of sensitizing an extrinsic quencher should increase with molecular weight because of the increased probability of an exciton encountering a quencher.

The inhomogeneity present in polymer, excited-state, quenching experiments of the type herein does not seem to have been explicitly recognized in earlier studies. It is difficult to treat this inhomogeneity more quantitatively than the simple estimate provided in the previous section, part A. Fluctuations around some average number of quenchers per polymer chromophore can be treated as a random event if no specific quencher–polymer solvation occurs.[12] Since not only the number of quencher contacts can vary, but also their "type" (i.e., orientation of the quencher–chromophore pair), it is doubtful that more than a qualitative theory of these contacts is possible for solids. For liquids, a number of quencher–chromophore orientations can be established during the excited state lifetime of the latter which may simplify the analysis of the effect of the quencher.

Work on other polymer systems using the technique described herein is continuing, as well as efforts to provide a convenient theoretical framework to describe the kinetics of the exciton population in an essentially inhomogeneous population.

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References and Notes

(1) J. Eisinger and R. G. Shulman, *Proc. Natl. Acad. Sci. U.S.A.*, **55**, 1387 (1966).

(2) G. I. Lashkov and V. L. Ermolaev, *Opt. Spektrosk.*, **22**, 462 (1967).

(3) The first report of intramolecular delayed fluorescence was by R. F. Cozzens and R. B. Fox (*J. Chem. Phys.*, **50**, 1532 (1969)) for poly(1-vinylnaphthalene). Later J. W. Longworth and M. D. C. Battista (*Photochem. Photobiol.* 11, 207 (1970)) reported the same phenomenon for poly(L-tyrosine) and poly(adenylic acid).

(4) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969). For related work on copolymers of P1VN, see: R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 2284 (1972); and R. B. Fox, T. R. Price, R. F. Cozzens, and W. H. Echols, *Macromolecules*, **7**, 937 (1974).

(5) N. F. Pasch and S. E. Webber, *Chem. Phys.*, **16**, 361 (1976).

(6) A. C. Sommerset and J. E. Guillet, *Macromolecules*, **6**, 218 (1973).

(7) N. F. Pasch and S. E. Webber, *Macromolecules*, **11**, 727 (1978).

(8) C. David, M. Lempereur, and G. Geuskens, *Eur. Polym. J.*, **8**, 417 (1972); some comparisons are made between poly(1-vinylnaphthalene) and poly(acenaphthylene) in this paper.

(9) For an earlier, preliminary report using this technique, see: S. E. Webber, *J. Photochem.*, **9**, 269 (1978). In this earlier report, the polymer sample was P2VN-6.

(10) The designations 3 and 6 are the same as those used in a previous publication (ref 5) for these polymer samples.

(11) In a recent paper, M. P. Schuh (*J. Phys. Chem.*, **82**, 1861 (1978)) includes quenching without energy transfer in the mechanism for *cis*-piperylene quenching of gas phase alkyl benzenes. In addition, this paper provides evidence for steric specificity for effective quencher action.

(12) If the probability of a quencher contacting a naphthalene moiety is random, then we would expect the distribution of quencher–polymer contacts to obey a Poisson distribution of the form $p_n = (L/N_{\mathrm{CH}})^n e^{-L/N_{\mathrm{CH}}}/n!$, where p_n is the probability of n quencher contacts with a polymer containing L chromophores.

(13) Similar to quencher contacts, photon excitation is a random event, such that the probability of n excitons occurring on a segment of length L is given by $p_n = (L/L_0)^n(e^{-L/L_0}/n!)$, where L_0 is the length of polymer required for an average of one excitation (a typical value of L_0 might be 50 to 200, depending on the excitation source). If $L/L_0 < 1$, then p_n for $n > 1$ is small.

(14) The decay rate of P2VN-6 is so enhanced by the presence of biacetyl that extracting a meaningful value of K_{E} for higher biacetyl concentrations is difficult.

(15) Fits of the data to a double exponential (with one decay rate constrained to equal the unquenched phosphorescence) were performed at the Center for Fast Kinetics Research at the University of Texas at Austin.

(16) The trend for P2VN-3 in lifetimes has certain "reversals" in it (i.e., compare the 1.23×10^{-3} and 2.61×10^{-3} data). This probably arises from the inaccuracies in fitting the data to a "constrained" double exponential function.

(17) The phosphorescence decay of P2VN-6 will be nonexponential at higher excitation intensities, where biexcitonic annihilation makes a significant contribution to the phosphorescence decay rate.

(18) N. F. Pasch, R. D. McKenzie, and S. E. Webber, *Macromolecules*, 11, 733 (1978).

Contribution to the Study of the Mean Square End-to-End Distance $\langle r_n^2 \rangle$ of a Polymer Chain

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ABSTRACT: A recurrence equation is proposed to calculate the mean end-to-end distance $\langle r_n^2 \rangle$ of a polymer chain of length n, when we know the mean end-to-end distance of a chain of length $n - 2$ and the mean end-to-end distance $\langle r_n^2 \rangle_0$ of the class of configurations of the chain n having $x = 0$ primary contacts between nearby segments. We have established for $\langle r_n^2 \rangle_0$ equations of the type $\langle r_n^2 \rangle_0 = n^{E_n^0}$ where the exponent is a function of n.

In a preceding work,[1] we have drawn systematically all the configurations that a polymer chain of n segments can take on a square-planar lattice. These drawings were made up to $n = 11$ (about 6000 configurations, after elimination of the configurations which are identical by symmetry). Then we classified the configurations, taking into account the number x of primary contacts, between nearby segments, presented by each of these configurations.[2] This type of primary contact occurs between neighboring segments of the chain (segments p and $p + 3$), if the distance between them is equal to the side of the lattice cell (Figure 1).

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Table I

	n = 2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\langle r_n{}^2\rangle$	1	2.4	3.88	5.553719	7.234295	9.070548	10.897236	12.845084	14.780576	16.817245	18.841373	20.952845	23.052131	25.228468

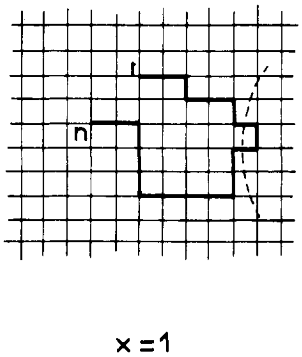

Figure 1. The cutting off of two beads decreases the chain length by 2 without alteration of the end-to-end distance. The number y of secondary contacts between nearby segments decreases by 2.

For each value of x, we also classified the configurations, taking into account the number y of secondary contacts between nearby segments (segments p and $p + 2$); the distance between these segments is equal to the diagonal of the lattice cell.

Proceeding in this way, we obtained $n/2$ classes of configurations for n even and $(n - 1)/2$ for n odd. Indeed, the number of primary contacts between nearby segments that can form a chain of length n varies between $x = 0$ and $x_{\max} = (n - 2)/2$ for n even and $(n - 3)/2$ for n odd.[2] For each of these classes of configurations, we measured, on the drawings, the end-to-end distances. We thus came to the following observation: a class of configurations of the chain of length n, presenting x primary contacts between nearby segments, has the same mean end-to-end distance as the class of configurations of a polymer chain of length $n - 2x$, having $x = 0$ primary contacts between neighboring segments. Figure 1 shows indeed that this can be explained by the fact that the presence of a first contact "shortens" the length of the chain by two segments (the two segments are separated on Figure 1 by a dotted line).

Thus, the mean end-to-end distance of the class of configurations of the chain n, with $x = 0$, will be specific for this chain length. But the mean end-to-end distance of the class of configurations of the chain n with $x = 1$ primary contacts will be the same as the mean end-to-end distance of the configurations of a chain of length $n - 2$ with $x = 0$ primary contacts; the mean end-to-end distance of the class of configurations of the chain n with $x = 2$ will be the same as the mean end-to-end distance of the configurations of a chain of length $n - 4$ with $x = 0$ primary contacts or of a chain of length $n - 2$ with $x = 1$ primary contacts. Similarly, the mean end-to-end distance of the class of configurations of the chain n with $x = 3$ is the same as the mean end-to-end distance of the configurations of a chain of length $n - 6$ with $x = 0$, or of the configurations of a chain of length $n - 4$ with $x = 1$, or of a chain $n - 2$ with $x = 2$, and so on. This reasoning is valid for any value of x and allows us to write the following recurrence relation:

$$\langle r_n{}^2\rangle = \gamma\,\langle r_n{}^2\rangle_0 + (1 - \gamma)\,\langle r_{n-2}{}^2\rangle \tag{1}$$

where: $\langle r_n{}^2\rangle_0$ is the mean end-to-end distance of the class of configurations of the chain n with $x = 0$ primary contacts; $\langle r_{n-2}{}^2\rangle$ is the mean end-to-end distance for all the configurations of a chain of length $n - 2$. For these configurations x varies between 0 and $x_{\max}$ and $\gamma = [N]_n{}^{x=0}/C_n$, where $[N]_n{}^{x=0}$ is the number of configurations of the chain of length n having $x = 0$ primary contacts and C_n is the total number of configurations of this chain.

For a cubic lattice, eq 1 is a good approximation (see below). In a preceding article,[3] we have shown how we can calculate $[N]_n{}^{x=0}$ and C_n, for every value of n and for a three-dimensional lattice. In order to be able to make use of the recursion eq 1, we must find an algebraic relation to determine $\langle r_n{}^2\rangle_0$ for every value of n.

The class of configurations with $x = 0$ primary contacts is the easiest to study among all of the classes of configurations of the chain of length n that we have defined above. With the help of drawings, we have established eq 2 and 3, valid for a cubic lattice chain. We had to take into account the parity of n. Indeed, there is a rather strong oscillatory behavior of $\langle r_n{}^2\rangle$ depending on the parity of n, as other authors have also noted.[4] Letting $\log \langle r_n{}^2\rangle_0 = E_n{}^0 \log n$ we have for n even

$$E_n{}^0 = \frac{6(n-1)}{5n} + (n-3)\left[(3/10n) + 1\Big/\left\{[(n-2) + (n-8) + (n-14) + \ldots]\left[n + A\left\{\frac{1}{n} + \frac{1}{n^3} + \frac{1}{n_5} + \ldots\right\}\right]\right\}\right] + \frac{(n-4)\frac{1}{n^3} + (n-8)\frac{1}{n_5} + (n-12)\frac{1}{n^7} + \ldots}{2 + n + \frac{1}{n} + \frac{3}{2}\frac{1}{n^2} + \frac{7}{4}\frac{1}{n^3} + \frac{11}{6}\frac{1}{n^4} + \ldots} - \frac{6}{5}\frac{1 + (n-4)C}{(n-1)^2 + 3(n-3)^2 + 5(n-5)^2 + \ldots}\frac{1}{n} - (n-3) \times \left\{\frac{1}{10}\frac{1}{n^3} + \frac{1}{29}\frac{1}{n^5}\left[\frac{1 + B\{(n-7) + (n-14) + \ldots\}}{n-2}\right]\right\} \tag{2}$$

where $A = (n - 4)(n - 6) + 2(n - 5)(n - 7) + 3(n - 6)(n - 8) + \ldots$; $B = 2(n - 5)(n - 6) + 3(n - 6)(n - 7) + 4(n - 7)(n - 8) + \ldots$; and $C = n - 1 + 2[\{(n - 3)/3n\} + [3(n - 4)/5n^3] + [5(n - 5)/7n^5] + [7(n - 6)/9n^7] + \ldots]$. For n odd

$$E_n{}^0 = \frac{6(n-1)}{5n} + (n-3)\left[(3/10n) + 1\Big/\left\{[(n-1) + (n-7) + (n-13) + \ldots]\left[n + A\left\{\frac{1}{n} + \frac{1}{n^3} + \frac{1}{n^5} + \ldots\right\}\right]\right\}\right] + \frac{(n-4)\frac{1}{n^3} + (n-8)\frac{1}{n^5} + (n-12)\frac{1}{n^7} + \ldots}{2 + n + \frac{1}{n} + \frac{3}{2}\frac{1}{n^2} + \frac{7}{4}\frac{1}{n^3} + \frac{11}{6}\frac{1}{n^4} + \ldots} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1}{n^6}\left[\frac{1 + B\{(n-7) + (n-14) + \ldots\}}{n-1}\right] \tag{3}$$

where $A = (n - 4)(n - 6) + 2(n - 5)(n - 7) + 3(n - 6)(n$

$- 8) + \ldots$ and $B = 2(n - 5)(n - 6) + 3(n - 6)(n - 7) + 4(n - 7)(n - 8) + \ldots$.

Discussion of Equation 1

Let us call $\langle r_{n-2}^2\rangle_{\text{bound}}$ the mean end-to-end distance of the population of configurations of chain $n - 2$ obtained by removing the two segments of a primary contact of the configurations of the chain n and $\langle r_{n-2}^2\rangle_{\text{free}}$ the mean end-to-end distance of the total number C_{n-2} of configurations of the chain $n - 2$. When in eq 1 we replace $\langle r_{n-2}^2\rangle_{\text{bound}}$ by $\langle r_{n-2}^2\rangle_{\text{free}}$ we make a good approximation, which rapidly becomes better as n increases. This allows us to determine rather good values of $\langle r_n^2\rangle_0$ since γ is known. These values can be calculated by eq 2 and 3. For numerical application, one has to remember that the terms $n - i$ can never be applied if they are negative. For $i > n$, the term disappears.

In the literature,[4] we can find values of $\langle r_n^2\rangle$ obtained by many authors, using exact enumeration. These values, considered as accurate up to $n = 15$, are given in Table I. They have been obtained for simple cubic lattice chains. These values allowed us to test the validity of our relations 2 and 3. The results given by these equations are practically the same as the values of Table I, from $n = 2$ to 15.

We now give some examples of numerical applications of eq 2 and 3: (1) For $n = 2$ (eq 2)

$$E_2^{\,0} = \frac{6(n-1)}{5n} - \frac{6}{5}\frac{1}{(n-1)^2}\frac{1}{n} = 0$$

$$\gamma = 0; \qquad \langle r_2^2\rangle = \langle r_2^2\rangle_0 = 2^0 = 1$$

(2) For $n = 3$ (eq 3)

$$E_3^{\,0} = \frac{6(n-1)}{5n} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1}{n-1}\frac{1}{n^6} = 0.79688615$$

For $n = 3$, there are no configurations presenting first contacts between nearby segments, then $\gamma = 1$ and $\langle r_3^2\rangle = \langle r_3^2\rangle_0$. (3) For $n = 5$, by eq 3

$$E_5^{\,0} = \frac{6(n-1)}{5n} + (n-3)\left[\frac{3}{10n} + \frac{1}{n(n-1)}\right] + \frac{1}{n^3}\left[n + 2 + \frac{1}{n} + \frac{3}{2}\frac{1}{n^2} + \frac{7}{4}\frac{1}{n^3} + \frac{11}{6}\frac{1}{n^4} + \ldots + \frac{35}{18}\frac{1}{n^{10}}\right]^{-1} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1}{n-1}\frac{1}{n^6} = 1.18069861$$

$$A = 0; \qquad B = 0$$

Then $\langle r_5^2\rangle_0 = 5^{1.18069861} = 6.68764045$

$$[N]_5^{\,0} = 534 \text{ and } C_5 = 726; \qquad \gamma = 0.73553719$$

Therefore by eq 1

$$\langle r_5^2\rangle = \gamma\langle r_5^2\rangle_0 + (1-\gamma)\langle r_3^2\rangle = 5.55371909$$

For $n = 15$

$$A = (n-4)(n-6) + 2(n-5)(n-7) + 3(n-6)(n-8) + 4(n-7)(n-9) + 5(n-8)(n-10) + 6(n-9)(n-11) + 7(n-10)(n-12) + 8(n-11)(n-13) + 9(n-12)(n-14) = 1.155$$

$$B = 2(n-5)(n-6) + 3(n-6)(n-7) + 4(n-7)(n-8) + 5(n-8)(n-9) + 6(n-9)(n-10) + 7(n-10)(n-11) + 8(n-11)(n-12) + 9(n-12)(n-13) + 10(n-13)(n-14) = 1.320$$

$$E_{15}^{\,0} = \frac{6(n-1)}{5n} + (n-3)\left[\frac{3}{10n} + \left[1/[(n-1) + (n-7) + (n-13)]\left[n + A\left\{\frac{1}{n} + \frac{1}{n^3} + \frac{1}{n^5} + \frac{1}{n^7}\right\}\right]\right]\right] + \left\{\left[(n-4)\frac{1}{n^3} + (n-8)\frac{1}{n^5} + (n-12)\frac{1}{n^7}\right]\Big/\left[n + 2 + \frac{1}{n} + \frac{3}{2}\frac{1}{n^2} + \frac{7}{4}\frac{1}{n^3} + \frac{11}{6}\frac{1}{n^4} + \frac{15}{8}\frac{1}{n^5} + \frac{19}{10}\frac{1}{n^6}\right]\right\} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1 + B[(n-7) + (n-14)]}{n-1}\frac{1}{n^6} = 1.36559806$$

Then $\langle r_{15}^2\rangle_0 = 15^{1.36559806} = 40.37085448$. In a preceding article,[3] we showed how to calculate $[N]_{15}^{x=0}$. We found $[N]_{15}^{x=0} = 984\,003\,000$. The value of C_{15} considered as accurate is $C_{15} = 4\,468\,921\,678$. Then $\gamma = 0.22018851$ and $\langle r_{13}^2\rangle = 20.952845$. Hence $\langle r_{15}^2\rangle = \gamma\langle r_{15}^2\rangle_0 + (1-\gamma)\langle r_{13}^2\rangle = 25.22846758$.

References and Notes

(1) M. Lautout-Magat, *J. Polym. Sci., Part C*, **4**, 453 (1963).
(2) M. Lautout-Magat, *J. Chim. Phys. Phys.-Chim. Biol.*, **66**, 1345 (1969).
(3) M. Lautout-Magat, *Macromolecules*, **10**, 1375 (1977).
(4) A. Bellemans, *Physica (Utrecht)*, **68**, 209 (1973).

Theory of Adsorption of Macromolecules. 1. The Desorption–Adsorption Transition Point

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ABSTRACT: The general theory of adsorption of a single long ideal polymer chain on the surface is developed. The basic equation for the adsorption–desorption phase transition point is derived. In the phase transition point the grand partition functions of sequences of units adsorbed on the surface or on the thread are shown to be equal to 1. The equations connecting the critical energy of adsorption with the conformational partition functions of units on the surface and in volume are obtained. In order to show the generality of the derived equations, they are applied to determination of the critical adsorption energies for a number of model chains considered previously elsewhere. The developed theory may be used as a base for the creation of the quantitative theory of adsorption of macromolecules (as far as the determination of the phase transition point is concerned).

I. Introduction

The process of adsorption of macromolecules is of considerable interest both with respect to its practical use and to theoretical aspects as an example of conformational transition. A single ideal polymer chain adsorbed on a homogeneous (and usually flat) surface is the simplest

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