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Application of the "Spectroscopic Ruler" to Studies of the Dimensions of Flexible Macromolecules. 2. Experimental Studies of Poly(methyl methacrylate) Chains

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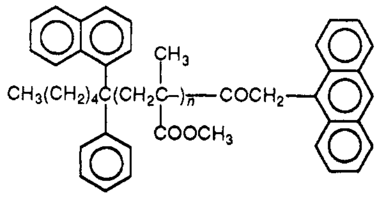
ABSTRACT: Energy-transfer efficiencies between end-labeled poly(methyl methacrylate) (PMMA) samples are determined in different media. With use of the formulas developed previously, they are then used to fit the root-mean-square end-to-end distances of PMMA chains. In nonviscous solvents, the values determined by the "spectroscopic ruler" technique are all considerably shorter than those from viscosity measurement. In a PMMA matrix, the end-to-end distances determined by this technique give a value close to that estimated from viscosity. Significant diffusion of the end groups during the donor excitation lifetime may be partially responsible for the observed discrepancies with static methods.

I. Introduction

The feasibility of using the "spectroscopic ruler" relation first derived by Förster[1] to measure directly the end-to-end distances of flexible organic polymer chains has been discussed in the first paper of this series.[2] Experimental studies of polymer I, a poly(methyl methacrylate) (PMMA) labeled with naphthalene on one end and anthracene on the other, are reported here. The root-mean-square end-to-end distances of polymer I in three different solvents, acetonitrile, ethyl acetate, and methylene chloride, and in a solid PMMA matrix are determined from this technique and compared with the results evaluated from viscosity measurement.



polymer I

It was shown that energy-transfer efficiencies experimentally measured, E, between energy donor (naphthalene) and acceptor (anthracene) groups attached to polymer chain ends are the statistical average given by

$$E = \langle E(n,R)\rangle = \int_0^\infty P(n)\int_0^\infty E(R)\,P(n,R)\,\mathrm{d}R\,\mathrm{d}n \quad (1)$$

where $E(R)$ is defined by[1]

$$E(R) = R_0^{\,6}/(R_0^{\,6} + R^6) \quad (2)$$

where R_0 is the critical energy-transfer distance, $P(n)$ is the number fraction of the chains with n repeating units, and $P(n,R)$ is the end-to-end distance, R, distribution function for polymer chains with n repeating units. When a Gaussian form was assumed for the end-to-end distance distribution function of PMMA chains, the numerical solution for $\langle E\rangle$ was shown to be[2]

$$\langle E\rangle = \sum_{n_1}^{n_2} P(n)\,\Delta n \sum_{i=1}^{m_x}(0.01i)^2 \times \exp[-1.5(0.01i)^2]\frac{R_0^{\,6}}{R_0^{\,6} + (0.01i)^6(2n\beta^2)^3}\Big/\sum_{i=1}^{m_x}(0.01i)^2 \times \exp[1.5(0.01i)^2] \quad (3)$$

where β is the statistical bond length of the PMMA backbone to be fitted, which is related to the root-mean-square end-to-end distance of the chain by

$$R_n = (2n)^{1/2}\beta \quad (4)$$

$P(n)$ is the fraction of chains with n repeat units, which can be determined from GPC measurement; m_x is defined by

$$m_x = m/(2n)^{1/2}\beta \quad (5)$$

where m is the contour length of a chain with n repeat units and R_0 the critical energy-transfer distance given by

$$R_0 = \left[\frac{9000 \ln 10\kappa^2\phi_D}{125\pi^5 \mathrm{n}^4 N_0}J\right]^{1/6} \quad (6)$$

according to Förster.[2] In eq 6, ϕ_D is the donor fluorescence quantum yield in the absence of energy transfer, n is the refractive index of the solvent at the wavelength of excitation, and N_0 is Avogadro's constant. The relative orientation of the donor group is characterized by κ^2. J is the overlap integral between the normalized fluorescence intensity, I_λ, and the acceptor extinction coefficient, ϵ_λ

$$J = \int_0^\infty \lambda^4 I_\lambda \epsilon_\lambda\,\mathrm{d}\lambda \quad (7)$$

where, by definition

$$\int_0^\infty I_\lambda\,\mathrm{d}\lambda = 1 \quad (8)$$

As discussed previously,[2] two methods can be used for the determination of the energy-transfer efficiency in

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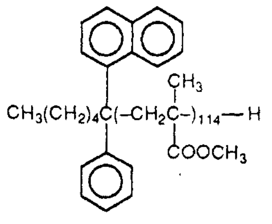
steady-state fluorescence measurements. In the first method, if the donor (naphthalene) fluorescence is solely quenched by energy transfer, the quenching efficiency, χ, would be equal to the energy-transfer efficiency, E. The value of χ was determined using

$$\chi = 1 - \phi_{NA}/\phi_N{}^0 \tag{9}$$

where ϕ_{NA} and $\phi_N{}^0$ denote the fluorescence quantum yields of the naphthyl group in polymers I and II, respectively.



polymer II

If fluorescence lifetimes are used for the calculation

$$\chi = 1 - \tau_{NA}/\tau_N{}^0 \tag{10}$$

symbols τ_{NA} and $\tau_N{}^0$ are the fluorescence lifetimes of the naphthyl group in polymers I and II, respectively.

In the second method, the energy-transfer efficiency, E, can be determined from the enhancement of anthracene fluorescence intensity. The equation

$$E = \frac{1}{P_T}\left[\frac{I_{Af}(\lambda_1)\, I_0(\lambda_2)\, (1 - 10^{-A(\lambda_2)})}{I_{Af}(\lambda_2)\, I_0(\lambda_1)\, (1 - 10^{-A(\lambda_1)})} - 1 + P\right] \tag{11}$$

can be used where λ_2 (348 or 364 nm) is the wavelength at which only the anthracene group absorbs. λ_1 (292 nm) is the wavelength at which naphthalene absorbs dominantly, the termination efficiency, T, accounts for the incomplete incorporation of anthracene groups in the synthesis of polymer I, and P is the fraction of totally absorbed radiation at λ_1, which is due to naphthalene absorption and is given by

$$P = \frac{1 - A^{-A_N(\lambda_1)}}{2 - 10^{-A_N(\lambda_1)} - 10^{-A_A(\lambda_1)}} \tag{12}$$

where $A_A(\lambda_1)$ and $A_N(\lambda_1)$ are the absorbances of the anthracene and naphthalene end groups at wavelength λ_1, $I_{Af}(\lambda_1)/I_{Af}(\lambda_2)$ is the ratio of anthracene fluorescence intensities observed in the direct mode by exciting at λ_1 and λ_2, respectively, and $I_0(\lambda_2)/I_0(\lambda_1)$ is the ratio of incident light intensities at these two wavelengths. If all spectra are recorded in ratio mode, eq 11 simplifies to

$$E = \frac{1}{P_T}\left[\frac{I_{Af}{}^R(\lambda_1)\, (1 - 10^{-A(\lambda_2)})}{I_{Af}{}^R(\lambda_2)\, (1 - 10^{-A(\lambda_1)})} - 1 + P\right] \tag{13}$$

where $I_{Af}{}^R(\lambda_1)$ and $I_{Af}{}^R(\lambda_2)$ are the anthracene fluorescence intensities from a polymer I sample in the ratio mode by exciting at wavelengths λ_1 and λ_2, respectively.

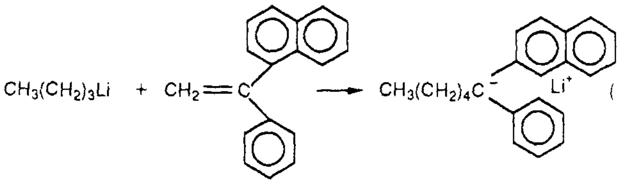
II. Experimental Section

All organic solvents were of spectrograde quality and used without further purification. Naphthalene (Fisher certified reagent) was recrystallized from methanol three times. 9-Methylanthracene (Aldrich, 95+%) was recrystallized twice from isopropyl alcohol. Methyl methacrylate (BDH, laboratory reagent) was first washed with dilute sodium hydroxide solution to colorless and then washed three times with distilled water. The inhibitor-free monomer was subsequently dried over anhydrous sodium sulfate (BDH, analytical reagent) and distilled under reduced pressure.

Synthesis of Poly(methyl methacrylate). The PMMA used for the supporting matrix of the end-labeled samples was synthesized by the addition of 0.05 g of azobis(isobutyronitrile) (AIBN) (Eastman Kodak), recrystallized from methanol, to 20 g of methyl methacrylate in 40-mL spectrograde ethyl acetate contained in an ampule. The mixture was degassed, filled with oxygen-free nitrogen (Canox), and reevacuated. This process was repeated three times before the ampule was sealed. The polymerization was run at 65 °C for 30 h. The polymer formed was purified by four precipitations from spectrograde methanol and dried in vacuo. A total of 8 g of product was obtained: yield 40%.

Preparation of Poly(methyl methacrylate) Films. PMMA films were formed by the slow evaporation of a polymer solution. Films with specific weight ratio of polymer I to matrix were prepared by the addition of PMMA to a known concentration of polymer I in spectrograde methylene chloride. The solution mixture was transferred to a 2-in.-diameter culture dish, covered, and left in the dark overnight. The film was peeled from the glass surface using distilled water or with gentle heating in the presence of water. Before any physical measurements were carried out, the free-standing films were annealed at 114 °C (around T_g) under vacuum for 6 h. This treatment was necessary to remove any remaining solvent and to relax the oriented conformations of the end groups, which possibly occurred on film surfaces during solvent evaporation.

Synthesis of Polymer I. The end-labeled polymers (polymers I and II) were synthesized using anionic polymerization.[3] Equal moles of butyl lithium and 1-phenyl-1-(α-naphthyl)ethylene were reacted in dry THF in the absence of O_2 and moisture to yield the initiator: The initiator reacts with methyl methacrylate and initiates the polymerization. The polymerization was then terminated with 2-(9-anthryl)acetyl chloride.



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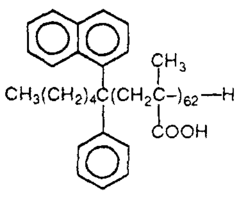
GPC Fractionation and Characterization of Polymer I. Polymer I was fractionated on a Waters high-pressure liquid chromatography using HPLC-grade toluene (Aldrich) and a series of ultrastyragel columns (Waters, 10^5, 10^4, 10^3, and 500 Å). Five fractions with polydispersity below 1.10 were obtained.

The calibration curve for another set of columns (10^4, 10^3, and 500 Å) was obtained from monodispersed PMMA standards ($\bar{M}_w/\bar{M}_n < 1.10$, M_p values given, Polymer Laboratories, Ltd.) in ethyl acetate, in the 2400–60 000 molecular weight range. Three fractions of the polymer with higher molecular weights were characterized for energy-transfer studies. The GPC calibration curve relating peak molecular weights, M_p, of PMMA standards and retention time, t, is given by

$$\ln M_p = -0.4187t + 19.34 \tag{15}$$

and is shown in Figure 1. GPC chromatograms of the three fractions are shown in Figure 2, and the weight- and number-average molecular weights are summarized in Table I.

NMR Characterization of Polymers I–III. NMR spectra were obtained for polymer I (fractions 2 and 3), polymer II, and polymer III using a Varian XL 400 NMR spectrometer. A



polymer III

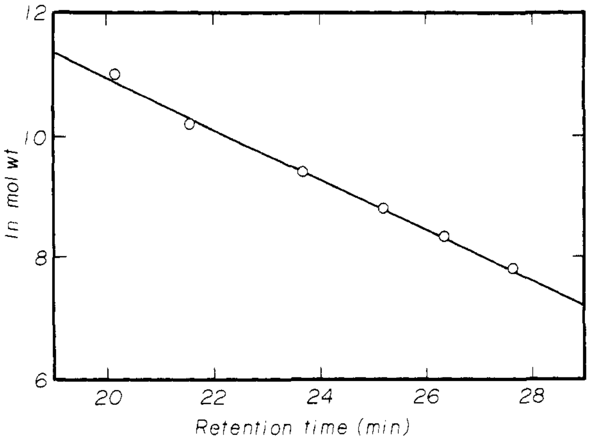


Figure 1. Calibration curve for Waters analytical columns (10^4, 10^3, and 500 Å) using PMMA standards.

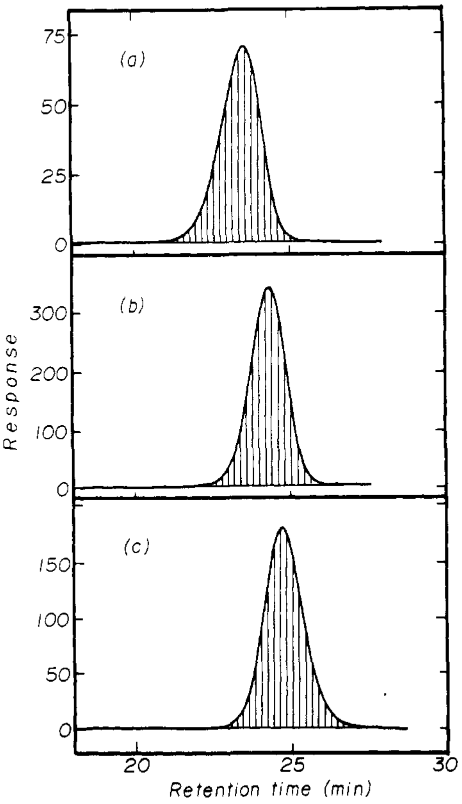


Figure 2. GPC chromatograms of an NA-PMMA-AN sample: (a) fraction 1, (b) fraction 2, and (c) fraction 3.

total of 200 or more pulses was required to get an acceptable signal-to-noise ratio. Approximately 20 mg of sample was needed for each measurement. The samples were either dissolved in deuterated dichloromethane (Aldrich, 99.5% CD_2Cl_2), deuterated acetonitrile, or deuterated methanol.

When the NMR peak area ratios between the aromatic end-group protons and the backbone protons are used, the number-average number of repeat units, $\bar{n}$, or molecular weight, $\bar{M}_n$, of each sample was determined. The average number of repeat units for fractions 2 and 3 of polymer I (fractions 2 and 3), polymer II, and polymer III are, respectively, 103 ± 2, 84 ± 2, 114 ± 3, and 62 ± 2, respectively. The corresponding average molecular weights are $(1.09 \pm 0.02) \times 10^4$, $(0.89 \pm 0.02) \times 10^4$, $(1.17 \pm 0.03) \times 10^4$, and $(0.56 \pm 0.02) \times 10^4$, respectively. Results for fractions of polymer I are tabulated in Table I.

Some peaks of naphthalene and anthracene are well resolved for fraction 2 of polymer I. From the peak area ratio, the anthracene to naphthalene concentration ratio was calculated to be 99 ± 5%. In subsequent calculations, termination efficiency is assumed to be 100% for polymer I.

UV-Visible Characterization of Polymer I. UV-visible spectra of all samples were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. The absorbances of 9-methylanthracene, polymer II, and polymer III were determined by preparing solutions of known concentrations. When a computer program in HP-85B Basic was used, the molar extinction coefficients at wavelengths of interest were calculated. The extinction coefficient of polymer II at 284 nm was calculated to be 7.07×10^3 L mol^{-1} cm^{-1}, which is in good agreement with the ϵ value of 6.98×10^3 L mol^{-1} cm^{-1} for polymer III. The extinction coefficients of 9-methylanthracene in acetonitrile at its maxima, 348, 366, and 386 nm, are 5.41×10^3, 8.55×10^3, and 7.91×10^3 L mol^{-1} cm^{-1}, respectively.

Figure 3 shows a comparison of the UV spectra of polymer I with those of its model compounds, 9-methylanthracene and polymer II. Curve (a) shows the UV spectrum of a 8.86×10^{-5} M solution of polymer I (fraction 1), curve (b) is the UV spectrum of a 8.60×10^{-5} M solution of polymer II, and curve (c) is that of a 6.74×10^{-5} M solution of 9-methylanthracene. The absorption spectrum of polymer I can be obtained by superimposing the absorption spectrum of polymer II on that of 9-methylanthracene. Curve (d), for example, is the summation of the absorption curves of polymer II (8.60×10^{-5} M) and 9-methylanthracene (7.55×10^{-5} M) and is very similar to the spectrum of fraction 1 × $\lambda > 280$ nm. The spectrum of fraction 1 has higher absorbances at $\lambda < 280$ nm, due to the absorption of toluene impurity, the existence of which was revealed from NMR measurement.

The extinction coefficient of the naphthalene end group in polymer I was assumed to be equal to those of polymer II at all wavelengths. This assumption is justified due to the close resemblance between the structure of polymer II and the naphthalene end group of polymer I. The termination efficiency has been established to be 100% from NMR measurement. It can then be concluded that the extinction coefficients of the anthracene group in polymer I are reduced by a factor of 7.55×10^{-5} M/8.60×10^{-5} M or 0.88, compared with those of 9-methylanthracene.

When the extinction coefficient of the naphthalene end group as determined from polymer II and the extinction coefficients of the anthracene end group as determined to be those of 9-methylanthracene multiplied by 0.88 are used, the number-average molecular weights for each fraction of polymer I can also be evaluated from end-group concentration determination using UV spectrophotometry. The $\bar{M}_n$ values for fractions 1-3 are 11600 ± 300, 9500 ± 300, and 7500 ± 200, respectively (see Table I).

Viscosity Measurement of Polymer I.[4] Viscosity molecular weights of the fractions of polymer I and the hydrodynamic radius of each fraction were measured using an automated viscometer.[5] The flow time, t, of a fluid through the capillary of the viscometer is related to its viscosity by

$$\eta_0 = k(t - 7.5631/t) \tag{16}$$

where k is a constant and the second term in the parentheses is due to correction for kinetic energy. The relative viscosity was calculated by inserting the flow times of each sample into eq 17 where η_s and η_0 are the viscosities of the polymer solu-

$$\eta_r = \eta_s/\eta_0 \tag{17}$$

tion and solvent, respectively. The specific viscosity was defined as

$$\eta_{sp} = \eta_r - 1 \tag{18}$$

Then, by use of eq 19,[6] the intrinsic viscosities, $[\eta]$, of fractions

$$[\eta] = (1/c)[2(\eta_{sp} - \ln \eta_r)]^{1/2} \tag{19}$$

2 and 3 were determined in a number of solvents at different temperatures. In eq 19, c is the concentration of the polymer solution in grams per deciliter.

Table II illustrates the calculation of the intrinsic viscosity of fraction 3 in acetonitrile at 45.20 °C. Exactly 9 runs were carried out for the polymer solution, and 31 runs, for the sol-

Table I
Characterization of Polymers

fraction	$\bar{M}_w$ (GPC)	M_n			M_w/M_n (GPC)	M_v
		GPC	UV[a]	NMR		
1[b]	1.42 × 10^4	1.32 × 10^4	1.16 × 10^4		1.08	
2[c]	1.00 × 10^4	0.94 × 10^4	0.95 × 10^4	1.09 × 10^4	1.06	1.03 × 10^4
3[c]	0.81 × 10^4	0.75 × 10^4	0.75 × 10^4	0.89 × 10^4	1.07	0.80 × 10^4

[a] Error ≃5%. [b] Insufficient sample for viscosity measurement. [c] Termination efficiency from NMR, 99%.

Table II
Calculation of the Intrinsic Viscosity of Fraction 3 in Acetonitrile at 45.20 °C

	flow time, s	η_r	η_{sp}	c, g/dL	[η], dL/g
solution	10.299	1.0152$_5$	0.0152$_5$	0.357	0.425
solvent	10.165				

Table III
Relative and Intrinsic Viscosities of Fractions 2 and 3

solvent	T, °C	c, g/dL	η_r	[η], dL/g
	Fraction 2			
acetonitrile	25.30	0.248	1.0114	0.0458
acetonitrile	45.20	0.248	1.0122	0.0489
methylene chloride	22.10	0.226	1.0199	0.0876
	Fraction 3			
acetonitrile	25.00	0.357	1.0147	0.0410
acetonitrile	45.20	0.357	1.0152	0.0425
methylene chloride	22.10	0.327	1.0240	0.0727
ethyl acetate	22.10	0.241	1.0143	0.0588

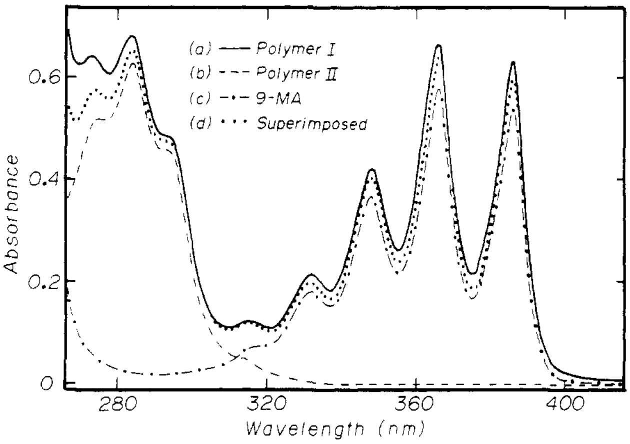


Figure 3. Comparison of the UV spectrum of polymer I and those of its model compounds, 9-methylanthracene and polymer II. The dashed curve (b) is superimposed from 8.6 × 10^{-5} M of polymer II and 7.55 × 10^{-5} M of 9-methylanthracene. The extinction coefficients of the anthracene group in polymer I are reduced by a factor of 0.88 relative to the values of 9-methylanthracene.

vent. The averaged flow times are 10.299 ± 0.002 s for the polymer solution and 10.165 ± 0.001 s for the solvent. The experimental precision of the viscometry measurements is high. The accuracy of the experiments is determined by inherent systematic errors and by assumptions made in the technique. Table III gives data on the relative and intrinsic viscosities of the samples.

The viscosity-average molecular weights for fractions 2 and 3 were calculated using eq 20 in acetonitrile. According to

$$\bar{M}_v = ([\eta]/k)^{1/\alpha} \tag{20}$$

Fox,[7,8] the k value is 4.8 × 10^{-5} dL/g at the Θ temperature of 45 °C. When this k value and the α value of 0.5 were used, the viscosity-average molecular weights were calculated to be 1.03 × 10^4 and 0.80 × 10^4, respectively, for fractions 2 and 3. These values are shown in Table I for comparison with the values obtained using other techniques.

Table IV
Results from Time-Correlated Single Photon Counting Experiments

sample	quantum yield	τ_f, ns	χ^2
	Polymer II		
in ethyl acetate	0.058	15.28	2.01
in PMMA film	0.211	46.41	1.99
	Polymer I		
in PMMA film[a]	0.041	31.12	2.46

[a] Polymer I to PMMA weight ratio = 1 × 10^{-3} g/g.

Fluorescence Measurements. All fluorescence spectra were recorded on a Spex Fluorolog 2 fluorometer. The emission spectrum of the naphthyl group in polymer II was corrected for relative response of the detecting system as a function of wavelength of emission. The correction curve was obtained by the local service center for the Spex fluorometer as follows. A small fraction of the light from a standard tungsten lamp source, calibrated at known color temperature, was reflected directly into the detecting system in order to evaluate the response factor at various wavelengths. The lamp profile of the exciting source for the fluorometer was monitored automatically by the instrument with the use of a quantum counter, rhodamine B.[9] For all fluorescence measurements, low optical densities (ca. 0.05) were used to minimize self-absorption. The front face mode was used for measurement of films.

Fluorescence Lifetime Measurements. The average fluorescence lifetimes of naphthalene groups in polymers I and II were measured by single photon counting.[10] The excitation source was a Thyratron-gated flash lamp operating at 5 kHz, 6 kV, 3.0-mm arc gap, and 25.0 Torr of research-grade deuterium. Naphthalene was excited by exciting the polymers at λ = 284 nm. Fluorescence was detected at 327 nm. Polymer films were placed in a cylindrical quartz test tube, which was rotated before data acquisition to minimize scattered light from reaching the detector.

Fluorescence lifetime measurements are summarized in Table IV. The large χ^2 (different from the square of quenching efficiency χ, a parameter indicating the degree of fitting of experimental data to a certain function) values indicate the poor fitting of the decay curve to a single exponential function.

Measurement of Fluorescence Quantum Yields. The absolute fluorescence quantum yield of the naphthalene group in polymer II in solution was determined by comparing its fluorescence intensity with that of naphthalene in argon-purged cyclohexane.[11] The expression used was[12]

$$\phi_N{}^0/\phi_N = \frac{I_{f2}(1 - 10^{-A_1})n_2{}^2}{I_{f1}(1 - 10^{-A_2})n_1{}^2} \tag{21}$$

where ϕ_N is the fluorescence quantum yield of naphthalene (0.23),[13] I_{f1} and I_{f2} are the fluorescence intensities of naphthalene and the naphthyl group in polymer II, respectively, A_1 and A_2 are the absorbances of the two species in solutions, and n_1 and n_2 are the refractive indexes of the two solvents that are used to dissolve the two samples. The fluorescence quantum yields of polymer II in different solvents and PMMA matrix are summarized in Table V.

Fluorescence quantum yields of the naphthyl groups of polymer II in films were evaluated by comparing their emission lifetimes. Hirayama and Phillips[14] showed that if the absorption spectrum of the naphthalene group does not change significantly with the medium, the fluorescence quantum yields of the naphthalene group in different media are related to one

Table V
Energy-Transfer Efficiency, *E*, and Quenching Efficiency, χ, in Different Solvents

fraction	χ, %	*E*, %
	In Acetonitrile	
1	17.1	16.4
2	27.1	24.5
3	31.0	28.7
	In Ethyl Acetate	
1	25.3	9.47
2	25.7	13.7
3	29.4	17.9
	In Dichloromethane	
1	16.2	4.79
2	18.3	6.70
3	19.8	9.02

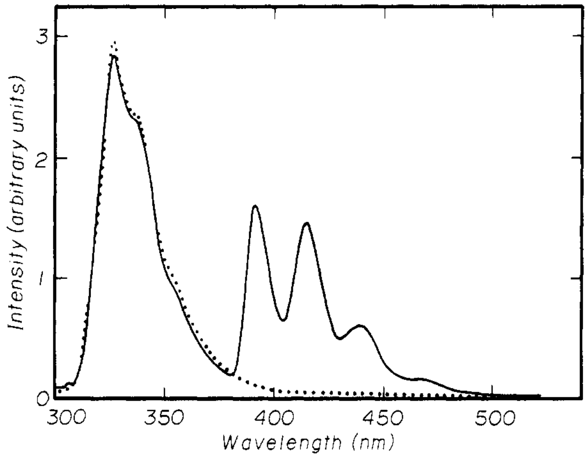


Figure 4. Fluorescence spectra of (—) polymer I and (···) polymer II are superimposed in the naphthyl group emission region. Subtraction of the fluorescence spectrum of polymer II from that of polymer I yields the anthracene emission spectrum.

another by

$$\phi_1/\phi_2 = n_1^2\tau_1/n_2^2\tau_2 \qquad (22)$$

where τ_1 and ϕ_1 are the fluorescence lifetime and quantum yield of the naphthyl group in medium 1, respectively, τ_2 and ϕ_2 are those in medium 2, respectively, and n_1 and n_2 are the refractive indices of the two media. Since the fluorescence quantum yield of polymer II in ethyl acetate was measured to be 0.059, using the data in Table IV from fluorescence lifetime measurement, the fluoresence quantum yield of polymer II in PMMA matrix was calculated to be 0.21.

Determination of Energy-Transfer Efficiencies. Since the Spex Florolog 2 spectrometer automatically monitors the relative lamp output at different wavelengths, eq 13 was used to determine the energy-transfer efficiencies. The light paths for the sample cell and the detector for lamp output are different and thus an attempt was made to generate the small residual correction. Using a quantum counter rhodamine B,[9] the correction was found to be within experimental error, ±5%. The $I_0(\lambda_2)/I_0(\lambda_1)$ value obtained from the fluorometer was accepted for all experimental results.

Fluorescence intensities were obtained by integration of the full spectra. The anthracene band was integrated from 370 to 520 nm. For excitation wavelengths at 292 or 285 nm, the naphthalene group emission band overlaps that of anthracene emission. This was corrected by using the fluorescence spectrum of polymer II. The fluorescence bands in polymers I and II were superimposed and the fluorescence spectrum of polymer II was subtracted from that of polymer I. The subtracted spectrum was that of anthracene emission alone. This is illustrated in Figure 4.

The calculation of energy-transfer efficiencies from eq 13 was aided by computation of the data. It was shown experimentally that errors in the results are mainly from the uncertainty in absorbance values, i.e., <3%. The results for the samples in three organic solvents are summarized in Table V.

Table VI
Energy-Transfer Efficiency, *E*, for Polymer I in PMMA Films

run	thickness, $\times 10^3$ g/cm^2	concn, $\times 10^5$ g/g	$I_f^R(284)/I_f^R(366)$	*E*, %
1	15.3	2	0.196	13.2
2	15.3	4	0.159	10.1
3	5.1	8	0.182	12.0
4	5.1	10	0.165	10.6
5	7.6	12	0.173	11.3
6	6.1	15	0.156	9.9
			av	11.2 ± 2.0

Table VI shows the energy-transfer efficiencies for fraction 3 of polymer I for different runs measured in PMMA films. The use of eq 13 is especially advantageous over other methods for calculating the energy-transfer efficiency in polymer films. The films have fluctuations in thickness from one point to another even for the same film. These variations in thickness therefore lead to fluctuations in the absolute absorbances of the sample. However, the absorbances appear in eq 13 as ratios. The ratio cancels fluctuations in the readings in the individual absorbances.

The *E* values in Table VI were determined for samples containing different amounts of fraction 3 and at different film thicknesses (expressed in terms of grams of PMMA per centimeters squared). The anthracene fluorescence intensity from each polymer sample was measured by exciting the sample with light of λ = 284 and 366 nm. The ratio of emission intensities, $I_{Af}^R(284)/I_{Af}^R(366)$, was calculated. Difficulties were encountered in obtaining the UV spectra of the samples listed in Table VI due to their low concentrations of fraction 3 and the thinness of the films. A UV spectrum for a more heavily loaded PMMA film was measured. Absorbance readings for the sample at 284 and 366 nm were divided by 100 and inserted into eq 13 for calculation of energy-transfer efficiencies for the samples for different runs. Adjustment for the absorbances of the individual samples was not necessary, because in eq 13, the absorbances at 284 and 366 nm appear in the ratio mode $(1 - 10^{-A(366)})/(1 - 10^{-A(284)})$. Absorbance at both wavelengths was very low for the extremely thin and dilute samples used. The ratio above is therefore well approximated by $A(366)/A(284)$, which is independent of fraction 3 concentration. The averaged energy-transfer efficiency for polymer I in the PMMA matrix in the absence of intermolecular energy transfer was found to be 11.2%.

Quenching Efficiencies. Quenching efficiencies for the fluorescence of the naphthyl group in polymer I were calculated using eq 9. If solutions with lower optical densities are used, a more convenient equation is

$$\chi_e = 1 - I_{1f}A_2/I_{2f}A_1 \qquad (23)$$

where I_{1f} and I_{2f} are the naphthyl group fluorescence intensities from solutions of polymers I and II with absorbances A_1 and A_2 at the excitation wavelength, respectively. The values of χ in each solvent for different fractions are summarized in Table V.

Computer Programming. Small programs like the calculation of the overlap integral were written in IBM Basic and carried out on an IBM XT personal computer. The program used for fitting the energy-transfer efficiencies involved double integrations and was written in Fortran and performed on a Gould computer.

III. Results and Discussion

Characterization of Polymer Samples. The molecular weights of fractions of polymer I determined using four different techniques are given in Table I. The number-average molecular weights for fractions 2 and 3 determined using GPC and UV spectrometry agreed very well with one another. Dividing the viscosity-average molecular weights with their polydispersity indices also yielded

Table VII
End-to-End Distances, R_{nv}, for Fractions 2 and 3 Calculated from Viscosity Data

solvent	T, °C	η_r	R_{nv}, Å	α_E
Fraction 2				
acetonitrile	25.30	1.0114	54.3	1.86
acetonitrile	45.20	1.0122	55.5	1.90
methylene chloride	22.10	1.0199	67.4	2.31
Fraction 3				
acetonitrile	25.00	1.0147	48.4	1.88
acetonitrile	45.20	1.0152	48.9	1.90
methylene chloride	22.10	1.0240	58.6	2.27
ethyl acetate	22.10	1.0143	54.6	2.11

the number-average molecular weights of these fractions determined from the previous two techniques. The molecular weights evaluated using NMR technique are, however, 15–20% higher than those obtained using other techniques. The reason is not known. In later calculations, the number-average molecular weights determined using the previous three techniques are accepted for fractions 2 and 3 due to their consistency.

A small uncertainty in the assessment of the absolute molecular weights will not affect experimental results on the root-mean-square end-to-end distances determined using the spectroscopic ruler technique. The root-mean-square end-to-end distances are determined by the quantities of energy-transfer efficiencies, the critical energy-transfer distances, and the choice of functional forms for molecular weight distribution and end-to-end distance distribution. If the energy-transfer efficiency, the critical energy-transfer distance, and the molecular weight distribution function are determined accurately and a Gaussian form is used for the end-to-end distance distribution function, any increase in the molecular weight of a sample will be accompanied by a decrease in the statistical bond length, β, in fitting eq 3. The root-mean-square end-to-end distance is not changed by a variation in the molecular weight.

End-to-End Distances from Viscosity Measurement. If PMMA coils can be assumed to be nondraining and noninteractive at low concentrations,[15] the hydrodynamic radii of the polymer coils were calculated from the relative viscosity, η_r, using

$$\eta_r - 1 = (10/3)N\pi R_h^3 \qquad (24)$$

where N is the number of coils per cubic centimeter, and R_h is the equivalent hydrodynamic radius of the coils. According to Flory and Fox,[7] the hydrodynamic radii, R_h, of polymer coils are related to radii of gyration, R_G, by

$$R_h = \xi R_G \qquad (25)$$

where ξ ranges from 0.775 to 0.875. Equation 25 has been experimentally proven for high molecular weight polymers.[16] The ξ value for PMMA was found to be 0.86 in a Θ solvent.[17] The values of ξ vary with molecular weights and solvents.[18] The value of 0.86 is used for all solvents as an approximation. After obtaining R_G, eq 26 derived for long chains was then used to calculate the end-to-end distances, R_{nv}, from viscosity measurements. The R_{nv} values for fractions 2 and 3 in different solvents are presented in Table VII.

$$R_{nv} = 6^{1/2}R_G \qquad (26)$$

Quantum Yields of the Naphthyl Group in Polymer I in the Absence of Energy Transfer. Quantum yields of the naphthyl group in polymer II are not necessarily equal to the quantum yields of the naphthyl group in polymer I in the absence of energy transfer. The introduction of the anthracene group into the polymer chain in polymer I might introduce not only a quenching mechanism for the naphthyl group due to energy transfer but also other quenching mechanisms such as the facilitation of intersystem crossing, etc. Furthermore, with polymer I there is a carbonyl group adjacent to the anthracene group. The carbonyl group is known to quench both naphthalene and anthracene fluorescence.[19] Additional quenching is defined as the quenching of the donor, naphthalene, fluorescence by the acceptor, anthracene, through mechanisms other than energy transfer (e.g., intersystem crossing). To obtain the quantum yields of the naphthyl group in polymer I in the absence of energy transfer, it is important to correct for any additional quenching.

Additional fluorescence quenching would result in greater quenching efficiencies, χ, when compared to E, energy-transfer efficiencies measured using eq 13. It is more serious for methylene chloride and ethyl acetate solutions than it is for acetonitrile solution judging from the values of χ and E values measured for different fractions in different solvents as summarized in Table V. The reason for this behavior is unknown.

It is important to correct for additional quenching in methylene chloride and ethyl acetate solutions if one wishes to obtain the fluorescence quantum yield, $\phi_{NA}{}^0$, of naphthalene groups in polymer I in the absence of energy transfer.[20] The quenching efficiency χ is given by eq 9. By definition,[19] the energy-transfer efficiency, E, in terms of naphthalene fluorescence quantum yield should be given by

$$E = 1 - \phi_{NA}/\phi_{NA}{}^0 \qquad (27)$$

where ϕ_{NA}'s are naphthalene fluorescence quantum yields in the presence of energy transfer. Combining eq 27 and eq 9 yields

$$\phi_{NA}{}^0 = [(1-\chi)/(1-E)]\phi_N{}^0 \qquad (28)$$

where $\phi_N{}^0$ is the fluorescence quantum yield of the naphthalene group in polymer II. The results for $\phi_{NA}{}^0$ in the two solvents are summarized in Table VIII for R_0 calculations.

A lifetime measurement is necessary to assess the degree of additional quenching of naphthalene fluorescence by anthracene for polymer I in PMMA films. Low concentrations of fraction 3 were used to measure energy-transfer efficiency (see Table VI) for a single photon counting measurement. Another film, which had a fraction 3 to PMMA weight ratio of 1 × 10^{-3} g/g, was made for this purpose, and lifetime measurement results are summarized in Table IV. The quenching efficiency, χ, calculated using eq 10 is then 32.9%, which is considerably higher than 11.2% where intermolecular energy transfer was absent. Using the technique described above, the energy-transfer efficiency for this sample was measured to be 30 ± 2%. Since the quenching efficiency (32.9%) agreed well with the energy-transfer efficiency (30 ± 2)%, additional quenching was not deemed important in the PMMA matrix.

Overlap Integral. The overlap of the fluorescence spectrum of the naphthyl group in polymer II with the absorption spectrum of 9-methylanthracene in acetonitrile is shown in Figure 5. The J integral for the naphthalene–anthracene pair in polymer I in acetonitrile is

Table VIII
Critical Förster Energy-Transfer Distances, R_0, for the Naphthalene–Anthracene Donor–Acceptor Pair of Polymer I

solvent	J integral, L cm^3/mol	$\phi_N{}^0$	$\phi_{NA}{}^0$	η_D	κ^2	R_0, Å
CH_3CN	1.98×10^{-15}	0.058	0.058	1.3442	2/3	16.5
$C_2H_3O_2C_2H_5$	1.73×10^{-15}	0.059	0.051	1.3723	2/3	15.7
CH_2Cl_2	1.68×10^{-15}	0.071	0.062	1.4242	2/3	15.7
PMMA matrix	1.85×10^{-15}	0.21	0.21	1.502	0.475	17.8

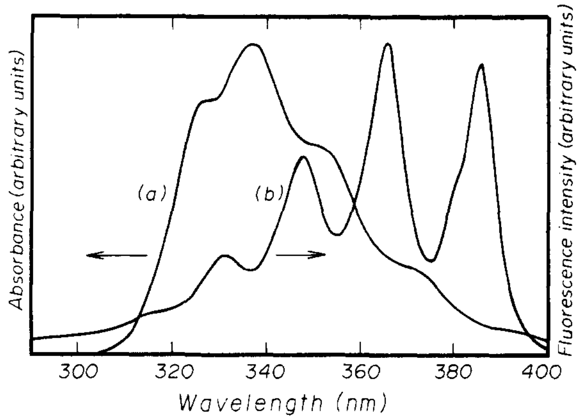


Figure 5. Overlap of the fluorescence spectrum of (a) polymer I with (b) the UV absorption spectrum of the model compound, 9-methylanthracene.

approximated by

$$J = \sum_{i=1}^{55} 2\epsilon(290 + 2i)(290 + 2i)^4 I(290 + 2i)10^{-28} \quad (29)$$

where 2 is the integration increment and $\epsilon(290 + 2i)$ is the extinction coefficient of the anthracene end group in polymer I at $\lambda = 290 + 2i$ nm. The extinction coefficient of the anthracene end group is obtained from the product of that of 9-methylanthracene and 0.88 as discussed in the Experimental Section. The summation was performed by a computer program. The value obtained was 1.98×10^{-15} L cm^3/mol. In a similar fashion, the J integrals in the other two solvents and in the PMMA matrix were calculated (Table VIII).

Error may arise from ϵ determination and the correction of the fluorescence spectrum for the relative response of the detecting system as a function of wavelength of emission. The estimated systematic error is within ±15%.

Critical Energy-Transfer Distance, R_0. All components needed for calculation of R_0 are listed in Table VIII. The experimental precision for fluorescence quantum yield, $\phi_{NA}{}^0$, measurement is within ±5%. The estimated systematic error is within ±15%.

The refractive index of each solvent at naphthalene excitation wavelength, typically 285 or 292 nm, was approximated using n_D values from the *Handbook of Chemistry and Physics*. Estimated error is less than ±3%.

The orientation factor, κ^2, in eq 6 is assumed to be two-thirds for solution studies[21] and 0.475 for R_0 calculation in a PMMA matrix.[22] R_0 values were obtained by inserting κ^2, J, $\phi_{ND}{}^0$, and n_D into eq 6 (see Table VIII).

The estimated systematic error in R_0 is ±0.5 Å. This is calculated using the simple error calculation formula

$$\frac{|\Delta R_0|}{R_0} = \frac{1}{6}\frac{|\Delta J|}{J} + \frac{4}{6}\frac{|\Delta n|}{n} + \frac{1}{6}\frac{|\Delta \phi_{NA}{}^0|}{\phi_{NA}{}^0} \quad (30)$$

where $|\Delta J|/J$, $|\Delta n|/n$, and $|\Delta \phi_{NA}{}^0|/\phi_{NA}{}^0$ are relative errors in the J integral evaluation, refractive indices (measured at the sodium line and used without correcting wavelength dependence), and the fluorescence quantum yield of the naphthalene group in the absence of energy transfer, respectively. In the measurement of the root-mean-square end-to-end distances using the modified spectroscopic ruler relation, the main error comes from the evaluation of R_0.

Evaluation of R_{nE}. Values for β, the statistical bond length to be fitted, were calculated by fitting eq 3 with measured energy-transfer efficiency, E or $\langle E \rangle$. The $P(n)$ terms in eq 3 are replaced with the GPC chromatographic data given in Figure 2. The summation terms in eq 3 were computed using a Fortran program on a Gould computer.

The root-mean-square end-to-end distance, R_n, for each fraction is obtained by inserting the fitted β parameter into eq 4. R_n values obtained using this method are denoted as R_{nE} and given in Tables IX and X for comparison with the R_{nv} values obtained from viscosity measurements.

R_{nT} in Acetonitrile. In acetonitrile, the expansion factor, α_E, relative to a freely rotating chain, for PMMA chains is 1.80.[23] Using this value, the root-mean-square end-to-end distances for PMMA chains can also be calculated from

$$R_{nT} = [2n[(1 - \cos \phi)/(1 + \cos \phi)]]^{1/2} \alpha_E l_B \quad (31)$$

where n and l_B are the number of repeating units and bond length and ϕ is the C–C bond angle (109° 47′). R_{nT} values are given in Table IX and compared with the R_{nv} measured in acetonitrile. The agreement is very good. This lends further support for the assignment of molecular weights to the fractions of polymer I and also for the calculations of R_{nv} values.

Expansion Factors α_E of PMMA. Using eq 31 and the R_{nv} values measured in ethyl acetate and in methylene chloride, the α_E factors in these two solvents were calculated (see Table VII).

Discussion of the Results. It appears from Tables IX and X that R_{nE} values correctly reflect the changes in R_{nv} while varying the molecular weight of the polymer and changing the solvent. For example, viscosity measurements revealed that R_{nv} values are the lowest in acetonitrile, increased in ethyl acetate, and are the highest in methylene chloride. The same trend is observed for R_{nE} values.

However, the average end-to-end distances R_{nE} calculated from energy-transfer efficiencies in the three organic solvents are consistently shorter than the corresponding ones from viscosity measurements, R_{nv}, and theoretical calculations, R_{nT}. In a PMMA matrix, the value determined using this technique are in closer agreement with those from viscosity measurement. It seems that the diffusion of the chain ends during the lifetime of naphthalene excitation[24] was partially responsible for the discrepancies.

Significant diffusion of the chain ends during the lifetime of naphthalene fluorescence (typically 20 ns) leads to higher energy-transfer efficiency and smaller R_{nE} values than would be otherwise observed for nondiffusing ends. This can be understood as follows. Before the naphthalene is excited by the absorption of incident light, the naphthalene and anthracene groups are separated by an ensemble-averaged distance, R_n. Following excitation, the

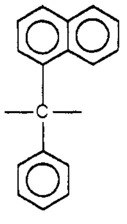
Table IX
End-to-End Distances for Polymer I in Various Solvents

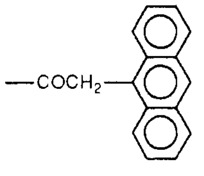
fraction	E, %	β, Å	$\bar{n}$	R_{nE},[a] Å	R_{nv}, Å	R_{nT}, Å	R_{nE}/R_{nv}
				In Acetonitrile			
1	16.4	2.25	111	33.5	*b*	59.2	
2	24.5	2.07	90	27.8	54.3	53.1	0.51
3	28.7	2.15	70	25.4	48.4	46.1	0.53
				In Ethyl Acetate			
1	9.47	2.70	111	40.2	*b*		
2	13.7	2.56	90	3.04	*b*		
3	17.9	2.57	70	30.4	54.6		0.56
				In Dichloromethane			
1	4.79	3.51	111	52.3	*b*		
2	6.70	3.42	90	45.9	67.4		0.68
3	9.02	3.4	70	40.8	58.6		0.70

[a] Experimental precision within ±0.5 Å; systematic error ≃±2 Å. [b] Insufficient sample for viscosity measurement.

relative diffusion motion of the end groups can be away from one another, stationary, and approaching one another. If the two groups diffuse away from one another, there is a chance that before they separate, the excitation energy would have been transferred. If they approach one another, this will increase the possibility of energy transfer.

Furthermore, the large end groups might distort the distribution function $P(n,R)$. The structures of the end groups (A and B) are significantly different from PMMA


A


B

units. The introduction of these groups into the ends of such chains might have some effect on the chain behavior, especially considering that the molecular weights of the samples studied are relatively low. In acetonitrile, the end-to-end distances from energy-transfer studies were found to be approximately 50% of the values determined from viscosity measurements. The ratio, R_{nE}/R_{nv}, increased in ethyl acetate and was the highest in methylene chloride since the end groups are relatively nonpolar. In polar solvents such as acetonitrile, there might be a net short-ranged attractive force acting between the naphthyl and the anthryl groups in polymer I, which distort the end-to-end distance distribution function of the polymer chain. Of course, a more rigorous explanation also needs to take the viscosity differences between the three solvents into account. These values at 25 °C are 0.441, 0.449, and 0.345 cP for ethyl acetate, methylene chloride, and acetonitrile, respectively. The similarity of these values suggests that the solvent polarity difference is mainly responsible for the different R_{nE}/R_{nv} ratios in the three solvents.

Errors may exist in the results determined from viscosity measurements. The application of eq 24 to polymer coils requires that the coils are nondraining and spherical in shape. The two conditions might well be satisfied with polymer samples with high molecular weights. A rough estimate of the lower limiting molecular weight below which eq 24 should not be used can be obtained by looking at the Kirkwood–Riseman treatment of the diffusion coefficient of polymer chains.[25,26] In the Kirkwood–Riseman model, a polymer chain is treated as n beads of radius r joined by a thread. Using this model, the diffusion coefficient, D, for the polymer coil was shown to possess two terms

$$D = D(\mathrm{s})(1 + \alpha) \tag{33}$$

where D(s) is the diffusion coefficient otherwise obtainable by treating the chain as a spherical coil and α is a term inversely proportional to the square root of the number of repeat units n. If one uses eq 24 when calculating R_h and makes the assumption that the polymer chain is nondraining and spherical (ignoring its detailed structure), the error estimated from the α term should be <8% for all of the samples studied.

Table X
Comparison of Root-Mean-Square End-to-End Distances Obtained Using the Spectroscopic Ruler Technique in a PMMA Matrix and from Viscosity Measurements

technique	β, Å	$\bar{n}$	R_n, Å	α_E
spectroscopic ruler	3.59	70	42.5	1.65
viscosity measurement		70	48.9	1.80[a]

[a] From ref 22.

IV. Conclusions

The technique known as the spectroscopic ruler for measuring molecular distances in systems with rigid backbones was modified and applied to polymer systems with flexible chains to measure directly the root-mean-square end-to-end distances. In the absence of significant diffusion of the end groups during the donor fluorescence lifetime, the technique gives results that are in good agreement with those obtained by viscosity measurements within experimental error. The success suports the Förster relationship given by eq 2 and the accuracy of the classical statistical models for describing polymer chains.

The values obtained from this method in nonviscous solvents correctly reflected the changes of end-to-end distances with variation of solvent and molecular weight. As indicated by viscosity measurements, fractions of polymer I were found to possess the largest expansion factors α_E in methylene chloride and the smallest in acetonitrile. This was confirmed by the R_{nE} values obtained in different solvents. The R_{nE} values experimentally obtained were, however, consistently shorter than those determined by viscosity measurements. It appears that diffusion of the end groups during the naphthalene excited-state lifetime is at least partially responsible for the discrepancies. The discrepancy, found to be the largest in acetonitrile, is less serious in ethyl acetate and the least serious in methylene chloride. It is also possible that PMMA end-group behavior is perturbed by the introduction of large chromophores such as naphthalene and anthracene. The other sources of error might arise from the application of formulas developed for infinitely long chains and from the assumption that a Gaussian form describes the end-to-end distance distribution.

For future studies, polymers with molecular weights up to five times greater should be used to minimize the effect of foreign chromophores on the behavior of the end group. Longer chains further justify the use of statistical treatments for polymer chains. It would also be informative to attach new donor–acceptor pairs with longer critical energy-transfer distances, e.g., 50 Å, to the polymer chain ends. Higher R_0 values not only ensure that significant energy transfer occurs in the polymer system but also that the distance the end groups diffuse in the donor fluorescence lifetime is much shorter than R_0. To minimize intermolecular energy transfer, it is desirable to use chromophores with high extinction coefficients so that only extremely low concentrations of the sample are required to perform the fluorescence measurement. Other improvements include the use of donors with extremely short fluorescence lifetimes and performance of the experiment in viscous solvents such as triacetin.

Finally, this research may lead to a new method for the measurement of diffusion coefficients of polymer end groups. In a nonviscous solvent, the diffusion of the end groups is significant during the donor fluorescence lifetime. This results in a dynamic component of energy-transfer efficiency and therefore reduces the end-to-end distances measured from the modified spectroscopic ruler. In viscous solvents or a solid matrix, the diffusion of the end groups may be assumed to be absent during donor fluorescence lifetime. With the correct model, the diffusion coefficients of the end groups could be evaluated from the dynamic energy-transfer component.

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Registry No. PMMA, 9011-14-7; 9-methylanthracene, 779-02-2.