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Energy-Transfer Studies of Donor–Acceptor-Labeled Polystyrene-*block*-Poly(methyl methacrylate) Diblock Copolymers in Solution

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There is a wide variety of fascinating experiments one could carry out with block copolymer systems if one had access to small amounts of the copolymer labeled with appropriate fluorescent dyes. One could study exchange dynamics in polymer micelles, as well as diffusion in lamellar structures and other ordered phases. In the special case of doubly labeled block copolymers containing donor and acceptor chromophores in specific sites, one could measure the extent of chain elongation that accompanies incorporation into these ordered phases.[1]

The sites where one would most like to have the fluorescent groups are at either chain end and at the junction point. Like Quirk and Mattice,[2,3] we recognized that derivatives of 1,1-diarylethylene in which one of the aryl groups was a donor (e.g., phenanthrene, Phe) or acceptor (e.g., anthracene, An) chromophore would serve to terminate anionic polymerization of monomers like styrene to form a diaryl anion capable of initiating polymerization of a second monomer. This strategy places the Phe or An group at the A/B junction of the A–B diblock copolymer. We report the synthesis of a series of polystyrene-*block*-poly(methyl methacrylate) [PS–PMMA] polymers containing Phe or An groups at the A/B junction as well as two doubly labeled polymers containing Phe as described above and an An group at the PMMA end. The An group here is introduced by terminating the second-stage anionic polymerization with 9-(bromomethyl)anthracene. These polymers and their characterization are described in Table I. To assess the suitability of these polymers for fluorescence studies of ordered systems, we have measured intramolecular energy-transfer efficiencies for these polymers in dilute solution. These measurements are the main topic of this report.

Experimental Section. Block copolymer syntheses and characterization will be reported in detail elsewhere. In brief, 1-(9-phenanthryl)-1-phenylethylene (**1**; Scheme I) was synthesized by Friedel–Crafts acylation of phenanthrene with benzoyl chloride ($AlCl_3$, CS_2) followed by reaction with methyllithium and then dehydration. 1-(2-Anthryl)-1-phenylethylene (**2**) was prepared by a similar acylation of anthracene with acetyl chloride under forcing conditions to generate the 2-isomer, followed by reaction with phenylmagnesium bromide and dehydration.

Polymers were prepared under argon by a combination of syringe and Schlenk techniques in which styrene (~5 g) polymerization in THF (−78 °C) was initiated with *sec*-butyllithium. After 30 min, a 2-fold excess of **1** or **2** in THF was added. After removal of an aliquot of this solution for analysis, MMA, carefully purified, was added slowly by vapor transfer. Some reactions were terminated by addition of methanol. Others, intended to produce doubly labeled polymer, were terminated by addition of 9-(bromomethyl)anthracene. The polymers were purified by repeated reprecipitation into methanol from CH_2Cl_2 solution and analyzed by gel permeation chromatography (GPC) using tandem refractive index and UV or fluorescence detectors. These samples occasionally contained a few percent of polystyrene homopolymer but always less than 0.01% low molecular weight UV-absorbing impurities. Since PMMA and PS have very similar calibration curves for GPC in tetrahydrofuran, M_n and M_w/M_n values for both the PS block and the entire block copolymer could be determined by GPC. Polymer composition was measured by ^1H NMR. The chromophore content was determined by UV spectroscopy in conjunction with polymer M_n values, using 1-(9-phenanthryl)-1-phenylethane (**3**) and 9-methylanthracene (**4**) as model compounds.

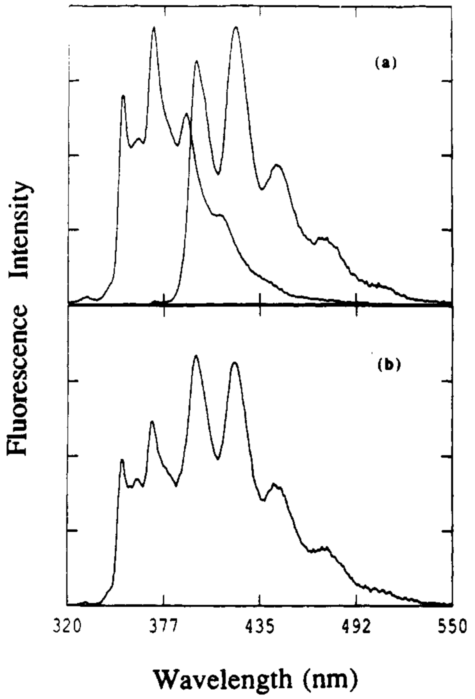

Figure 1. (Top) Superimposed fluorescence spectra showing Phe emission from sample C-26 (λ_{ex} = 300 nm) and An emission from sample C-22 (λ_{ex} = 360 nm). (Bottom) Fluorescence spectrum of sample C-22 excited at 300 nm.

Results and Discussion. One of the most effective ways of ensuring 100% fluorescent group incorporation into a specific site of a polymer is to use a dye derivative as an initiator for anionic polymerization.[4–6] 1,1-Diarylethylene derivatives serve a dual function of terminating an ionic PS polymerization and producing an anion sufficiently reactive to initiate MMA polymerization. Thus all block copolymers should in principle contain the diaryl substituent. Termination of the polymerization with $AnCH_2Br$ occurs in high yield but does not guarantee quantitative chromophore substitution. One normally characterizes chromophore content by UV spectroscopy in conjunction with molecular weight measurements. The former relies on model compounds, here **3** and **4**,[7] and the assumption of identical extinction coefficient values. The latter has the usual molecular weight uncertainties. Within these strictures we note from Table I that the degree of Phe substitution at the A/B junction appears to be less than quantitative but that of An at the chain end is indeed very high.

Figure 1a shows the Phe fluorescence spectrum of the copolymer sample C-26 at λ_{ex} = 300 nm and the An fluorescence spectrum of the copolymer sample C-22 at λ_{ex} = 360 nm. These spectra are characteristic of those for the model compounds **3** and **4**, respectively. We do not observe any significant shift (<1 nm) in either the

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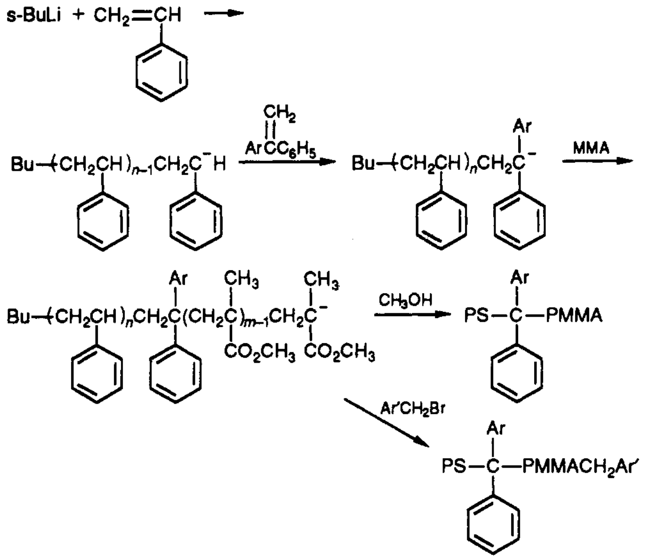
Table I
Characterization of Labeled PS–PMMA Block Copolymers

sample	$M_{n,PS}$	M_w/M_n[a]	$M_{n,PMMA}$	PS/PMMA[b]	M_n (UV)[c]	$f_{Phe,An}$[d]	
			PS–Phe–PMMA				
C-18	2800	1.09	11 000	30/70	20 000	0.69	
C-19	3300	1.08	13 000	20/80	17 000	0.96	
C-26	3000	1.	10 000	22/78	16 000	0.81	
			PS–Phe–PMMA–An				
C-22	2700	1.08	10 000	19/81	13 100/12 500	0.97	1.01
C-24	11000	1.12	4 000	77/23	17 600/16 000	0.85	0.94

[a] From SEC analysis of the PS precursor. [b] From ^{1}H NMR. [c] From UV analysis, using 1-(9-phenanthryl)-1-phenylethane for the Phe group and 9-methylanthracene for the An group. [d] From the ratio of the number-average molecular weight determined by SEC and by UV.

Scheme I[a]



[a] Ar = 9-phenanthryl (1); 2-anthryl (2). Ar′ = 9-anthryl.

absorption or emission spectra[7] when these chromophores are attached to the copolymers. For the copolymer sample C-22 excited at 300 nm, its fluorescence spectrum (Figure 1b) is characterized, as expected, by a superposition of Phe and An emissions. However, the interpretation of this spectrum in terms of energy transfer would require a correction for the parasitic effects from radiative energy transfer and an accurate value (ϕ_D/ϕ_A) of the Phe and An fluorescence quantum yield ratio. It is easier and less ambiguous to use Phe fluorescence decay measurements to characterize the energy-transfer efficiency for the doubly labeled block copolymers.

In a solution containing a Phe-labeled block copolymer such as C-26, the Phe fluorescence decay profile is monoexponential with a lifetime of 44 ns in benzene and 45.5 ns in THF (Table II). The introduction of an An group to the PMMA end of the block copolymer (e.g., C-22 and C-24) enhances the Phe fluorescence decay rate and makes the Phe fluorescence decay nonexponential. In highly dilute solutions such as those used in the present experiments (10^{-5} M block copolymer), energy transfer from the excited Phe to An is intramolecular. Since the rate of energy transfer depends on the D–A distance,[8] we would expect that the Phe fluorescence decay profiles obtained in our study reflect both the D–A distance probability distribution dictated by the nature of the copolymer in solution and the rate of diffusion of D toward A through the time-dependent change in the conformations of the block copolymers.[1,9]

It is, in principle, possible to factor apart the end-group distribution and the chain-end diffusion.[9,10] This is one of our objectives for future work. There is, however, no simple analytical expression which would allow us to analyze the Phe decay profile in this way. Rather, we fit the decays to a sum of exponential terms

Table II
Energy-Transfer Data for the Labeled PS–PMMA Block Copolymers in Benzene and THF

sample	solvent	τ_D	$\tau_M^{(2)}$	E_q	$\tau_M^{(1)}$	E_{ET}
C-26	benzene	43.9 ± 0.1				
	THF	45.5 ± 0.3				
C-22	benzene		40.5	0.08	39.3	0.11
	THF		42.4	0.07	40.4	0.11
C-24	benzene		29.6	0.33	27.2	0.38
	THF		31.1	0.32	27.7	0.39

$$I_D(t) = \sum \alpha_i \exp(-t/\tau_i) \qquad (1)$$

(two suffice) and calculate the first ($\tau_M^{(1)}$) and second moments ($\tau_M^{(2)}$) of the intensity decay. The second moment

$$\tau_M^{(2)} = \sum_i \alpha_i \tau_i^2 / \sum_i \alpha_i \tau_i \qquad (2)$$

is the mean lifetime and, in a Stern–Volmer sense, measures the intramolecular quenching rate

$$(\tau_M^{(2)})^{-1} = (\tau_D)^{-1} + k_T[A]_{local} \qquad (3)$$

where $[A]_{local}$ is an averaged local quencher concentration. From this point of view, one can define the intramolecular quenching efficiency as

$$E_q = 1 - \tau_M^{(2)}/\tau_D \qquad (4)$$

In our system we anticipate that energy transfer is the only quenching process contributing to the enhanced Phe decay. By definition then

$$E_{ET} = 1 - \frac{\int_0^\infty \sum_i \alpha_i \exp(-t/\tau_i)\, dt}{\int_0^\infty \exp(-t/\tau_D)\, dt} \qquad (5)$$

which leads to

$$E_{ET} = 1 - \sum_i \alpha_i \tau_i / \tau_D = 1 - \tau_M^{(1)}/\tau_D \qquad (6)$$

Equations 5 and 6 calculate the energy-transfer efficiency E_{ET} by evaluating the area under the experimentally measured Phe fluorescence decay profile. Under suitable conditions, this parameter can be compared to those derived from the steady-state fluorescence measurements.[11]

Table II lists the numerical values of the parameters $\tau_M^{(1)}$, $\tau_M^{(2)}$, E_q, and E_{ET} for the two doubly labeled block copolymers C-22 and C-24 in benzene and THF, respectively. It is immediately clear that there is significantly more energy transfer for C-24 with a shorter PMMA block than for C-22 with a longer PMMA block. The effect of solvent on energy-transfer efficiency is very small and is expected to be small since both benzene and THF are good solvents for PMMA and PS. As long as other processes do not contribute to quenching,[12] such as the formation of ground-state dimers, the E_{ET} value can be interpreted in terms of the Phe–An distance probability distribution and how it varies with the chain-end diffusion of the block copolymer.

In conclusion, a general synthetic technique for the construction of singly and doubly labeled PS–PMMA block copolymers has been described. These preliminary studies indicate that these labeled block copolymers are suitable for fluorescence studies. We are currently looking forward to future experiments of these block copolymers in selective solvents, in viscous media, and in solid matrices.

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Registry No. PS–PMMA (block copolymer), 106911-77-7.