Table III
Photoinduced pK Increase ($\Delta pK = pK^* - pK$) for Quinoline in 2MQ and P2VQ

	$\Delta pK_{exptl}{}^{a}$	$\Delta pK_{em}{}^{b}$	$\Delta pK_{ex}{}^{b}$	$\Delta pK_{av}{}^{c}$
2MQ	0	9.9	9.3	9.7
P2VQ	1.4	9.2	3.5	7.1

[a] Experimental results. [b] Calculated by the Förster cycle using emission (ΔpK_{em}) and excitation (ΔpK_{ex}) data. [c] Calculated by the Förster cycle using the average of excitation and emission wavelengths.

averages[1] of those two values. The closest approach to experimental results in the P2VQ case corresponds to excitation data, in agreement with previous arguments about the electronic excited state involved in proton-transfer reactions, the Franck–Condon level. For 2MQ, ΔpK calculated values overestimate the experimental result. Perhaps solvent relaxation in this case is faster than the proton-transfer reaction and the equilibrium excited state is not able to react.

Differences in ground-state basicity and excited-state behavior for the polymer and the monomer analogue suggest that the chromophore approach by solvent molecules is very different in the two cases. Chromophore packing in the polymer chain and steric hindrance of the backbone, which is especially important in position 2,[15] make the quinoline–solvent interaction difficult. As a consequence, local dielectric constant and ground-state basicity are different for the polymer and the monomer analogue, and that influences too the rate of proton-transfer reaction with respect to the rate of solvation atmosphere relaxation.

Conclusions

Several polymer effects have been observed from comparison of the ionization equilibria of P2VQ and its monomer analogue 2MQ. (i) Ground-state basicity is much smaller for the polymer than for the small compound. (ii) P2VQ suffers proton-transfer reactions in the first singlet excited state and 2MQ does not. (iii) Charge-transfer complexes with counterions quench the emission at lower acid concentrations for the polymer than for 2MQ.

These effects are explained by the following arguments: (i) Excitation produces chromophore conformational changes both in the polymer and in the monomer analogue. (ii) Proton-transfer reactions occur from Franck–Condon excited states and compete with solvent relaxation, both in the polymer and in the monomer analogue. (iii) Solvent molecule approach to quinoline is different in 2MQ and P2VQ. As a consequence, proton-transfer reactions are faster than solvent relaxation processes in the polymer case, but the opposite is true for 2MQ. This also explains the ground-state behavior of both compounds.

These interpretations are in agreement with Stokes shifts and calculated pK values.

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Registry No. 2MQ, 91-63-4; P2VQ, 33638-30-1.

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Photophysics of Polystyrene. 1. A Monte Carlo Study

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ABSTRACT: Investigations have been carried out on intramolecular excimer formation, quantum yields, times of fluorescence decay, and energy migration (EM) in polystyrene (PS) as a function of molecular weight by using the Monte Carlo method. Mechanisms (resonance and exchange) that may be responsible for PS luminescence have been discussed, and it has been shown that the exchange (Dexter's) mechanism is more appropriate in the description of the EM process. The observed differences in quantum yield obtained by experiment and by Monte Carlo simulation have been explained by PS chain dynamics, which are not taken into account in the simulation. The following photophysical parameters of PS have been determined: concentration of excimer-forming sites, average time of energy hop between chromophoric groups, average number of energy hops, and average square of the angle between electronic transition moments in phenyl groups.

I. Introduction

Investigations of migration and transfer of electronic excitation energy have been conducted on a number of substances, which, owing to the distribution of luminescent molecules, may be divided into homogeneous and nonhomogeneous substances.

The study of luminescence processes in nonhomogeneous systems, which include, among others, biological cells, micelles, microemulsions, and natural and synthetic macromolecules, is important both from the scientific and from the application point of view.

Previous efforts to describe theoretically the energy-transport processes in synthetic macromolecules may be divided into three groups. In the first group of works,[1] the authors have applied a phenomenological scheme based on simple kinetics of luminescence processes. The proposed models allowed the determination of deactivation rate constants of the macromolecule's excited states and made the analysis of the kinetics of these processes possible. In the second group of works,[2] a description of energy migration (EM) aided by the diffusion process has allowed the determination a number of macromolecular luminescence parameters. However, application of the diffusion approximation of copolymers[3,4] containing short sequences of luminescently active monomers leads to difficulties in interpretation. Finally, in the third group of works,[5,6] the authors have used a model of energy random walk, where the walk is limited by physical ends of the macromolecule or intramolecular excimers.

One may notice that the above-mentioned models almost completely neglect the macromolecule's topology. From the luminescence point of view, there exist at least two topological factors that distinguish diluted solid or liquid solutions of macromolecules from the same solutions of small molecules. First, chromophoric groups of a macromolecule do not form a random set but are correlated by covalent bonds forming the chain. Chromophoric groups bonded in this way in vinyl macromolecules are well described by configurational statistics worked out by Flory.[7] Second, a macromolecule is a spatially finite object, and the number of chromophores sampled by excitation energy is limited. For these reasons, in the case of solutions of macromolecules, the application of theoretical models worked out for homogeneous and infinite systems seems to be difficult to justify.[8]

Recently,[9] during investigation of the energy transport time dependence of the fluorescence depolarization of copolymers of vinylnaphthalene and methacrylate in poly(methyl methacrylate) and poly(ethyl methacrylate), the proposed theoretical description of energy transport in macromolecules[10,11] was tested. It was shown that the key problem is to take a proper account of distribution of chromophoric groups in the macromolecule.

In spite of a few works questioning the EM process in polystyrene[12] and poly(2-vinylnaphthalene),[13] many experimental works[14-18] have shown that the EM process takes place in the aforementioned and other macromolecules. However, both theoretical and experimental studies have failed to supply explicit information concerning the mechanism responsible for the EM process in synthetic vinyl macromolecules. Very few authors[19,20] have mentioned the possibility of EM taking place in real macromolecules through the resonance mechanism,[21] which assumes long-range resonance interaction between electric dipoles of chromophoric groups. However, justification of the resonance mechanism of EM in view of close-packing of chromophoric group as well as overlapping of electron clouds seems to be rather difficult.[14,22]

The Monte Carlo method, often called a numeric experiment,[23] offers interesting possibilities of detailed analysis of luminescent processes in macromolecules. The Monte Carlo method allows one to take into account in a natural way the macromolecules' topology, which, as has already been mentioned, decides the specific character of luminescent processes. This is well illustrated by the recent works of Frank et al.,[5,6] in which Monte Carlo simulation was used to analyze a model of energy random walk in poly(2-vinylnaphthalene) and polystyrene (PS).

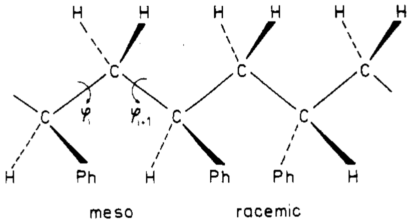

Figure 1. Protion of the PS chain with meso and racemic diads.

Table I
Averaged Conformation Angles $\langle\varphi_i\rangle$ and $\langle\varphi_{i+1}\rangle$ at $T = 300$ K and $\sigma = 5.0$ Å[25]

conformation	$\langle\varphi_i\rangle$, $\langle\varphi_{i+1}\rangle$, deg	conformation	$\langle\varphi_i\rangle$, $\langle\varphi_{i+1}\rangle$, deg
meso tt	22, 22	racemic tt	9, 9
meso tg	6, 110	racemic tg	20, 87
meso gt	110, 6	racemic gt	87, 20
meso gg	92, 92	racemic gg	105, 105

In this paper, we have carried out a Monte Carlo simulation of photophysical processes in a diluted solution of PS. Section II contains a description of the method of simulation of PS and estimation of excimer-forming population. Section III describes the method of simulation of photophysical processes in PS. Results of Monte Carlo calculations and their analysis, stressing the EM mechanism, are presented in section IV. In section V we have summarized the results of the paper.

II. Simulation of a Polystyrene Macromolecule

1. Description of the Method. A Monte Carlo simulation of a macromolecule may be carried out on the basis of lattice or off-lattice spatial arrangement.[24] In the first case, the chain is simulated by a random walk in various lattice systems such as cubic, tetrahedral, and others. In the second case, the chain is generated in a continuous space. The relative directions of two successive bonds may be chosen either completely at random or with fixed bond angles.

A single polystyrene chain has been generated in a continuous space in an off-lattice manner. Successive joining of the following segments of the simulated chain is carried out by the random-number generator.

Relative directions of neighboring bonds of the chain are determined by conformational properties of polystyrene.[25] Each diad of neighboring styrene mers is a meso or racemic type (Figure 1) depending on the relative position of phenyl groups. Additionally, each diad is in one of four conformations, which is a combination of trans (t) and gauche (g) states. Individual conformations have different values of torsional angles of skeleton bonds φ_i and φ_{i+1} (Table I). The torsional angles φ_i and φ_{i+1} are measured in right- and left-handed directions, respectively (Figure 1).

At the beginning of simulation, the distribution of meso and racemic diads was determined randomly, while the fraction of meso diads was assumed a priori. Conformation of each diad was determined randomly on the basis of probabilities given by Flory. The probability that meso or racemic diad r is in conformation $\beta\gamma$ on a chain made of x repeating units is given by[26]

$$P_{(\beta\gamma)r} = Z^{-1}\mathbf{J}^*\Big(\prod_{n=1}^{r-1}\mathbf{U}_n{}^{(2)}\Big)(\mathbf{U}'_r\mathbf{U}''_{(\beta\gamma)r})\Big(\prod_{n=r+1}^{x-1}\mathbf{U}_n{}^{(2)}\Big)\mathbf{J} \quad (1)$$

where Z is the partition function

$$Z = \mathbf{J}^*\Big(\prod_{n=1}^{x-1}\mathbf{U}_n{}^{(2)}\Big)\mathbf{J} \quad (2)$$

and the matrices are defined as

$$\mathbf{J}^* = [1 \quad 0 \quad 0 \quad 0] \qquad \mathbf{J} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad \mathbf{U}^{(2)} = \mathbf{U}'\mathbf{U}'' \tag{3a}$$

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \qquad \mathbf{U}''_{\mathrm{meso}} = \begin{bmatrix} w'' & 1/n \\ 1/n & w/n^2 \end{bmatrix}$$
$$\mathbf{U}_{\mathrm{racemic}} = \begin{bmatrix} 1 & w'/n \\ w'/n & 1/n^2 \end{bmatrix} \tag{3b}$$

The matrix $\mathbf{U}''_{\beta\gamma}$ is formed from the matrix $\mathbf{U}''$ by setting all elements except the statistical weight for state $\beta\gamma$ equal to zero. The values of the statistical weights have been reported as[25]

$$\begin{aligned} w = w' &= 1.3 \exp(-1000/T) \\ w'' &= 1.8 \exp(-1100/T) \\ n &= 0.8 \exp(200/T) \end{aligned} \tag{4}$$

where T is the absolute temperature.

The diad in the drawn conformation has been constructed by successive joining of CH_2 and CHPh (Ph stands for phenyl) groups to the simulated macromolecule.

Each group is assigned four vectors in a tetrahedric position corresponding to the bonds between atoms (Figure 2). The vectors are joined in the position of a skeleton carbon atom. The Cartesian coordinates of these vectors for the CHPh group at the beginning of the chain are as follows:

$$\begin{array}{lll} [\ \ 1 & 0 & 0] \\ [-1/3 & 0 & 2(2)^{1/2}/3] \\ [-1/3 & (2/3)^{1/2} & -(2)^{1/2}/3] \\ [-1/3 & -(2/3)^{1/2} & -(2)^{1/2}/3] \end{array} \tag{5}$$

The length of each of these vectors is 1, a conventional unit of length corresponding to the real length of the bond between carbon atoms. It has been assumed that interatomic distances and angles between bonds are the same for all conformations. The bond length is 1.5 Å,[25] while the angle between bonds is 109.47 Å.

The joining of CH_2 and CHPh groups was achieved by adding the described tetrahedric vectors rotated through an angle of φ_i or φ_{i+1} corresponding to the conformation of the constructed diad. The axis of rotation was formed by the vector determining the direction of skeleton chain bond (Figure 2). Rotation of vector **X** through an angle φ around the axis determined by the vector having Cartesian coordinates (a, b, c) is made according to the formula

$$\mathbf{X}' = \mathbf{T}^{\mathrm{T}}\mathbf{O}\mathbf{T}\mathbf{X} \tag{6}$$

where matrices are described as follows

transition matrix from normal base to rotated base

$$\mathbf{T} = \begin{bmatrix} \dfrac{c}{R_2} & \dfrac{c}{R_2} & -\dfrac{a+b}{R_2} \\ -\dfrac{(a+b)b+c^2}{R_1R_2} & \dfrac{(a+b)a+c^2}{R_1R_2} & \dfrac{(a-b)c}{R_1R_2} \\ \dfrac{a}{R_1} & \dfrac{b}{R_1} & \dfrac{c}{R_1} \end{bmatrix} \tag{7}$$

where $R_1 = (a^2 + b^2 + c^2)^{1/2}$ and $R_2 = ((a + b)^2 + 2c^2)^{1/2}$

rotation matrix

$$\mathbf{O} = \begin{bmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{8}$$

The phenyl group was joined to the polymer chain by a vector chosen on the basis of whether the diad was of meso or racemic type.

During the simulation of polystyrene macromolecule the excluded volume effect was taken into account. This was done in the following way: the next successive diad in the drawn conformation was not joined to the chain if the distance of the new phenyl group from each of the remaining groups was smaller than the assumed distance. In such a case, due to elasticity of the chain, the remaining possible conformations are drawn. If, however, in each of the four possible conformations the new diad collides with the excluded volume, the whole simulated macromolecule is rejected.

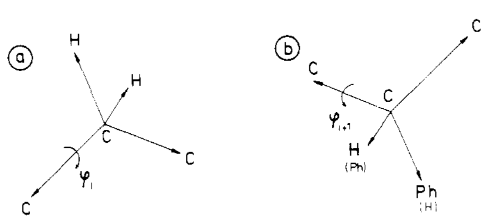

Figure 2. Vectors in tetrahedric position corresponding to groups CH_2 (a) and CHPh (b).

Table II
Fraction of Excimer-Forming Sites (q) in Polystyrene

no. of mers in PS (N)	fraction of EFS (q)	no. of mers in PS (N)	fraction of EFS (q)
10	0.021 ± 0.009	60	0.026 ± 0.003
20	0.025 ± 0.007	70	0.028 ± 0.003
30	0.029 ± 0.004	80	0.036 ± 0.004
40	0.024 ± 0.005	90	0.035 ± 0.004
50	0.024 ± 0.004	100	0.036 ± 0.003

The polystyrene macromolecule was simulated with a 45% meso diad content, which is consistent with the results obtained recently from nuclear magnetic resonance.[27] Statistical weights (eq 4) were calculated for a temperature of 300 K, and the distance at which the solvent shields the macromolecule–macromolecule interaction was taken to be $\sigma = 5$ Å. The critical distance for excluded volume was assumed to be 3 Å.

The complexity of the problem of PS chain generation required costly and time-consuming computer calculations. The photophysical parameters of PS determined in the latter part of this work were averaged for the set of chains constituting a satisfactory statistical sample. Additionally, we have given the values of standard deviation for the estimated parameters.

2. Estimation of Excimer-Forming Site (EFS) Population. The problem of determination of the EFS population in synthetic macromolecules has been discussed in a number of papers, both for copolymers and for homopolymers.[2-6,14,16-18] For homopolymers, the EFS has been estimated on the basis of conformational conditions of excimer formation.[28] Analysis of the conformational energies of meso and racemic PS diads in the ground state has shown[5,6] that only in meso tt diads is excimer formation possible due to a nearly parallel placing of chromophoric groups. Recently,[29] on the basis of a modified version of the Pariser, Parr, and Pople (PPP) method, we have calculated the energy of the two lowest electron transitions in different conformations of meso and racemic PS diads. It has been shown that for electronically excited states the excimer formation is possible only in meso tt diads.

Values of EFS (meso tt diads) obtained during PS simulation are compiled in Table II as a function of the number of mers (N) in the chain. Taking into account the standard deviation determined during the simulation, one may see that the values of EFS (denoted by q) do not depend on the molecular weight of PS. One may note that while estimating the values of EFS, Gelles and Frank[6] also concluded that they do not depend on the molecular weight of PS. The correlation of these results suggests that the excluded volume effect, accounted for in our simulation, has a negligible influence on the probability of meso

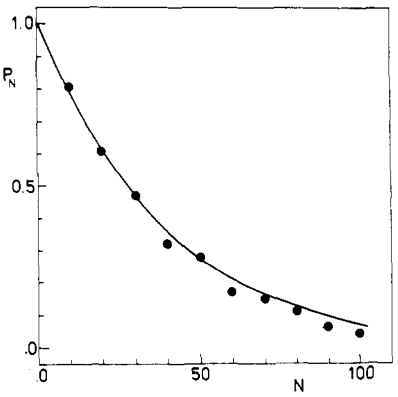

Figure 3. Probability of finding a chain without meso tt diads (P_N) in the set of PS chains as a function of number of mers in PS chain (N). The solid line has been calculated for q = 0.0259, taken from ref 6.

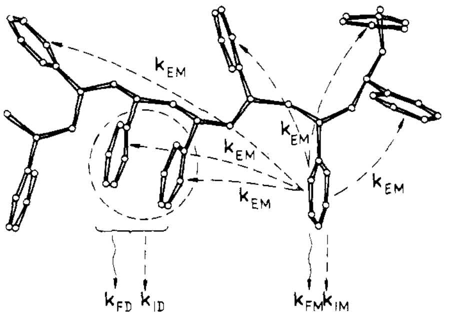

Figure 4. Elementary photophysical processes in PS taken into account in Monte Carlo simulation.

tt diad formation in the PS chain.

In the case of chains of low molecular weight, part of the generated chains did not contain meso tt diads. Gelles and Frank[6] have recently mentioned such effects. The cause of this is the low value of statistical weight of the meso tt diad in comparison with the remaining diads.[25] In Figure 3 we have shown the changes of probability (P_N) of finding a chain without meso tt diads in the set of PS chains as a function of number of mers (N) in the chain. The solid line denotes changes of P_N calculated from the equation $P_N = (1 - q)^{N-1}$, which was recently applied in the analysis of random walk of energy in PS and poly(2-vinylnaphthalene).[5]

III. Simulation of Photophysical Processes in Polystyrene Macromolecules

Macromolecules of PS formed as described in section II have been used to carry out a simulation of photophysical processes. The elementary luminescence processes, given in Table III and shown in Figure 4, have been taken into account in the simulation. It has been assumed that in PS the intramolecular excimers are formed only in meso tt diads[5,6,29] and that the excimer is a nondissociating trap. The neglect of excimer dissociation constitutes a simplification of the problem. However, it seems to be appropriate in the case of PS because the rate constant of excimer dissociation in this macromolecule at room temperature is about 100 times lower than the association rate constant.[30]

Table III
Elementary Photophysical Processes in PS

process	description	rate constant, s^{-1}
$M + h\nu_{ex} \rightarrow M^*$	absorption by monomer	
$-[M-M]- + h\nu_{ex} \rightarrow D^*$	direct excitation of an excimer-forming site	
$M^* \rightarrow M + h\nu_M$	monomer fluorescence	k_{FM}
$M^* \rightarrow M$	monomer internal conversion	k_{IM}
$D^* \rightarrow -[M-M]- + h\nu_D$	excimer fluorescence	k_{FD}
$D^* \rightarrow -[M-M]-$	excimer internal conversion	k_{ID}
$M^* + M \rightarrow M + M^*$	singlet energy migration	k_{EM}
$M^* + -[M-M]- \rightarrow M + D^*$		

The simulation of photophysicl processes in PS has been carried out in the following way. The primary excitation of any phenyl group was chosen by the random-number generator. Next, we checked whether the drawn phenyl group was in meso tt conformation. If not, then a radiative or nonradiative transition of the excited phenyl group to the ground state or an excitation energy hop to another group was possible. The time of energy hop (τ_h) and the time of monomer fluorescence decay (τ_{0M}) resulting from these processes have been estimated according to equations derived from the distribution function of the random process[31] taking the form

$$\tau_h = \frac{-1}{k_{FM} + k_{IM} + \sum k_{EM}} \ln \xi \qquad (9)$$

$$\tau_{0M} = \sum \tau_h - \frac{1}{k_{FM} + k_{IM} + \sum k_{EM}} \ln \xi \qquad (10)$$

where $\xi \in \langle 0,1 \rangle$ and is the random variable of uniform distribution.

EM allows the excitation energy to reach the meso tt diads that form excimers. Excimers may also be formed as a result of direct absorption by phenyl groups in a meso tt diad. The time of excimer fluorescence decay has been simulated by using the following relation:

$$\tau_{0D} = \sum \tau_h - \frac{1}{k_{FD} + k_{ID}} \ln \xi \qquad (11)$$

Quantum yields of monomer and excimer fluorescence, Φ_M and Φ_D, respectively, have been estimated by determining the ratio of the emissions to the total number of excitations.

Electronic excitation EM has been simulated by assuming the resonance or exchange mechanisms. In the case of the resonance mechanism, the EM rate constant has been estimated by using the well-known Förster formula[21] in the form

$$k_{EM} = \frac{3\kappa^2}{2\tau_M}(R_0/R)^6 \qquad (12)$$

where R_0 is the critical radius at which emission and transfer of energy are equally likely, R is the separation between pendant chain groups, $\tau_M = (k_{FM} + k_{IM})^{-1}$, and κ^2 is an orientational factor dependent on the relative orientation of the transition moments.

The rate constant resulting from the exchange mechanism has been estimated by using Dexter's equation[22] in the form

$$k_{EM} = (2\pi/\hbar)KJ \exp(-2R/L) \qquad (13)$$

Here L is an effective average van der Waals radius for the initial and final states, and K is a quantity in units of energy. Usually K cannot be related to experimentally obtainable spectroscopic quantities. J is an overlap integral of the type

$$J = \int_0^\infty F_M(\bar{\nu})\epsilon_M(\bar{\nu})\, d\bar{\nu} \qquad (14)$$

where $F_M(\bar{\nu})$ and $\epsilon(\bar{\nu})$ are the normalized monomer fluorescence (model compound for PS) and normalized monomer absorption spectrum, respectively.

Table IV
Photophysical Parameters Used in Monte Carlo Calculations

k_{FM},[a] s^{-1}	k_{IM},[a] s^{-1}	k_{FD},[b] s^{-1}	k_{ID},[b] s^{-1}	R_0,[c] Å	L, Å	$(2\pi/\hbar)KJ$, s^{-1}
0.55×10^7	7.15×10^7	8.44×10^5	5.06×10^7	6.47	3.0	0.5×10^{12}

[a] Taken from ref 32. [b] Average values taken from ref 33. [c] Taken from ref 34 for isopropylbenzene/isopropylbenzene.

Table V
Photophysical Parameters of PS Obtained from Monte Carlo Simulation under Assumption of EM Exchange Mechanism

N[a]	q[b]	κ^2[c]	$\Phi_M \times 10^2$[d]	$\Phi_D \times 10^2$[e]	τ_{0M},[f] $\times 10^9$ s	τ_{0D},[g] $\times 10^9$ s	$\langle n \rangle$[h]
20	0.025 ± 0.007	0.356 ± 0.006	4.3 ± 0.7	0.6 ± 0.2	0.54 ± 0.07	15.9 ± 0.2	30 ± 4
40	0.024 ± 0.005	0.349 ± 0.003	2.4 ± 0.5	0.8 ± 0.2	1.3 ± 0.2	16.6 ± 0.3	90 ± 14
100	0.036 ± 0.004	0.337 ± 0.002	0.9 ± 0.2	1.1 ± 0.2	2.6 ± 0.6	17.1 ± 0.4	172 ± 40
20	0		7.1 ± 0.5		13.4 ± 0.5		802 ± 30
40	0		4.6 ± 0.9		13.5 ± 0.8		851 ± 66

[a] Number of mers in PS chain. [b] Fraction of EFS. [c] Orientational coefficient. [d] Monomer quantum yield. [e] Excimer quantum yield. [f] Monomer fluorescence decay time. [g] Excimer fluorescence decay time. [h] Number of energy hops.

The values of parameters used in the following section of this paper, found in formulas 9–13, are given in Table IV. The values of monomer and excimer rate constants given in Table IV correspond to intrinsic quantum yields of monomer (Q_M) and excimer (Q_D) fluorescence and are defined by relations

$$Q_M = k_{FM}/(k_{FM} + k_{IM}) \qquad Q_D = k_{FD}/(k_{FD} + k_{ID})$$

Values of rate constants k_{FM} and k_{IM} have been assumed for ethylbenzene in dichloroethane.[32] In the case of excimer vaules of rate constants k_{FD} and k_{ID}, calculated by Ishii et al.[33] on the basis of a comparison of a simple kinetic model with experimental studies, there is only a slight dependence on the molecular weight of PS. The observed negligible changes of k_{FD} and k_{ID} are probably within experimental error, which the authors do not analyze. One may expect that values of intrinsic quantum yield[6] do not depend on PS molecular weight and in the case of styrene copolymers do not depend on the luminescently inactive comonomer.[4] Therefore the values of k_{FD} and k_{ID} assumed in this work represent average values of those given by Ishii et al.[33]

IV. Results and Discussion

1. Energy Migration. Resonance Mechanism. The simulation of luminescence of PS has been carried out by applying eq 12 as a rate constant of EM. The respective parameters are summarized in Table IV. Equation 12 also contains a parameter κ^2 whose value is not known for PS. In Table V we have summarized the average values of orientational coefficient κ^2, estimated during simulation, taking into account that the transition moment in the phenyl group is oriented in the direction of the CH_2 substituent of the benzene ring. This assumption undoubtedly requires an experimental verification, but from general considerations, it may be supposed that the benzene symmetry disordered by the CH_2 group can lead to distinction of the mentioned direction of the transition moment.[35]

Assuming critical radius $R_0 = 6.47$ Å (see Table IV), the following values of quantum yields and times of fluorescence decay have been estimated for PS with $N = 100$ and $q = 0.029 \pm 0.006$:[36]

$$\Phi_M = (6.0 \pm 0.3) \times 10^{-2} \qquad \Phi_D = (0.19 \pm 0.05) \times 10^{-2} \tag{15a}$$

$$\tau_{0M} = 10.9 \pm 0.4 \text{ ns} \qquad \tau_{0D} = 20.9 \pm 0.6 \text{ ns} \tag{15b}$$

These values are very different from those obtained by experiment. The latter are[33]

$$\Phi_M = 0.42 \times 10^{-2} \qquad \Phi_D = 1.84 \times 10^{-2} \tag{16a}$$

$$\tau_{0M} = 1.85 \text{ ns} \qquad \tau_{0D} = 17.2 \text{ ns} \tag{16b}$$

The mentioned differences are the result of close values of k_{EM} and $k_{FM} + k_{IM}$, which leads to a restriction of the EM process and an increase of monomer quantum yield (eq 15a). In this case, the probability of capture of excitation energy by EFS is small. It is reflected by the estimated average values of the number of energy hops $\langle n \rangle = 8.8 \pm 0.4$.

It must be stressed that the small energy migration obtained for the resonance mechanism does not allow description of the luminescence of PS. This result does not correspond to recent studies in which it shown that the energy-migration process was necessary to describe the luminescence of this macromolecule.[2-4,6,14,20,30,33,37-39] A more efficient energy-migration process may be sought by changing the critical radius (R_0). Fitting the results of simulation to the experimental data yields a satisfactory agreement for $R_0 \approx 13.6$ Å. While the value of the critical radius for styrene has not been estimated, in comparison with ethylbenzene ($R_0 = 7.27$ Å)[34] or isopropylbenzene ($R_0 = 6.47$ Å),[34] the value $R_0 \approx 13.6$ Å seems to be difficult to justify. Similarly, changes of κ^2[40] (if our assumption is not fully correct) for $R_0 = 6.47$ Å do not lead to important changes of the energy-migration rate constant.

2. Energy Migration. Exchange Mechanism. The simulation of PS luminescence has been carried out by applying eq 13 for the rate constant of EM. The respective parameters are shown in Table IV. It has been assumed that excitation energy can migrate from an excited chromophoric group no further than to the fifth neighboring group in either direction along the chain under the condition that the chromophoric group is not a terminal group. For PS with 100 mers the following average values of EM rate constants have been estimated: to the first group, $(1.7 \pm 0.2) \times 10^9$ s^{-1}; to the second, $(1.6 \pm 0.3) \times 10^9$ s^{-1}; to the third, $(0.7 \pm 0.1) \times 10^9$ s^{-1}; to the fourth, $(1.4 \pm 0.3) \times 10^7$ s^{-1}; and to the fifth $(8 \pm 3) \times 10^6$ s^{-1}.

In Figure 5 we have shown the values of monomer (Φ_M) and excimer (Φ_D) fluorescence quantum yield as a function of the PS molecular weight, obtained from simulation. The given values of quantum yields were obtained by neglecting the set of PS chains not containing meso tt diads (see Figure 3). The respective experimental data obtained by Ishii et al.[33] have also been noted there. The observed differences for small molecular weights of PS between simulated and experimental values of quantum yields (as has been mentioned before) may be associated with the possibility of dynamic formation of excimers. In the case of PS with $N = 100$, the agreement between simulated and experimental values of quantum yields is also not satisfactory, although observed differences are not as large as in the case of short PS chains.

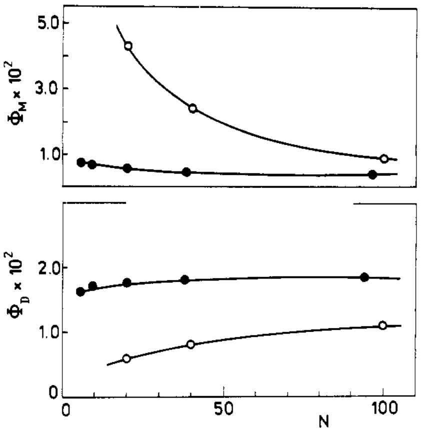

Figure 5. Results of simulation (○) and experimental values[33] (●) of quantum yields of monomer (Φ_M) and excimer (Φ_D) fluorescence as a function of number of mers in PS chain.

Univocal interpretations of the observed differences between quantum yields is presently not possible. We suppose that the main reason for the mentioned differences is the fact that chain dynamics is not taken into account in our simulations. One may also note that recently some authors[4,15,20] mentioned the possibility of a fluorescence self-quenching process occurring in PS. This rather unspecified process has also not been taken into account in our simulations, but from the analysis of Figure 3, one may conclude that taking into consideration the fluorescence self-quenching should lead to a decrease of Φ_M values obtained from Monte Carlo simulations. In order to illustrate the influence of chains not containing excimers, we have shown in Table V the times of monomer (τ_{0M}) and excimer (τ_{0D}) fluorescence decay obtained from the simulation of photophysical processes in PS chains with and without ($q = 0$) excimers. In the case of PS chains for which $q = 0$, the time of monomer fluorescence decay is, within an accuracy obtained in simulation, equal to the lifetime of ethylbenzene (see Table IV). This result was expected for the case in which $q = 0$. For the set of PS chains that did not contain excimerless chains, the times of monomer and excimer fluorescence decay are comparable with experimental investigations of those parameters.[20,30] An increase of τ_{0M} along with an increase of PS molecular weight is due to an increase of the average distance between excimers in spite of the fact that the concentration of EFS remains unchanged. This leads to an increase of probability of the deactivation of electronic excitation on the monomer. It is illustrated by values of the average number of energy hops ($\langle n \rangle$) given in Table V.

In order to see the full picture concerning times of PS fluorescence decay, one must consider chains with and without EFS, in proper proportion. For PS in diluted solution, certain authors observed a one-exponential monomer fluorescence decay,[20] while others suggest a two-exponential decay.[30] A two-exponential monomer fluorescence decay was explained by excimer dissociation. Recently,[41] it has been suggested that a lengthy monomer fluorescence decay as compared with the time of excimer fluorescence may be due to the tail of excimer fluorescence for the wavelength at which monomer fluorescence decay is measured. Analysis[42] of the results of theoretical studies concerning the process of energy transfer has shown that the presence of an acceptor (excimer) leads to a nonexponential donor fluorescence decay, even when back-transfer from an acceptor (excimer) to a donor does not occur. One may consider the case in which the overlap of monomer and excimer fluorescence spectra for the wavelength at which the decay is measured to be eliminated. The PS monomer fluorescence decay should be nonexponential. Taking into account the possibility of the existence of excimerless chains (or long monomeric sequences) greatly complicates the analysis of the fluorescence decay of PS, and the problem requires further studies.

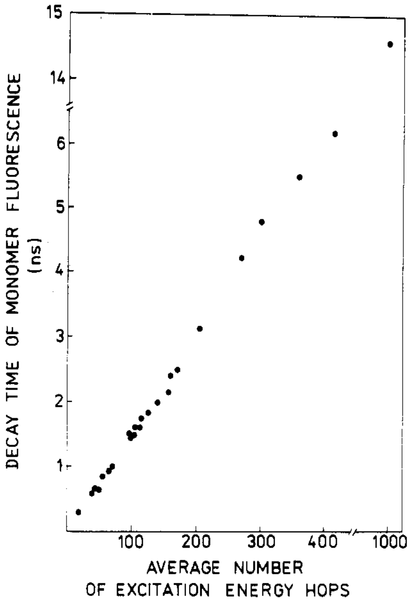

Figure 6. Results of decay-time simulation of monomer fluorescence (τ_{0M}) as a function of average number of energy hops ($\langle n \rangle$).

The average decay time of monomer fluorescence, simulated for the ith macromolecule, may be expressed[2]

$$\langle \tau_{0M} \rangle_i = \langle \tau_h \rangle (1 + \langle n \rangle_i) \tag{17}$$

where $\langle n \rangle_i$ denotes the average number of energy hops. Relation 17 has been shown in Figure 6, from which $\tau_h = 14.8 \pm 0.1$ ps for correlation coefficient $\rho = 0.9996$. The determined value of τ_h is close to the values estimated by other authors, e.g., $\tau_h = 30$ ps[20] or $\tau_h = 1.5$ ps.[2]

The time of the excitation energy hop may be expressed by rate constants (Figure 4)

$$\langle \tau_h \rangle = \frac{1}{k_{FM} + k_{IM} + \langle \sum k_{EM} \rangle} \tag{18}$$

where $\langle \sum k_{EM} \rangle$ is the average total rate constant of EM in the neighboring 10 chromophoric groups. Using $\langle \tau_h \rangle$ obtained from eq 17 and 18, we have obtained $\langle \sum k_{EM} \rangle = 6.7 \times 10^{10}$ s^{-1}. This value is close to 3×10^{10} s^{-1} obtained by Itagaki et al.[20]

The difference between EM rate constants determined from the simulation of photophysical processes in PS (eq 13) and EM rate constants calculated by formal averaging of eq 17 and 18 is not surprising. This difference results from the fact that the EM process occurs between chromophoric groups which are in the most suitable position for this process.

Comparing the results of simulation under the assumption of resonance (eq 12) and exchange (eq 13) interactions, one may notice that exchange interactions may satisfactorily describe the process of EM in polystyrene. This result is also justified by the fact of close-packing of phenyl groups.

V. Summary

The simultion of photophysical processes in polystyrene as a function of molecular weight has been carried out. The mechanisms (resonance and exchange) that may be responsible for the EM process have been analyzed. The analysis of the obtained results shows that the exchange mechanism is responsible for the EM process in PS.

The difficulties in interpretation of the mechanisms leading to excimer formation, mentioned in the paper, may be in part omitted by investigating rigid diluted solutions, macromolecules of large molecular weights, or block copolymers of the PS–B type, where B is a luminescently inactive polymer of large molecular weight.

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Diffusion of Polystyrene Latex Spheres in Polymer Solutions Studied by Dynamic Light Scattering

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ABSTRACT: The diffusional behavior of latex spheres (radius 720 Å) in both dilute and semidilute solutions of the following linear polymers is reported: (hydroxyethyl)cellulose (HEC), (hydroxypropyl)cellulose (HPC), (carboxymethyl)cellulose (CMC) (pH 4 and 9) at different ionic strengths, and nonionized poly(acrylic acid) (PAA) (pH 3.5). In these systems the scattering is dominated almost entirely by the latex component. In very dilute solutions ($<10^{-3}\%$) of HEC and HPC, the average diffusion coefficient of latex decreases strongly with increasing polymer concentration, and the relative variance shows a concomitant increase. Multiexponential analysis of the time correlation function gave a bimodal fit as the simplest model: (a) fast mode, a polymer concentration-independent D value equal to that of the latex monomer at infinite dilution; (b) slow mode, diffusion coefficient corresponding to aggregate species with apparent radii 2–3 times that of the latex monomer. The aggregation behavior is consistent with a bridging mechanism. In semidilute solutions of nonionized CMC at pH 4 in the salt-free system, latex diffusion follows the theoretically predicted $C^{1/2}$ dependence: $D/D_0 = \exp(-AC^{1/2})$. With HEC and HPC, the adsorptive interactions lead to characteristic deviations from this dependence. Qualitatively similar behavior is observed with CMC in the fully neutralized form (salt free) at pH 9, where electrostatic repulsive forces are operative. In the presence of a low molar mass electrolyte (at pH 9), CMC adsorbs to the individual latex particles and there is a strong positive deviation from the $C^{1/2}$ dependence. The scaling index in $D/D_0 = \exp(-AC^{\delta})$ provides a sensitive index to the interactions in the system.

Introduction

The diffusion of latex spheres in polymer solutions has been the subject of numerous investigations in both the dilute and semidilute regions of polymer concentration. Some recent examples are the studies in ref 1–8, 14, and 30–34. At the dilute end of the scale, dynamic light