earlier spectra of aqueous NaOH- and NaCl-containing Nafion perfluorosulfonate membranes.[4] If the lowest frequency peak for the filled membranes is likewise associated with the relaxation of the interfacial polarization of isolated clusters, in this case containing nanometers in extent silicon oxide "networks", the suppression of this peak might then be associated with the eventual intergrowth of these clusters. This might not appear to be an unreasonable mechanistic assignment if the seemingly corresponding low-frequency peak seen in the absorption spectra for the unfilled membranes would not exhibit the same general behavior. Of course, to salvage this notion, one might imagine that both systems would contain clusters of about the same size and having the same protonic charge carriers. As the temperature increases, one might further imagine that the motions of these charge carriers in both systems would eventually become delocalized to such an extent that they are no longer confined within individual cluster boundaries. This view, conveniently of course, is not strongly linked to the chemical composition of either of the clusters. Finally, we are presently unable to offer an explanation for the origin and strange temperature response of the high-frequency peak for either filled or unfilled membranes.

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Application of the "Spectroscopic Ruler" to Studies of the Dimensions of Flexible Macromolecules. 1. Theory

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ABSTRACT: This paper explores the feasibility of using the Förster "spectroscopic ruler" relation for measuring the end-to-end distances of flexible organic polymer chains. The experimental techniques for measuring the energy-transfer efficiencies from the naphthalene donors, attached at one end of polymer chains, to anthracene acceptors at the other end of the chains are established. Numerical solutions are obtained for the theoretical expression for energy-transfer efficiencies. Replacing the theoretical energy-transfer efficiencies in the theoretical expression with experimentally measured values should enable one to fit the root-mean-square end-to-end distances of polymer chains.

I. Introduction

The root-mean-square end-to-end distances, R_n, of macromolecules in solution are important measures of the dimensions of polymer coils. Knowledge of R_n is of both experimental and theoretical importance. Three principal methods have been used for the determination of dimensions of macromolecules: light scattering,[1] viscosity,[2] and diffusion coefficient[3] measurements. Determination of inelastic scattered light intensity versus angle yields the radius of gyration, R_G. For long chains, if the correlation between bond pairs diminishes rapidly with sequence separation, R_G is related to R_n by

$$R_G = (1/6)^{1/2} R_n \qquad (1)$$

The diffusion coefficient, D, for polymer coils can be measured by either dynamic light scattering experiments[4] or measurement of the sedimentation velocity.[3] If nondraining coils are assumed, the coefficient D can be related to another effective radius R_D, equal to the hydrodynamic radius, R_H (related to R_G and therefore R_n), through the Stokes relation for a sphere by

$$D = \frac{kT}{6\pi\eta_0 R_D} \qquad (2)$$

where kT is thermal energy and η_0 is the viscosity of the solvent. The viscosity measurement makes use of eq 3, first derived by Einstein,[5] where R_h is the equivalent hydrodynamic radius of the nondraining coil, N is the number

$$\eta_s = \eta_0[1 + (10/3)N\pi R_h^{\,3}] \qquad (3)$$

of coils per cubic centimeter, and η_s and η_0 are the viscosities of the polymer solution and solvent, respectively. The use of eq 3 implicitly assumed that polymer concentrations are low and coils can be assumed to be nondraining.

The statistically averaged root-mean-square end-to-end distance of Gaussian chains is defined by

$$R_n = \langle R^2\rangle^{1/2} = [\int R^2 P(n,R)\,\mathrm{d}R]^{1/2} = (nl^2)^{1/2} \qquad (4)$$

where

$$P(n,R) = 4\pi R^2[3/2\pi R_n^{\ 2}]^{3/2}\exp[-(3/2)(R/R_n)^2] \qquad (5)$$

is the Gaussian end-to-end distance distribution function.

Real chains are more expanded, due to the fixed bond angles and to the excluded-volume effect of the chain segments.[1] In Θ solvent, the distribution of end-to-end distances for these chains remains Gaussian,[1] e.g., given by eq 5, but R_n is more expanded than $(nl^2)^{1/2}$

$$R_n = (n\beta^2)^{1/2} \qquad (6)$$

where β is the effective bond length, which is typically longer than l by a factor of 3–5. Equation 4 also applies for real chains except that the end-to-end distance distribution function in eq 4 is replaced by one that describes real chains.

This paper explores the possibility of using the Förster "spectroscopic ruler"[6] (eq 7) for the direct measurement of end-to-end distances of organic polymer chains

$$E(R) = R_0^{\ 6}/(R_0^{\ 6} + R^6) \qquad (7)$$

where $E(R)$ denotes the energy-transfer efficiency from an excited donor, D^*, to an acceptor, A, through the dipole–dipole interaction mechanism at a separation distance of R. The value of R_0 is the critical resonance energy-transfer distance at which the probability of energy transfer $E(R_0)$ is 50%. The expression for R_0 is given by

$$R_0 = \left(\frac{9000\ln 10\kappa^2\phi_D}{125\pi^5\eta^4N_0}J\right)^{1/6} \qquad (8)$$

where ϕ_D is the donor fluorescence quantum yield in the absence of energy transfer, η 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

$$J = \int_0^\infty \lambda^4 I_\lambda \epsilon_\lambda\,\mathrm{d}\lambda \qquad (9)$$

where, by definition

$$\int_0^\infty I_\lambda\,\mathrm{d}\lambda = 1 \qquad (10)$$

The spectroscopic ruler relation has been used directly in probing intramolecular distances in biological systems for polymer chains with specific conformations.[7] In doing so, the sites of interest are labeled at one point with a donor and at another point with an acceptor. For example, Stryer and Haugland[8] synthesized homologous proline oligopeptides with donors and acceptors attached at two ends. Since the proline peptides are stiff and linear, with knowledge of the transfer efficiency, E, the end-to-end distance, R_n, was calculated using

$$R_n = [(1/E) - 1]^{1/6}R_0 \qquad (11)$$

The use of eq 7 for systems with flexible chains is complicated by the distribution of distances between the sites of interest. Cantor and Pechukas[9] first discussed the possibility of actually determining the distance distribution functions using eq 7. It was proposed that a series of polymers with equivalent molecular weight and molecular weight distribution be made and labeled on two ends with different donor–acceptor pairs. By this approach, a series of R_0 values is obtained. Grinvald et al.[10] took a different approach and proposed to determine the end-to-end distance distribution function for flexible chains by analyzing the transient donor fluorescence decay of end-labeled chains. The experiment was performed by Katchalski-Katzir et al.[11] In their work, donors and acceptors were attached on a series of homologous peptide oligomers. The energy transfer between donor and acceptor governed by eq 7 was used to explain the behavior of the donor fluorescence decay of the end-labeled oligomers. Information was extracted with regard to the end-to-end distance distribution function, $P(R)$, for an ensemble of molecules representing, at equilibrium, the various conformations attained by a given peptide in solution. From the distribution function, $P(R)$, the root-mean-square end-to-end distance for a given peptide in solution was calculated using

$$R_n = [\int_0^m R^2P(R)\,\mathrm{d}R]^{1/2} \qquad (12)$$

where m is the maximum length of the outstretched peptide chain.

Peterson et al.[12] have determined the radius of gyration of poly(methyl methacrylate) (PMMA) chains in the amorphous solid state using time-resolved fluorescence depolarization measurements. In their experiment, methyl methacrylate was copolymerized with a small fraction of 2-vinylnaphthalene. The copolymerized sample was molded with host PMMA. The naphthalene groups were excited with a polarized short pulse (nanoseconds in duration), and the fluorescence decay along the parallel and perpendicular directions was monitored. The remaining degree of polarization at time t, obtained from the decay curves, is related to the parameter $G^s(t)$, the ensemble-averaged probability that an orginally excited chromophore is still excited at time t. Assuming that the spectroscopic ruler relation determines the energy-transfer probability, the functional form of $G^s(t)$ was previously found to be related to the radius of gyration of the polmer coils.[13–15] The radius of gyration of PMMA chains was obtained by fitting the experimentally observed $G^s(t)$.

In the present work, the spectroscopic ruler technique was modified to measure the end-to-end distances of a flexible, high molecular weight, synthetic organic polymer, namely poly(methyl methacrylate). Since the theory for the form of the end-to-end distance distribution for polymers has already been reasonably well established, it was not intended to derive the exact expressions for them but rather to establish a new technique, which enables the direct measurement of end-to-end distances of polymer chains in solution or solid media.

II. Theoretical Considerations

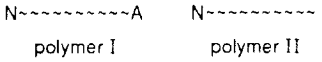
These studies used PMMA chains with ~100 repeating units, labeled on one end with a fluorescence donor, naphthalene (N), and on the other with an energy acceptor, anthracene (A). The N → A energy-transfer efficiencies experimentally measured, E, are the statistical average given by

$$E = \langle E(n,R)\rangle = \int_0^\infty P(n)\int_0^\infty E(R)\,P(n,R)\,\mathrm{d}R\,\mathrm{d}n \qquad (13)$$

where $E(R)$ is defined by eq 7, $P(n)$ is the distribution function for the number of repeating units n or the relative number fraction of the polymer chains with repeating units n, and $P(n,R)$ is the end-to-end distance distribution function for polymer chains with n repeating units. Integration with respect to n in eq 13 was performed to account for the dispersity in molecular weights of polymer samples. With the correct choice of the distribution function $P(n,R)$, the energy-transfer efficiency, E, experimentally observed can be fitted using the above equation and thus the root-mean-square end-to-end distances can be obtained.

A numerical expression for the theoretical energy-transfer efficiencies and the formulas used for calculating the experimental energy-transfer efficiencies are derived below. A new method is developed for the measurement of energy-transfer efficiencies between energy donors and acceptors, which is believed to be superior for both its convenience and accuracy.

In the steady-state fluorescence technique, two methods are commonly used for the measurement of energy-transfer efficiency.[16] In one, the energy-transfer efficiency from naphthalene to anthracene in polymer I is determined from the decrease in naphthalene fluorescence quantum yield for polymer I. If the quenching of naphthalene fluorescence were solely due to energy transfer, the quenching efficiency, χ, would be equal to the energy-transfer efficiency, E. The value of χ is determined using



$$\chi = 1 - \phi_{NA}/\phi_N{}^0 \tag{14}$$

where ϕ_{NA} and $\phi_N{}^0$ denote the fluorescence quantum yields of naphthalene in polymers I and II, respectively. The selective excitation of naphthalene was best achieved by irradiating with incident light at $\lambda_1 = 284$ or 292 nm. At these wavelengths, about 95% of the light is absorbed by the naphthalene moiety.

If the incorporation of the anthracene group is less than 100%, the observed quenching efficiency, χ_e, is

$$\chi_e = \chi P_T \tag{15}$$

where P_T is the fraction of the total light absorbed at the excitation wavelength by chains with terminators, i.e., the anthracene group. P_T is given by

$$P_T = \frac{1 - 10^{-A_1}}{2 - 10^{-A_1} - 10^{-A_2}} \tag{16}$$

where A_1 and A_2 are the absorbances of chains with and without terminators, respectively. If low absorbances are used in fluorescence measurement, P_T is equal to the termination efficiency, T. Then

$$\chi_e = \chi T \tag{17}$$

or

$$\chi = \chi_e/T \tag{18}$$

Table I
Energy-Transfer Efficiencies, *E*, Calculated Using Equation 24 for Polymer I in Methylene Chloride[a]

fraction	$\bar{n}$	E,[b] %	E,[c] %
1	111	4.76	4.82
2	90	6.58	6.82
3	70	8.96	9.08

[a] See ref 19. [b] $\lambda_1 = 285$ nm, $\lambda_2 = 365$ nm. [c] $\lambda_1 = 292$ nm, $\lambda_2 = 350$ nm.

In the second method, the energy-transfer efficiency, E, is determined from the enhancement of anthracene fluorescence intensity. A brief description of the technique is as follows. A molecule incorporating both donor and acceptor molecules such as polymer I is used. Excitation of the donor group leads to emission by the acceptor. The intensity from the acceptor is then measured. One also needs a reference molecule with only the acceptor attached. With the reference compound excited at the same wavelength, the emission intensity from the acceptor is again measured. When the fluorescence intensities from the acceptor group in both cases are compared, the energy-transfer efficiency from the donor to the acceptor can be evaluated. This procedure is tedious and requires reference samples, e.g., PMMA attached at one end with an anthracene group.

We propose an improvement to the latter method, as follows. Consider now excitation of polymer I at wavelengths $\lambda_2 = 348$ or 364 nm, where naphthalene has negligible absorption and anthracene is excited by direct excitation. The observed fluorescence intensity of anthracene should be

$$I_{Af}(\lambda_2) = \kappa' I_0(\lambda_2)(1 - 10^{-A(\lambda_2)})\phi_{Af} \tag{19}$$

where κ' is an instrument constant, which varies with the fluorescence observation angle, filter, and monochromator efficiency, etc. The parameter ϕ_{Af} is the fluorescence quantum yield of anthracene, which is assumed to be independent of the excitation wavelength of the incident light.[17] $I_0(\lambda_2)$ is the incident light intensity at λ_2. The value $A(\lambda_2)$ is the absorbance of the studied solution at λ_2.

Excitation of polymer I at $\lambda_1 = 284$ or 292 nm results in an observed anthracene fluorescence emission, the intensity of which is given by[18]

$$I_{Af}(\lambda_1) = \kappa' I_0(\lambda_1)(1 - 10^{-A(\lambda_1)})(PET + 1 - P)\phi_{Af} \tag{20}$$

where $I_0(\lambda_1)$ is the incident light intensity at wavelength λ_1 and P is the fraction of the total light absorbed at wavelength λ_1, which is absorbed by naphthalene. P is given by

$$P = \frac{1 - 10^{-A_N(\lambda_1)}}{2 - 10^{-A_N(\lambda_1)} - 10^{-A_A(\lambda_1)}} \tag{21}$$

where $A_N(\lambda_1)$ and $A_A(\lambda_1)$ are the absorbances of naphthalene and anthracene groups at wavelength λ_1, respectively. In eq 20 $1 - P$ is the fraction of total light absorbed due to direct anthracene absorption, E is the energy-transfer efficiency, and T is the termination efficiency or the percent of chains with both an anthracene and a naphthalene group. Dividing eq 20 by eq 21 gives

$$\frac{I_{Af}(\lambda_1)}{I_{Af}(\lambda_2)} = \frac{[1 - 10^{-A(\lambda_1)}][PET + 1 - P]I_0(\lambda_1)\phi_{Af}}{[1 - 10^{-A(\lambda_2)}]\phi_{Af}I_0(\lambda_2)} \tag{22}$$

Rearranging and simplifying eq 22 gives

$$E = \frac{1}{PT}\left[\frac{I_{Af}(\lambda_1)\, I_0(\lambda_2)\, (1 - 10^{-A(\lambda_2)})}{I_{Af}(\lambda_2)\, I_0(\lambda_1)\, (1 - 10^{-A(\lambda_1)})} - 1 + P\right] \tag{23}$$

where $I_{Af}(\lambda_1)/I_{Af}(\lambda_2)$ 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 the incident light intensities at these two wavelengths. If all spectra are recorded in ratio mode, eq 23

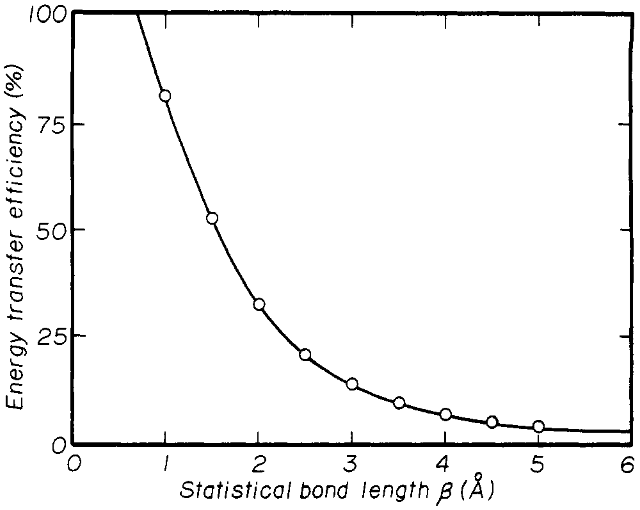


Figure 1. Increasing the statistical bond length of a polymer chain decreases energy-transfer efficiencies experimentally observed: R_0 = 17 Å, n = 80.

simplifies to

$$E = \frac{1}{PT}\left[\frac{I_{\mathrm{Af}}{}^{\mathrm{R}}(\lambda_1)\ (1 - 10^{-A(\lambda_2)})}{I_{\mathrm{Af}}{}^{\mathrm{R}}(\lambda_2)\ (1 - 10^{-A(\lambda_1)})} - 1 + P\right] \tag{24}$$

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

Equation 24 has been used in the determination of energy-transfer efficiencies for a few fractions of end-labeled PMMA samples dissolved in methylene chloride. The results are summarized in Table I.[19] The values of E were found to decrease with increasing average repeat units, $\bar{n}$, of the fractions. When two sets of λ_1 and λ_2 values were used for the measurement, the E values obtained are quite reproducible.

The theoretical expression for energy-transfer efficiencies in polymer sample I is given by eq 13. Assuming a Gaussian form for the end-to-end distance distribution function of these chains, eq 13 then becomes

$$\langle E\rangle = \int_{n_1}^{n_2} P(n)\,\mathrm{d}n \int_0^m 4\pi R^2\left[\frac{3}{4n\pi\beta^2}\right]^{3/2} \times \exp\left[-\frac{3}{2}\left[\frac{R^2}{2n\beta^2}\right]\right]\frac{R_0{}^6}{R^6 + R_0{}^6}\,\mathrm{d}R \tag{25}$$

where β is the statistical bond length to be fitted and

$$m = 2nL_{\mathrm{B}} \sin(\Phi/2) \tag{26}$$

where Φ is the C–C bond angle, 109°47′. The value m is the contour length of a polymer chain with n repeating units, i.e., the length of the fully stretched chain. Letting $x = R/(2n\beta^2)^{1/2}$, eq 25 becomes

$$\langle E\rangle = \int_{n_1}^{n_2} P(n)\,\mathrm{d}n \int_0^{m_x} 4\pi x^2\left[\frac{3}{2\pi}\right]^{3/2} \times \exp[-1.5x^2]\left[\frac{R_0{}^6}{R_0{}^6 + (2n\beta^2)^3x^6}\right]\mathrm{d}x \tag{27}$$

where m_x is given by

$$m_x = m/(2n\beta^2)^{1/2} \tag{28}$$

Table II
Energy-Transfer Efficiencies Calculated Using Various Parameters

different statistical bond lengths, β (R_0 = 17 Å, n = 80)		different no. of repeating units, n (β = 4.0 Å, R_0 = 17 Å)		different critical energy-transfer distances, R_0 (β = 4.0 Å, n = 80)	
β, Å	E, %	n	E, %	R_0, Å	E, %
1.0	80.6	40	15.3	12	2.55
1.5	52.0	50	11.8	14	3.89
2.0	32.1	60	9.40	16	5.55
2.5	20.3	70	7.73	17	6.51
3.0	13.4	80	6.51	18	7.55
3.5	9.16	90	5.58	20	9.85
4.0	6.51	100	4.85	22	12.4
4.5	4.77	110	4.27	24	15.3
5.0	3.59	120	3.80	26	18.3

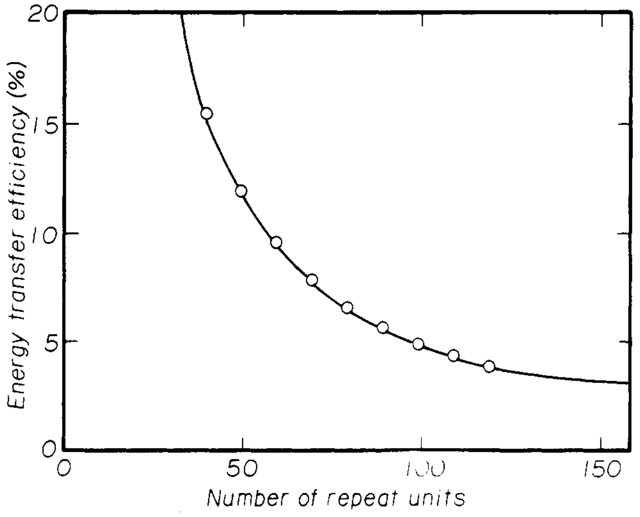


Figure 2. Increasing the number of repeat units of a polymer chain decreases energy-transfer efficiencies experimentally observed: β = 4.0 Å, R_0 = 17 Å.

Since the upper integration limit for x in eq 27 does not go to infinity, the integral

$$\int_0^{m_x} 4\pi x^2(3/2\pi)\exp[-1.5x^2]\,\mathrm{d}x \tag{29}$$

is not equal to unity. A normalization factor is needed for eq 25. Dividing the right-hand side of eq 25 by expression 29 and simplifying leads to

$$\langle E\rangle = \frac{\int_{n_1}^{n_2} P(n)\,\mathrm{d}n \int_0^{m_x} x^2 \exp[-1.5x^2]\left[\frac{R_0{}^6}{R_0{}^6 + (2n\beta^2)^3x^6}\right]\mathrm{d}x}{\int_0^{m_x} x^2\exp[-1.5x^2]\,\mathrm{d}x} \tag{30}$$

Analytical solution of eq 30 for β and the subsequent calculation of R_n using

$$R_n = (2n)^{1/2}\beta \tag{31}$$

is difficult. The integrals in eq 30 can be approximated by

$$\langle E\rangle = \sum_{n_1}^{n_2} P(n)\,\Delta n \sum_{i=1}^{m_x}(0.01i)^2 \times \exp[-1.5(0.01i)^2]\frac{R_0{}^6}{R_0{}^6 + (0.01i)^6(2n\beta^2)^3}\Big/\sum_{i=1}^{m_x}(0.01i)^2 \times \exp[-1.5(0.01i)^2] \tag{32}$$

The increment in integration, δx, is given a value 0.01.

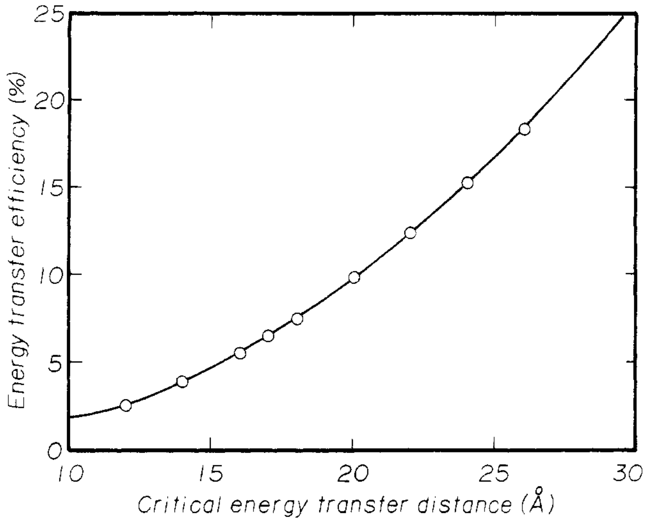


Figure 3. Increasing critical energy-transfer distances increases energy-transfer efficiencies experimentally observed: $R_0 = 4.0$ Å, $n = 80$.

Using $P(n)$ from GPC, this expression can be evaluated by computation.

If monodispersed samples are used, eq 32 is simplified to

$$\langle E\rangle = \sum_{i=1}^{m_x}(0.01i)^2 \exp[-1.5(0.01i)^2]\frac{R_0^{\,6}}{R_0^{\,6} + (0.01i)^6(2n\beta^2)^3}\Big/ \sum_{i=1}^{m_x}(0.01i)^2 \exp[-1.5(0.01i)^2] \quad (33)$$

Using a critical energy-transfer distance, R_0, of 17 Å, the energy-transfer efficiencies between the donor and acceptor end groups are calculated from the above equation for a hypothetical chain with 80 repeat units and different statistical bond length, β. The results are presented in Table II and Figure 1. It is obvious from the results that the energy-transfer efficiency calculated is a sensitive function of β. Upon changing the statistical bond length from 1.0 to 5.0 Å, the energy-transfer efficiency is decreased from 80.6 to 3.59%. In Table II and Figure 2, the energy-transfer efficiencies calculated are shown to decrease with an increasing number of repeat units of the polymer chain. Finally, in Table II and Figure 3 the energy-transfer efficiencies calculated are demonstrated to vary sensitively with the critical energy-transfer distances, R_0.

III. Conclusions

It appears to be experimentally feasible to use the spectroscopic ruler to measure directly the root-mean-square end-to-end distances of flexible organic polymer chains. For the system discussed, a flexible organic polymer chain labeled at one end with a fluorescence donor, naphthalene, and the other end with an acceptor, anthracene, experimental measurement of the energy-transfer efficiency is convenient and precise. The energy-transfer efficiency calculated from the numerical equation is a sensitive function of the statistical bond length, β, and therefore the root-mean-square end-to-end distances.

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Registry No. Naphthalene, 91-20-3; anthracene, 120-12-7.