Study of Poly(methyl methacrylate) Stereocomplex Formation by Nonradiative Energy Transfer

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Introduction. It is well-known that syndiotactic and isotactic poly(methyl methacrylate) (s-PMMA and i-PMMA) form in some solvents a stereocomplex. The formation and structure of this stereocomplex have been studied by a variety of methods,[1] i.e., turbidimetry, light scattering, sedimentation, osmometry, GPC, viscometry, DSC, X-ray diffraction, NMR, and IR spectroscopy.

Nonradiative energy transfer (NET) observed when the emission spectrum of one fluorophore (the donor) overlaps the absorption spectrum of a second fluorophore (the acceptor) depends in a characteristic way on the donor–acceptor spacing[2] and has been utilized to characterize a number of equilibrium and kinetic properties of polymer systems, such as described in a recent review.[3] Here we used NET to study the PMMA stereocomplex formation and compare the results with those obtained by other methods.

Experimental Section. Unlabeled Polymers. Atactic poly(methyl methacrylate) (at-PMMA) was prepared by free-radical polymerization of methyl methacrylate (MMA) in toluene at 60 °C using azobis(2,2′-dimethylpropionitrile) initiator. The polymer was reprecipitated into methanol. Isotactic PMMA (i-PMMA) was prepared by anionic polymerization of MMA in toluene in −78 °C using *tert*-butylmagnesium bromide initiator.[4] Syndiotactic PMMA (s-PMMA) was prepared by polymerization of MMA initiated by $TiCl_4$–Et_3Al at −78 °C in toluene.[5]

Labeled Polymers. Fluorescent labels were introduced into PMMA by copolymerization of MMA with 2-(9-carbazoyl)ethyl methacrylate or (9-anthryl)methyl methacrylate. Copolymerizations were carried out in the same way as polymerizations of unlabeled polymers. at-PMMA was labeled with carbazole (at-PMMAc) or anthracene (at-PMMAa), i-PMMA with anthracene (i-PMMAa), and s-PMMA with carbazole (s-PMMAc). Molecular weights were determined by GPC in THF, tacticities were determined by ^1H NMR spectroscopy[6] in chloroform at 60 °C, and the content of the labels was determined by UV spectroscopy in dioxane. The main characteristics of the polymers used in this study are given in Table I.

Sample Preparation and Fluorescence Measurements. Labeled polymers were diluted with the corresponding unlabeled polymers to attain the desired concentration and i- to s-PMMA ratio. The molar ratio of the anthracene and carbazole fluorophores was 1:1. The complexation was studied in dioxane, dimethylformamide (DMF), and chloroform.

Reflectance fluorescence spectra were measured on a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer at 24 °C. The donor was excited at 292 nm, and the energy transfer efficiency was characterized by the ratio of the emission intensity of the donor at 345 nm and the acceptor at 411 nm.

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Table I
Content of Fluorophores in Polymer, Triad Tacticity, and Molecular Weights of the Polymers

polymer	label content (mol %)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	tacticity (%) I	H	S
at-PMMA	0	53.6	143.9	3.9	34.1	62.0
at-PMMAc-1	1.12	50.6	123.2	3.9	32.6	63.5
at-PMMAa-1	1.09	56.7	135.8	4.6	34.7	60.7
at-PMMAc-2	5.24	23.0	37.6	5.0	32.0	63.0
at-PMMAa-2	4.98	23.0	42.0	5.0	31.5	61.5
i-PMMA	0	13.30	21.60	95.0	3.0	2.0
i-PMMAa	2.46	5.26	10.30	83.3	6.3	10.4
s-PMMA	0	143.6	244.6	0.8	9.0	90.2
s-PMMAc	2.42	57.4	207.0	0.9	9.6	89.5

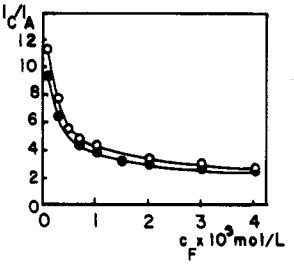

Figure 1. Dependence of I_C/I_A on c_F for at-PMMAa,c-1 (●) and at-PMMAa,c-2 (○) in dioxane (immediately after mixing of solutions containing carbazole and anthracene labels). Concentration of polymer: 74 g/L.

Results and Discussion. Figure 1 represents the ratio of carbazole and anthracene emission intensities (I_C/I_A) in solutions containing the C- and A-labeled atactic polymers as a function of the global fluorophore concentration c_F. As c_F increases, I_C/I_A decreases due to an increasing efficiency of NET. As the label content of the polymers is raised, keeping the molecular weight of the polymer and c_F constant, the number of labeled polymer chains per unit volume is reduced, the mean donor–acceptor spacing is increased, and the NET efficiency declines. Similar concentration dependences have been found for labeled at-PMMA mixtures in the solid state.[7,8] The difference between I_C/I_A values when using polymers with different label contents is largest when c_F is low; as c_F increases, the mutual interpenetration of the polymer coils reduces this difference. When using atactic PMMA, the I_C/I_A ratio remains constant for 50 days after mixing solutions containing carbazole- and anthracene-labeled polymers in both dioxane (a poor medium for stereocomplex formation) or DMF (a strong stereocomplex-forming medium).

The study of stereocomplex formation from labeled isotactic and syndiotactic PMMA was carried out by reflectance fluorescence from a triangular cell. Lower solution concentrations had to be used since gel formation in more concentrated systems may be accompanied by a detachment from the wall of the cell, leading to irreproducible results. The decay of I_C/I_A with time reflects the stereocomplex formation (Figure 2). This demonstrates that fluorescent labels of i-PMMA and s-PMMA approach each other as the complex is formed. Also, the figure shows qualitatively that the complex is formed faster in DMF than in dioxane, as found by other methods.[9] Unfortunately the initial phase of stereocomplex formation is too fast to be followed by our experimental method. The initial value of I_C/I_A before the stereocomplex is formed can be obtained using atactic PMMA with the same fluorophore content in labeled polymers, comparable molecular weight,

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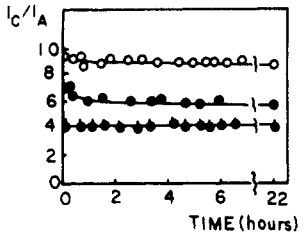

Figure 2. Dependence of I_C/I_A on incubation time for stereoregular PMMA (65 wt % of s-PMMA) in dioxane (○) and DMF (●), (concentration of polymer, 5.6 g/L; $c_F = 1.2 \times 10^{-4}$ mol/L) and in chloroform (●) (concentration of polymer, 22 g/L; $c_F = 0.5 \times 10^{-3}$ mol/L).

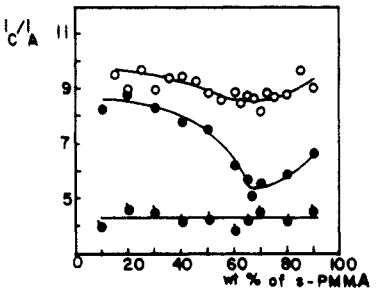

Figure 3. Dependence of I_C/I_A on the weight percent of s-PMMA in dioxane (○) and DMF (●) 22 h after mixing solutions of i-PMMA and s-PMMA (concentration of polymer, 5.60 g/L; $c_F = 1.2 \times 10^{-4}$ mol/L) and in chloroform (●) 15 min after mixing (concentration of polymer, 22.0 g/L; $c_F = 0.5 \times 10^{-3}$ mol/L).

and equal overall concentration of polymer. The ratio I_C/I_A for atactic PMMA is 10.5 and 9.9 in dioxane and DMF, respectively, so that ~65% of the change in this ratio took place before the first reading could be taken in the solution containing the mixture of isotactic and syndiotactic PMMA. In chloroform I_C/I_A is constant, since no stereocomplex is formed in that medium.[10] Since chloroform is a fluorescence quencher, a high polymer concentration had to be used.

The dependence of I_C/I_A on the weight percent of s-PMMA in the mixture confirms the relative tendency for stereocomplex formation in various solvents (Figure 3). The I_C/I_A minimum is lower in DMF than in dioxane and is located at a i-PMMA/s-PMMA ratio of $^1/_2$. This stoichiometry of the stereocomplex was also found by other methods.[10]

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