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Application of the "Spectroscopic Ruler" to Studies of the Dimensions of Flexible Macromolecules. 5. Experimental Measurement of Chain-End Diffusion Coefficients

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ABSTRACT: Diffusion coefficients of poly(methyl methacrylate) chain ends in different solvents are evaluated by using the model developed in a previous paper in this series. The significance of the results is discussed.

Introduction

Knowledge of the diffusion coefficients of polymer ends is of both experimental and theoretical importance. Theoretically, knowledge of this coefficient makes it possible to verify experimentally existing theoretical predictions. According to Kirkwood–Riseman–Flory theory,[1,2] the diffusion coefficient $D(s)$ of a chain segment s distance away from the center of mass is given by

$$D(s) = D_t \exp\left[-\frac{9}{2n}(s/\beta)^2\right] + D^\circ(s)\left[1 - \exp\left[-\frac{9}{2n}(s/\beta)^2\right]\right] \quad (1)$$

where n is the number of bonds in the chain and β is an effective bond length. $D^\circ(s)$ in eq 1 is the diffusion coefficient of a hypothetically free segment; D_t, the translational diffusion coefficient of the center of mass of a Gaussian chain, is related to $D^\circ(s)$ by

$$D_t = \frac{4(2/3\pi)^{1/2}}{n^{1/2}\alpha} D^\circ(s) \quad (2)$$

where α is the ratio between β and bond length L

$$\alpha = \beta/L \quad (3)$$

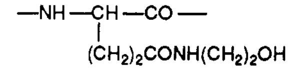
The diffusion coefficient of the center of mass of polymer coils can be determined by techniques such as photon correlation spectroscopy,[3] sedimentation,[4] and NMR pulse-gradient spin–echo experiments.[5] Techniques for the measurement of $D^\circ(s)$ or small molecules are well established[6] or can even be calculated from the Einstein–Stokes relation[7] if the size of the molecule is significantly larger than those of solvent molecules

$$D = \frac{kT}{6\pi\eta_0 R_h} \quad (4)$$

where kT is thermal energy, η_0 is solvent viscosity, and R_h is the hydrodynamic radius of the diffusing molecule.

Experimentally, knowledge of end-group diffusion coefficients can contribute to a better understanding, for instance, of cyclization reaction kinetics[8,9] and termination kinetics in free-radical polymerization.[1,10,11]

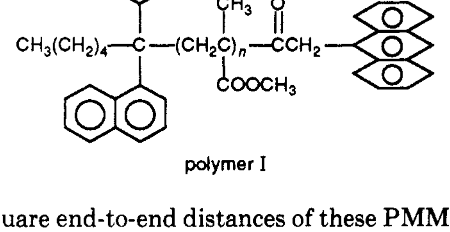
Despite the fundamental importance of end-group diffusion coefficients, there have been only scattered reports of their experimental measurement. Katchalski-Katzir et al.[12] monitored the effect of diffusion on the decay of donor fluorescence. The donor group was attached to one end of an oligopeptide chain that was labeled at the other end with an acceptor group. In cases involving significant end-group diffusion, the fluorescence of the donor group decayed much faster. By fitting the decay curves, the effective coefficient of relative diffusion between fluorescence donor and acceptor end groups could be estimated. According to Katchalski-Katzir et al.,[12] in trifluoroethanol (η = 1.0 cP) as the number of intervening repeat units (A) between the donor and acceptor end groups increased from four to nine, the effective coefficient D of relative diffusion between the end groups increased from 0.9 × 10^{-7} to 6.4 × 10^{-7} cm^2/s. Xu and Winnik[13] studied the kinetics of diffusion-controlled exciplex formation between pyrene and *N,N*-dimethyltoluidine end-labeled polymer using pyrene monomer and exciplex decay measurement. The time dependence of the rate constant for exciplex formation skewed the decay curves. By incorporating a time-dependent rate constant into the kinetic equations, a method was developed for end-group diffusion coefficient measurements. For polystyrene chains of molecular weights 1.97 × 10^3 (16 repeat units) and 3.25 × 10^3 (28 repeat units) in cyclohexane at 22 °C (η = 0.98 cP), the effective coefficients D of relative diffusion had the values of (1.3 ± 0.3) × 10^{-6} and (0.25 ± 0.03) × 10^{-6} cm^2/s, respectively.



$$\text{—NH—}\underset{\displaystyle (CH_2)_2CONH(CH_2)_2OH}{\underset{|}{CH}}\text{—CO—}$$

A

In a previous paper in this series,[14] we reported energy-transfer efficiencies measured in various media from naphthalene to anthracene groups attached to the ends of poly(methyl methacrylate) (PMMA) samples of three different molecular weights. In an attempt to fit the root-mean-square end-to-end distances of these PMMA chains



polymer I

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Table I
Characterization of Polymers

fraction	$\bar{M}_w$ GPC	$\bar{M}_n$ GPC	$\bar{M}_n$ UV[a]	$\bar{M}_n$ NMR	$\bar{M}_w/\bar{M}_n$ GPC	$\bar{M}_v$
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 $\simeq$ 5%. [b] Insufficient sample for viscosity measurement. [c] Termination efficiency from NMR, 99%.

using energy-transfer efficiencies determined in nonviscous media, it was found that the values determined from the so-called "spectroscopic ruler" technique were consistently shorter than the root-mean-square end-to-end distances determined from viscometry measurements. It was concluded that significant diffusion of the chain end groups during the donor fluorescence lifetime was responsible for the discrepancies.

In a subsequent paper in the series,[15] it has been demonstrated theoretically that energy-transfer efficiencies between polymer end groups increases if the mobility of the end groups increases. The energy-transfer efficiencies, E, between the end groups of a polymer chain have been shown to be a function of the root-mean-square end-to-end distances of polymer chains, R_n, Förster critical energy-transfer distances, R_0,[16] the coefficient of relative diffusion betwen the chain ends, D, and the lifetime τ of donor fluorescence in the absence of energy transfer. That is

$$E = E(R_n, R_0, D, \tau) \tag{5}$$

rather than

$$E = E(R_n, R_0) \tag{6}$$

as was used in a previous paper.[14]

In this paper, we estimate the coefficients of relative diffusion between PMMA chain ends from the expression of energy-transfer efficiency developed in the preceding paper.[15] In doing so, we assume that the root-mean-square end-to-end distances of the polymer chains, R_{nV}, determined by viscometry are correct.

Experimental Section

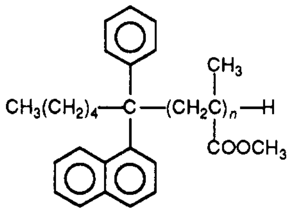
Polymer Characterization. Three fractions of polymer I were used for energy-transfer studies. The samples were characterized by GPC, viscometry, NMR, and UV spectrometry.[14] Molecular weights determined from the various techniques for the samples are summarized in Table I.

Critical Energy-Transfer Distances R_0. The calculation of the critical distances for Förster energy transfer involves the evaluation of the overlap integrals between the fluorescence spectrum of energy donors and the absorption spectrum of energy acceptors. It also requires the determination of fluorescence quantum yields of the donor group in the absence of energy transfer. The procedures for R_0 evaluation have been discussed in detail in a previous paper.[14] In the solvents acetonitrile, ethyl acetate, and dichloromethane, the R_0 values for polymer I were estimated to be 16.5 ± 0.5, 15.7 ± 0.5, and 15.7 ± 0.5 Å, respectively.

Lifetimes of the Donor Groups in the Absence of Energy Transfer. In a previous paper,[14] the fluorescence quantum yield ϕ°_{NA} of the naphthyl group, the energy donor, in the absence of energy transfer in each solvent was determined and tabulated. The fluorescence quantum yield ϕ°_N and the lifetime τ°_N of the naphthyl group of polymer II in ethyl acetate were determined to be 0.058 and 15.28 ns, respectively. The fluorescence lifetime τ°_{NA} of the naphthyl group of polymer I in any other solvent in the absence of energy transfer can then be calculated by using eq 7,[17] where n_2 and n_1 are the refractive indices of ethyl acetate and any other solvent in which ϕ°_{NA} were determined. The resultant τ°_{NA} values in these solvents are presented in Table II.

Table II
Fluorescence Lifetimes of the Naphthyl Groups in Polymer I in the Absence of Energy Transfer in Different Solvents

solvent	n	ϕ°_{NA}	τ°_{NA}, ns
ethyl acetate	1.3723	0.051	13.2
acetonitrile	1.3442	0.058	15.6
dichloromethane	1.4242	0.062	14.9



polymer II

$$\frac{\phi^\circ_{NA}}{\phi^\circ_N} = \frac{n_1^2 \tau^\circ_{NA}}{n_2^2 \tau^\circ_N} \tag{7}$$

R_{nV} Values. The R_{nV} values, R_n determined by viscometry, for the samples have been calculated from viscosity measurements by assuming that the polymer chains can be treated as non-draining random coils. Upon the determination of the viscosity η of a very dilute polymer solution and the viscosity η_0 of the solvent, an equivalent hydrodynamic radius R_h for polymer coils can be calculated according to Einstein's equation[18]

$$\eta/\eta_0 = 1 + (10/3)N_c\pi R_h^3 \tag{8}$$

where N_c is the number of polymer coils per cubic centimeter. According to ter Meer and Burchard,[19] R_h and R_G, the radius of gyration, for PMMA samples of high molecular weight are related by

$$R_G = \xi R_h \tag{9}$$

where ξ is a proportionality coefficient and varies with solvent but not with molecular weight, provided that the molecular weight is sufficiently high. The value of ξ for PMMA in a Θ-solvent, butyl chloride at 34.5 °C, has been determined to be 1.156. It changes to 1.555 in a good solvent, acetone at 20 °C, for PMMA. R_{nV}, root-mean-square end-to-end distances of PMMA chains from viscometry measurements, can then be calculated by using the asymptotic equation for chains of infinite length given by[20]

$$R_{nV} = 6^{1/2}R_G \tag{10}$$

The three PMMA samples studied have $\bar{M}_w$ of 1.42×10^4, 1.00×10^4, and 0.81×10^4, respectively. The ξ values for samples of these molecular weights are not very accurately known, and therefore a ξ value of 1.156 was used previously[14] for all three solvents, neglecting the fact that acetonitrile is a Θ-solvent, methylene chloride is a good solvent, and ethyl acetate is a fairly good solvent for PMMA. This approximation was used in calculating the R_{nV} values presented in Table III.

Energy-Transfer Efficiency. Energy-transfer efficiencies from the naphthyl group to the anthryl group in polymer I were monitored from the enhanced fluorescence emission of the acceptor group due to energy transfer. In a typical experiment, the donor group is selectively excited. Due to energy transfer, fluorescence emission intensity from the acceptor group increased over that which would have been observed in the absence of energy transfer. The experimental procedure for measurement of E has

Table III
Coefficient of Relative Diffusion between the Chain Ends in Different Media ($T = 20$ °C)

fraction	R_{nV}, Å	$\bar{n}$[a]	R_0, Å	τ, ns	E, %	D[b]	D_{end}[b]
			In Acetonitrile				
1	60.6	111			16.4	8.0	4.0
2	54.3	90	16.5	15.6	24.5	10.4	5.2
3	48.4	70			28.7	8.3	4.1
			In Ethyl Acetate				
1	68.8[c]				9.47	7.3	3.6
2	61.6[c]		15.7	13.2	13.7	8.5	4.2
3	54.6				17.9	7.6	3.8
			In Dichloromethane				
1	74.3[c]				4.79	2.6	1.3
2	67.4		15.7	14.9	6.70	2.8	1.4
3	59.0				9.02	2.5	1.2

[a] Number-averaged number of repeat units. [b] In units $\times 10^{-6}$ cm²/s. [c] Data may be slightly in error because they are extrapolated from those fractions with lower molecular weights assuming that $R_{nV} \propto M^{1/2}$.

already been described in detail.[14] The values for the three fractions in different solvents are summarized in Table III.

End-Group Diffusion Coefficients. It has been demonstrated[15] that as end-group diffusivity increases the value of E, energy-transfer efficiency between the end groups increases. Thus, energy-transfer efficiency is a function of D, τ, R_0, and R_n. For each given set of D, τ, R_0, and R_n values, a numerical solution for E is possible. If we accept R_{nV}, R_n determined from viscometry measurements, as the correct root-mean-square end-to-end distances of the samples, the effective end-group diffusion coefficient D is then the only parameter required to uniquely specify the value of E. The D values thus determined from measurement of E are given in Table III.

The change in end-to-end distance between the end groups has been visualized as being caused by the Brownian motion of one end of the chain in space. The diffusional motion of the moving end in space was further pictured as being comprised of many small jumps of distance δ_r along the radial direction occurring with high frequency ψ.[21] The effective diffusion coefficient of the end group is defined as

$$D = (1/2)\psi\delta_r^{\,2} \tag{11}$$

Actually, both ends make jumps in space. The effective diffusion coefficient of the end groups is the sum of the diffusion coefficients, D_{end}, of the individual ends

$$D = D_{end\ 1} + D_{end\ 2} = 2D_{end} \tag{12}$$

In eq 12, equality in end-group diffusion coefficients has been assumed. This assumption is rigorously satisfied if polymer chain end groups possess the same structure.

Discussion

D_{end}, diffusion coefficients of individual chain ends, have been calculated with eq 12 and are summarized in Table III. Two trends can be noticed for the sets of D_{end} values from Table III: (1) D_{end} is the highest in acetonitrile, lower in ethyl acetate, and the lowest in dichloromethane, and (2) as the polymer chain length increases, D_{end} first increases and then decreases.

At 20 °C, the temperature at which these experiments were performed, ethyl acetate ($\eta = 0.455$ cP) is more viscous than acetonitrile ($\eta = 0.359$ cP), and D_{end} of each fraction should therefore be higher in acetonitrile than in ethyl acetate. This is in agreement with experimental results. Dichloromethane is less viscous than ethyl acetate. D_{end} values in dichloromethane are, however, much lower than those in ethyl acetate. It appears that the D_{end} values either in ethyl acetate and acetonitrile or in dichloromethane are erroneous.

In Table IV, the end-group diffusion coefficients of fraction 1 in different solvents are compared with the translational diffusion coefficients of a sample of $\bar{M}_w = 1.6 \times 10^4$ measured by ter Meer and Burchard.[19] According to eq 1, the coefficient of end-group diffusion is higher than the translational diffusion coefficient of the corresponding polymer chain but lower than that of a free segment. D_{end} values of our samples are on the order of 10^{-6} cm²/s, which is 1 order of magnitude smaller than the diffusion coefficient of small molecules.[6] The D_t values of the polymer coils are the lower limit for the diffusion coefficients D_{end} of the end groups. Comparison between D_{end} and D_t suggests that D_{end} measured in ethyl acetate and acetonitrile appears to be correct.

Table IV
Comparison of the Translational Diffusion Coefficient D_t of a PMMA Sample ($\bar{M}_w = 1.6 \times 10^4$) with the End-Group Diffusion Coefficient of Fraction 1

solvent	$\bar{M}_w$	η (cP)/T (K)	D_t, cm²/s	D_{end}, cm²/s
butyl choride	1.6×10^4	0.391/307.5	2.24×10^{-6}	
acetone	1.6×10^4	0.324/293	2.71×10^{-6}	
acetonitrile	1.4×10^4	0.359/293		4.0×10^{-6}
ethyl acetate	1.4×10^4	0.455/293		3.6×10^{-6}
dichloromethane	1.4×10^4	0.429/293		1.3×10^{-6}

The inaccuracy in D_{end} values measured in dichloromethane can be attributed to the inaccuracy in R_{nV} calculations. When calculating R_G from R_h using eq 9 in all solvents including methylene chloride, a good solvent for PMMA, we have used the ξ value for high molecular weight samples in a Θ-solvent. In acetone, a good solvent for PMMA, the ξ value has been determined to be 1.555 for high molecular weight PMMA samples. If higher ξ values are used in eq 9 for calculating R_G in methylene chloride, the R_{nV} obtained in dichloromethane will be higher and the D_{end} fitted from eq 5 will be higher. The increase in D_{end} values fitted by using increasing R_n values has been demonstrated by an iso-energy-transfer-efficiency curve illustrated in Figure 1 generated from the data given in Table V. For each set of D_{end} and R_n values, the energy-transfer efficiency fitted is always 16.4%, the experimentally measured one in acetonitrile for fraction 1.

In all three solvents, D_{end} values of fraction 2 were highest among the three fractions. This could be an experimental artifact and may be accounted for by the errors in R_{nV} values as well. As molecular weight decreases, the assumption that polymer coils are nondraining is more erroneous. According to Kirkwood and Riseman,[20,22] the draining parameter for a polymer coil is given by

$$X = \frac{n^{1/2}\zeta}{(6\pi^3)^{1/2}\eta_0\beta} \tag{13}$$

where ζ is the friction coefficient of each individual segment

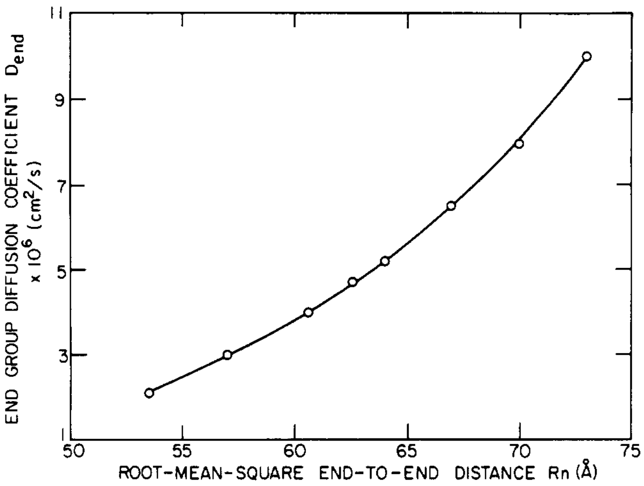


Figure 1. Iso-energy-transfer-efficiency curve illustrating the increase in D_{end} values fitted by using increasing R_n values.

Table V
R_n and D_{end} Readings on an Iso-Energy-Transfer-Efficiency Curve[a]

R_n, Å	$D_{end} \times 10^6$, cm^2/s	R_n, Å	$D_{end} \times 10^6$, cm^2/s
53.5	2.1	64.0	5.2
57.0	3.0	67.0	6.5
60.6	4.0	70.0	8.0
62.6	4.7	73.0	10.0

of a polymer chain possessing n segments, η_0 is the viscosity of the solvent, and β is the effective length of the segment. The coil is nondraining if $X \rightarrow \infty$ and free draining if $X \rightarrow 0$. Since X is proportional to $n^{1/2}$, as n decreases, X decreases and the polymer coils become more draining.

In acetonitrile, a Θ-solvent for PMMA, the R_n determined from our viscometry measurements for fraction 1 yields a value of 60.6 Å. In a previous paper,[14] the root-mean-square end-to-end distance of fraction 3 in a PMMA matrix, a Θ-solvent, was determined to be 48.4 Å by the spectroscopic ruler technique. If we assume that $R_n \propto n^{1/2}$ holds for samples in this molecular range, R_n for fraction 1 can be extrapolated to be 53.5 Å. According to ter Meer and Burchard,[19] R_h, the hydrodynamic radius measured for high molecular weight samples in a Θ-solvent from dynamic light scattering experiment, is related to $\bar{M}_w$ by

$$R_h = 0.191\bar{M}_w^{0.498} \text{ (Å)} \qquad (14)$$

For fraction 1, $\bar{M}_w$ has been determined to be 14 000, and the R_h value is therefore extrapolated to be 22.1 Å. By using eqs 9 and 10, one obtains an R_{nV} value of 62.6 Å. The average of the R_n from the three different techniques is 58.9 Å.

The D_{end} values fitted with R_n values from the three different techniques are 4.0×10^{-6}, 2.1×10^{-6}, and 4.7×10^{-6} cm^2/s, respectively. The average D_{end} value is 3.6×10^{-6} cm^2/s, and the standard deviation for D_{end} is 1.3×10^{-6} cm^2/s. The standard deviation for fractions 2 and 3 should be of the same magnitude. In ethyl acetate and dichloromethane higher percentage errors are expected due to greater uncertainty in the ξ value in eq 9.

Conclusions

The feasibility of a new method for end-group diffusion coefficient measurement has been demonstrated. With PMMA samples in the $\sim 10^4$ molecular weight range, diffusion coefficients of the right order of magnitude have been obtained. The main error in D_{end} evaluation arises from uncertainty in R_{nV} measurement for samples of this molecular range. For future studies, polymer samples of higher molecular weight range should be used. Additional experiments with the samples studied would involve the determination of the diffusion coefficients of polymer chain end chromophores using NMR pulse-gradient spin–echo experiments and would use them to fit root-mean-square end-to-end distances, R_{nE}. The fitted R_{nE} values can be used to relate to R_{nV} and therefore allow the determination of ξ factors in eq 9.

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Registry No. PMMA, 9011-14-7; butyl chloride, 109-69-3; acetone, 67-64-1; acetonitrile, 75-05-8; ethyl acetate, 141-78-6; dichloromethane, 75-09-2.