backbone segments is important for evaluation of the rotational correlation time of the side chain bearing the fluorophore moiety. The rotational correlation times of polymer segments in s-PMMA-9,10-A for several solvents are summarized in Table II. In chloroform neither self-aggregation of s-PMMA nor stereocomplex formation between i-PMMA and s-PMMA takes place [1]. Therefore, we can assume that the rotational correlation time of the anthracene fluorophore in s-PMMA-9,10-A characterizes the segmental mobility of the backbone of syndiotactic PMMA. As shown in Table II, the increase in the

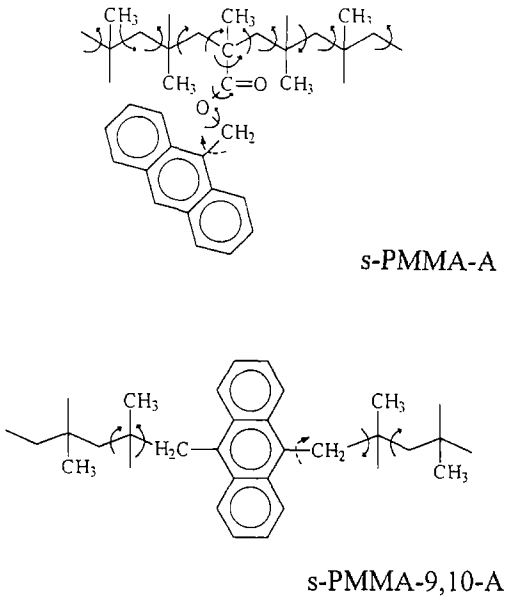

Fig. 1. Relative backbone geometries. Solid arrows represent motions resulting in depolarization of emitted radiation. Dashed arrows represent motions which do not result in fluorescence depolarization.

Table II. Rotational Correlation Time of the Anthracene Fluorophore (ϕ), Limiting Emission Anisotropy (r_∞), and Solvent Viscosity (η) for s-PMMA-9,10-A in Different Solvents at 30°C

Solvent	ϕ (ns)	r_∞	η (10^{-3} Pa·s)
Chloroform	2.9	0.02	0.514
Dimethylformamide	3.9	0.03	0.750
Dioxane	4.7	0.03	1.087

Table III. Rotational Correlation Times (ϕ_1, ϕ_2) and Limiting Emission Anisotropy (r_∞) for the Anthracene Fluorophore in the Polymer Side Chain[a]

	a-PMMA/ a-PMMA-A	i-PMMA/s-PMMA-A = 1/2	
Solvent	Dimethylformamide	Chloroform	Dimethylformamide
c_{pol}(g/L)	8.143	5	5
r_∞	0.00	0.00	0.05
ϕ_1(ns)	1.8	1.1	11.9
ϕ_2(ns)	—	—	2.0
Rel. B_2 (%)	—	—	31.7

[a] Concentration of the anthracene fluorophore $c_A = 6.00 \times 10^{-4}$ M; c_{pol}, overall concentration of polymers; rel. B_2, percentage of ϕ_2.

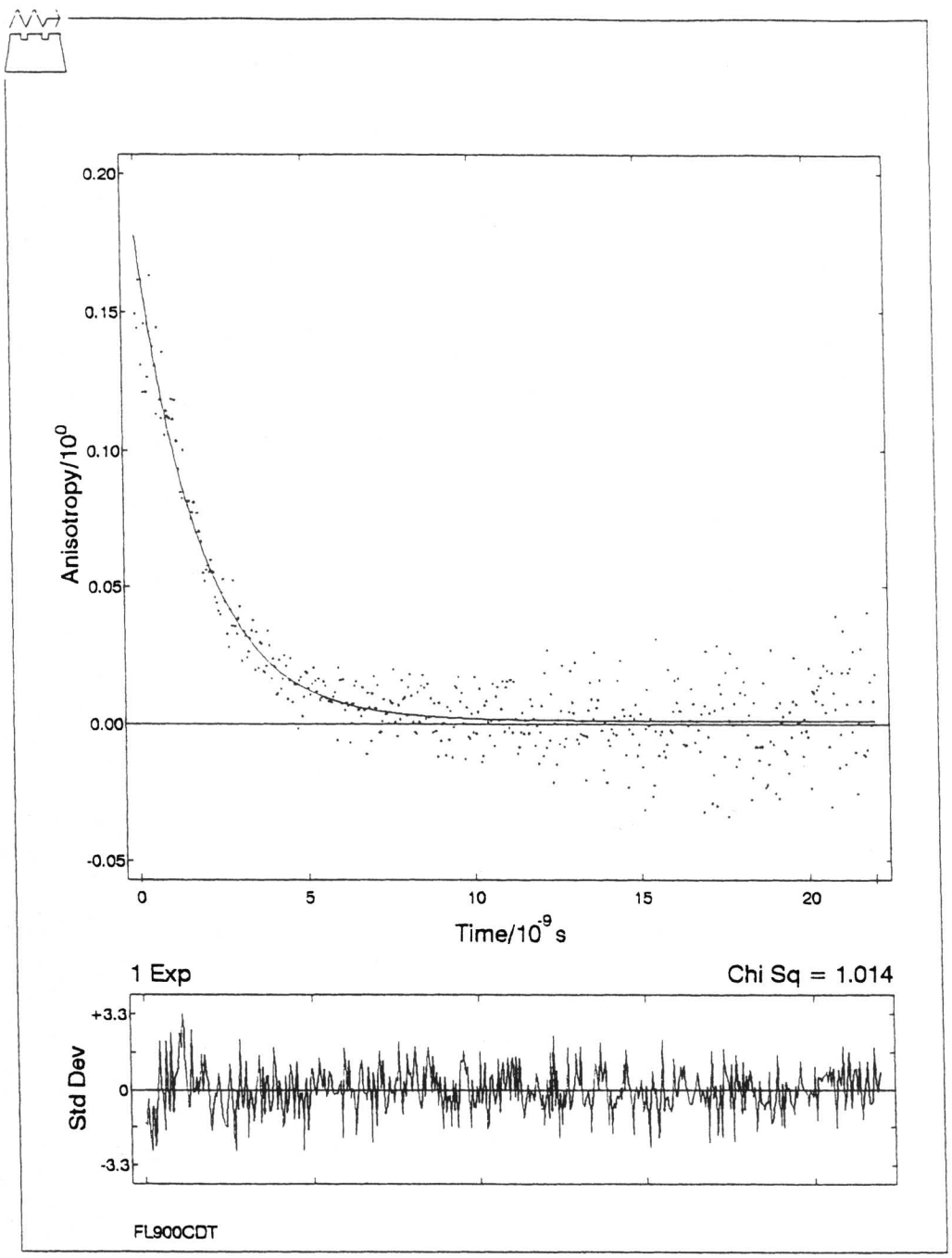

Fig. 2. Time dependence of the emission anisotropy (r) for a-PMMA/a-PMMA-A in dimethylformamide (c_{pol} = 8.143 g/L, $c_A = 6.00 \times 10^{-4} M$). Excitation wavelength, 398 nm; emission wavelength, 427 nm.

rotational correlation times of segmental motion in s-PMMA-9,10-A follows the order of increasing solvent viscosity. The solvent viscosities (γ) in Table II were taken from Ref. 12.

In s-PMMA-A the transition dipole corresponding to absorption and emission is not oriented parallel to the bond of attachment to the chain. Therefore, a motion independent of the chain should produce depolarization

in addition to that caused by the mobility of polymer segments.

It should be noted that the rotational diffusion of the macromolecule as a whole is much slower than local conformational transitions [13–15], and the depolarization of fluorescence may be interpreted in terms of the conformational mobility of the polymer chain segments and mobility of the side group with attached fluorescence label.

The intramolecular motion in which fluorophore participates may then be expressed [14] as

$$\frac{1}{\phi_i} = \frac{1}{\phi_s} + \frac{1}{\phi_b} \tag{3}$$

where ϕ_s and ϕ_b are rotational correlation times of the side chain of polymer and polymer backbone segment, respectively. The time-resolved decay of anisotropy for polymer s-PMMA-9,10-A (Table II) and for the mixture of noncomplexing atactic polymers (Table III, Fig. 2) in dimethylformamide can be assumed to be monoexponential. Low values of the rotational correlation times evaluated for anthracene fluorophore in the mixture of noncomplexing PMMA can be assigned to fast relaxation motion of the side chain with attached anthracene fluorophore and segmental relaxation of the polymer backbone. For comparison the rotational correlation time of low molecular weight 9,10-dimethyl anthracene in chloroform is 0.4 ns.

A dramatic change in the time-resolved decay of anisotropy was observed for mixtures of labeled tactic PMMA in complexing solvent (dimethylformamide) (Tables III and IV, Figs. 3 and 4). The limiting emission anisotropy (r_∞) for the anthracene fluorophore is larger than zero. Values larger than zero demonstrate steric hindrance for rotation caused by formation of the stereocomplex. The time-resolved decay curves are double exponential for solvent, which supports the formation of the stereocomplex (dimethylformamide) and monoexponential for noncomplexing solvent (chloroform). The long rotational correlation time (ϕ_1) demonstrates formation of the stereocomplex. In the noncomplexing solvent, chloroform, no long-time component has been found. The formation of a stereocomplex brings about a decrease in the mobility of the polymer segments and the side chains of polymers, producing the increase in the rotational correlation time.

The role of solvent in PMMA aggregation is not quite clear. Solvents are classified according to their tendency to stimulate PMMA stereocomplex formation [16]: strongly complexing (dimethylformamide), weakly complexing (dioxane), and noncomplexing (chloroform) solvents. The solvent can probably affect aggregation of PMMA [1] in two ways:

- change of the conformational structure of stereoregular sequences with promotion or hindrance of sterically complementary interactions and
- hindrance (or promotion) of stereocomplexation by specific interactions with certain functional groups.

Aggregation is not observed in solvents which interact strongly with carbonyl groups (chloroform). The fact that a PMMA stereocomplex was also obtained in a bulk [17] indicates that solvent is not necessary for aggregation. But when we discuss stereocomplex formation in a solution, the solvent plays an important role. The arrangement of PMMA stereocomplexes in solution is influenced by polymer–solvent interaction because the solvent determines a certain minimum length of stereoregular sequences which are necessary for stereocomplex formation [1].

The correlation time of segmental motion for polymer s-PMMA-9,10-A of 2.9–4.7 ns is in agreement with that obtained for PMMA in toluene at 298 K from dielectric relaxation data [18] and from fluorescence depolarization studies by North *et al.* [19] and Kettle *et al.* [20]. From NMR studies [21] effective correlation times τ_{eff} = 2 and 0.2 ns of methylene groups in the polymer backbone in deuterium acetonitrile at 27°C were evaluated for s-PMMA and i-PMMA, respectively.

The polymer with a label bound to the end of the side chain containing the ester group, s-PMMA-A, yields a correlation time in chloroform ϕ_i = 1.1 ns. A correlation

Table IV. Rotational Correlation Times (ϕ_1, ϕ_2) and Limiting Emission Anisotropy (r_∞) for the Anthracene Fluorophore in the Polymer Backbone[a]

i-PMMA/ s-PMMA-9,10-A	Chloroform	Dimethylformamide	
	r_∞	r_∞	Rel. B_2 (%)
1/1	0.02	0.28	—
1/1.5	0.02	0.28	—
1/2[b]	0.02	0.28	—
1/2.25	0.02	0.23	1.5
1/3	0.02	0.16	2.8
—	ϕ = 2.9 ns	$\phi_1 \sim$ 30 ns	$\phi_2 \sim$ 2 ns

[a] Concentration of the anthracene fluorophore $c_A = 5.8 \times 10^{-5}$–8.8×10^{-5} *M*; overall concentration of polymers c_{pol} = 10 g/L; rel. B_2, percentage of ϕ_2.

[b] Stoichiometric ratio for stereocomplex formation in dimethylformamide.

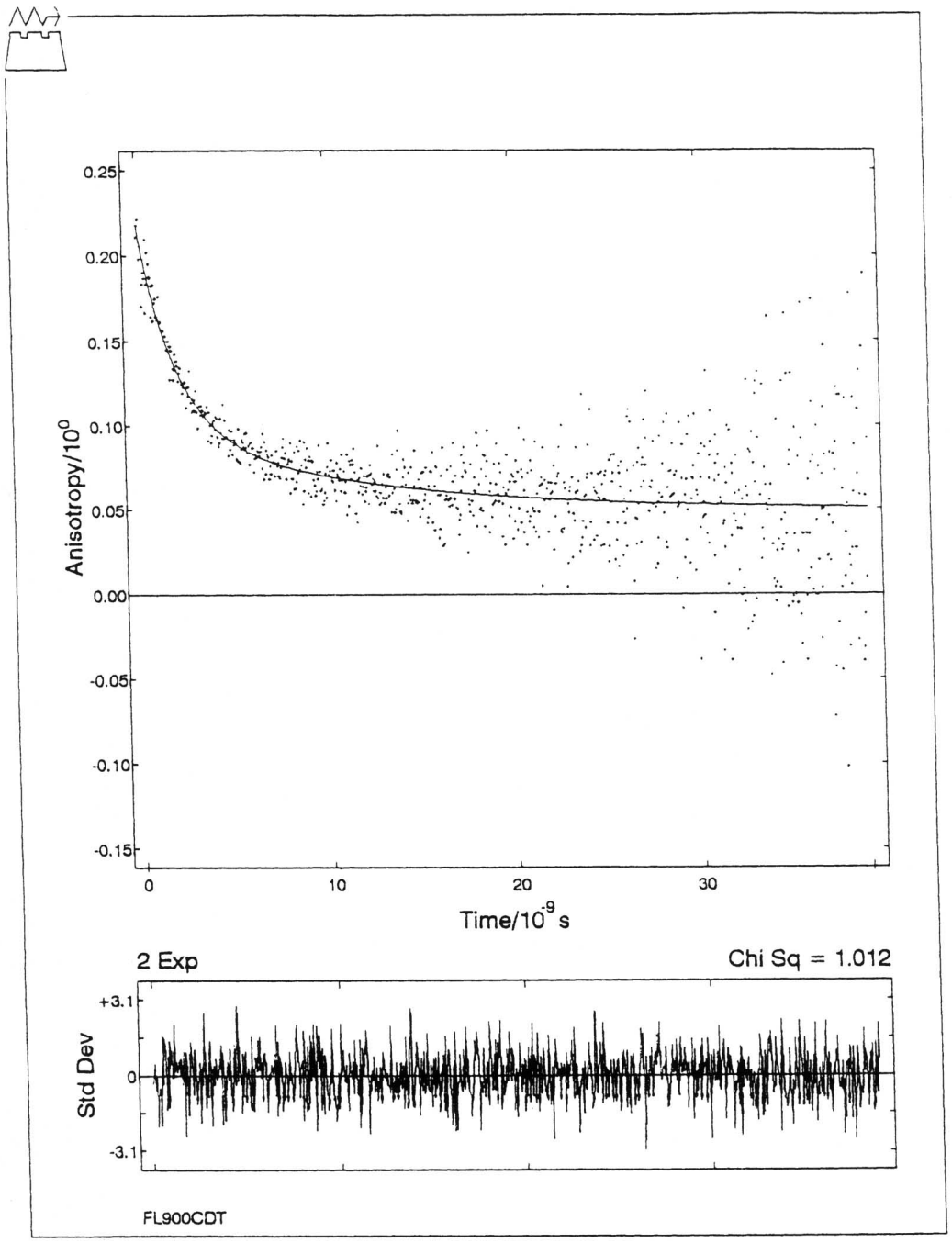

Fig. 3. Time dependence of the emission anisotropy for i-PMMA/s-PMMA-A = 1/2 in dimethylformamide (c_{pol} = 5.0 g/L, $c_A = 6.00 \times 10^{-4}$ M). For excitation and emission wavelengths see the legend to Fig. 2.

time ϕ_s, of 1.8 ns was calculated from Eq.(3) for the side chain motion containing the anthracene fluorophore.

At i-PMMA/s-PMMA-9,10-A ratios of 1/1–1/2 (Table IV) the labeled polymer s-PMMA-9,10-A participates completely in the stereocomplex (the stoichiometric ratio i-PMMA/s-PMMA in the stereocomplex in dimethylformamide is 1/2 [22]). In this case the time decay of emission anisotropy is strictly monoexponential. For the ratio of i-PMMA/s-PMMA-9,10-A 1/2.25 and 1/3, i.e., for a higher amount of s-PMMA-9,10-A in the mixture

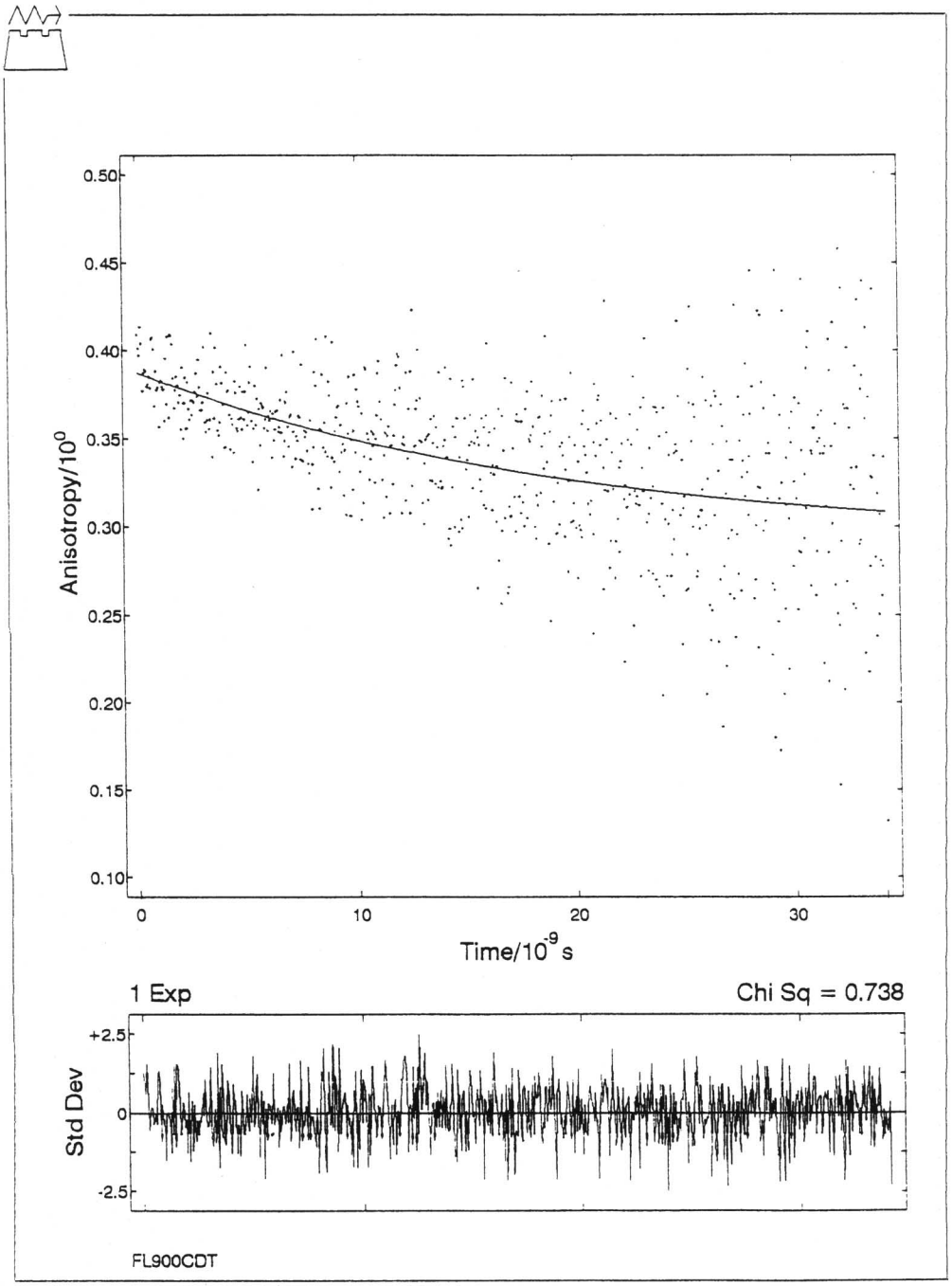

Fig. 4. Time dependence of the emission anisotropy for i-PMMA/s-PMMA-9,10-A = 1/1 in dimethylformamide (c_{pol} = 10 g/L, $c_A = 5.8 \times 10^{-5}$ M). For excitation and emission wavelengths see the legend to Fig. 2.

than corresponds to the stoichiometric ratio, some of the syndiotactic chains are loosely bound in a stereocomplex or are excluded from a stereocomplex. For this reason the time decay of the emission anisotropy obeys the two-exponential fit.

CONCLUSIONS

(1) The rotational correlation times of anthracene fluorophores attached at the end of side chains and embedded in the polymer backbone of s-PMMA unambiguously

prove the formation of a stereocomplex between s-PMMA and i-PMMA in dimethylformamide.

(2) Atactic PMMA does not form aggregates in chloroform or dimethylformamide.

(3) The rotational correlation time of the polymer backbone segments of s-PMMA determined from the time-resolved emission anisotropy data is in agreement with that obtained by other methods.

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