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Fluorescent Energy Transfer in a Scattering Medium

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ABSTRACT: A theory is presented which takes into account the effects of scattering and radiative energy transfer on nonradiative fluorescent energy transfer for multiphase materials. The results indicate that both radiative transfer and scattering affect substantially the observed acceptor and donor fluorescent emission intensities. The ramifications of these results on the interpretation of fluorescent energy-transfer experiments for the study of polymer blend miscibility are briefly discussed.

The technique of nonradiative energy transfer (NET) has been employed widely in the study of configurations of synthetic and biological macromolecules.[1] The utility of the technique arises primarily from the fact that the probability of NET, between an excited donor and a ground-state acceptor, is highly dependent on the relative orientation and separation distance between the two chromophores. The efficiency of energy transfer may be expressed as[2] $E = 1/[1 + (R/R_o)^6]$ where R is the separation distance between donor and acceptor and R_o is the so-called Förster distance for which the transfer efficiency is 0.5.

From this expression it is apparent that the efficiency of NET is a sensitive "spectroscopic ruler" for distances of the order of R_o. Experimentally, the efficiency can be determined by measuring the fluorescence emission intensities of the acceptor (F_a) and donor (F_d) under conditions wherein the illumination excites only the donor chromophore. In practice, however, the ratio F_a/F_d can also be affected by additional processes including radiative energy transfer and scattering of the incident emitted radiation. Horsky and Morawetz,[4] for example, studied energy transfer in solutions containing a mixture of poly(methyl methacrylate-*co*-methacrylic acids) labeled with carbazole and anthracene, respectively, and found that radiative processes make a predominant contribution to energy transfer. Melhuish[5] points out that scattering of the incident and emitted radiation has a strong influence on the fluorescent properties of textiles, lacquers, and paints.

Scattering effects are especially important for heterogeneous media for which the relative acceptor–donor emission ratio can be affected by the phase structure and optical properties of the components. Amrani[6] for instance studied phase-separated mixtures of carbazole-labeled poly(styrene-*co*-acrylonitrile) with anthracene-labeled poly(methyl methacrylate) (PMMA). As the acrylonitrile content of the copolymer was varied, the change in degree of mixing or miscibility of the two polymers was monitored by measuring the acceptor–donor fluorescence emission ratio. Albert et al.[7] have claimed that NET emission ratios in similar blends of naphthalene-labeled syndiotactic PMMA and anthracene-labeled poly(vinyl chloride) can be used to provide an estimate of the domain size.

A quantitative treatment of the fluorescence of donors and acceptors in a hetergeneous medium must take into account several factors. The most important of these is the spatial distribution of the two chromophores. When the host polymers are completely immiscible, NET can only occur within the interphase separating the two polymers, wherein the donor and acceptor chromophores can approach to within a separation distance of the order of the Förster distance. The intrinsic probability of energy transfer, in this case, is related to the total volume of interphase in the material (i.e., the phase dimensions) as well as the degree of overlay of the two species within the interphase. The latter property can in principle be used to study the form of the concentration profile in the interphase region[8] if the specific interfacial area is known. Radiative energy transfer may also occur if the fluorescence emission spectrum of the donor chromophore overlaps with the adsorption band of the acceptor. If radiative transfer is significant, the ratio of donor to acceptor fluorescence emission will not be directly related to the probability for NET. Scattering effects will similarly affect the fluorescence emission ratio.

The scattering power of phase-separated media is a function of the size of the phases, the difference in polarizability (i.e., refraction index), and the wavelength. The effect of scattering upon the acceptor–donor fluorescence emission ratio will necessarily be complex.

The experimental fluorescence emission ratio, F_a/F_d, is therefore influenced by three processes: radiative energy transfer, scattering, and nonradiative energy transfer. If nonradiative energy transfer is to be used as a tool to study macromolecular chain configurations in phase-separated systems, the effects of scattering and radiative energy transfer must be understood quantitatively. In this work, we present calculations that take into account the effects of both scattering and radiative energy transfer (i.e., emission followed by reabsorbtion) on the acceptor–donor fluorescence emission ratio. The treatment adopted follows closely the theory developed by Kubelka[9] for light absorption in a turbid medium and that developed by Allen[10] for fluorescence in a scattering medium. The intrinsic efficiency of NET is presumed to be unaffected by these additional processes but related only to the physical phenomena that dictate the separation distances between donor and acceptor fluorophores. In the case of the multiphase system, considered herein, E is related to the form of the interphase concentration profile and the specific interfacial area.

Fluorescence of Donors and Acceptors in a Scattering Medium

Light absorption and emission will depend on three parameters: the absorption coefficient k, the scattering

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coefficient (cross section per unit volume) s, and the film thickness L. Here s can be assumed to be independent of the film thickness if the dimensions of the phase domains are much smaller than L. In order to simplify the calculation, we also assume that the excitation and emission flux are monochromatic. Throughout this paper, unprimed quantities refer to the excitation wavelengths and primed and double-primed quantities to the emission wavelength of donor and acceptor, respectively.

Consider a phase-separated film of thickness L which contains fluorescent donors (d) and acceptors (a). Let x be the distance from the film surface, I_0 the intensity of monochromatic incident light normal to the film surface, k_a the absorption coefficient of the acceptor, k_d the absorption coefficient of the donor, and $k = k_a + k_d$. All absorption coefficients are of the general form $k = 2.303\epsilon C$, where ϵ is the molar absorptivity and C is the chromophore concentration. The light intensity $I(x)$ at a distance x from the film surface can be shown to be given by[9]

$$I(x) = I_0(1 + R_\infty)(e^{bs(2L-x)} - R_\infty e^{bsx})/(e^{2bsL} - R_\infty{}^2) \quad (1)$$

where $a = (s + k)/s$, $b = (a^2 - 1)^{1/2}$, and $R_\infty{}' = a - b$. The fluorescence of donor and acceptor are calculated by taking into account the scattering and absorption of both donor and acceptor fluorescence and the reemission of acceptors excited by absorbing the donor fluorescence. Let s' and s'' be the scattering coefficients of donor and acceptor fluorescence, respectively, k' and k'' be the absorption coefficients of donor and acceptor fluorescence, respectively, and $k_a{}'$ be the absorption coefficient of the acceptor at the donor emission wavelength. k' is equal to $k_a{}'$ when self-quenching of the donor fluorescence can be neglected. The relative acceptor–donor emission intensity is given by (see Appendix)

$$\frac{F_a}{F_d} = \frac{q_a(k_a + k_dE)(1 + R_\infty{}'')(e^{2b's'L} - R_\infty{}'^2)f_A}{q_dk_d(1 - E)(1 + R_\infty{}')(e^{2b''s''L} - R_\infty{}''^2)f_D} + \frac{q_ak_a{}'\alpha}{b's'f_D} \quad (2)$$

where q_a and q_d are fluorescence quantum efficiencies of the acceptor and donor, respectively, and f_D, f_A, and α are defined by

$$f_D = \frac{[e^{(bs+b's')L} + R_\infty R_\infty{}'e^{-(bs+b's')L}][e^{(bs+b's')L} - 1]}{bs + b's'} - \frac{[1 - e^{(b's'-bs)L}][R_\infty e^{2bsL} + R_\infty{}'e^{2b's'L}]}{bs - b's'} \quad (2a)$$

$$f_A = \frac{[e^{(bs+b''s'')L} + R_\infty R_\infty{}''e^{-(bs+b''s'')L}][e^{(bs+b''s'')L} - 1]}{bs + b''s''} - \frac{[1 - e^{(b''s''-bs)L}][R_\infty e^{2bsL} + R_\infty{}''e^{2b''s''L}]}{bs - b''s''} \quad (2b)$$

$$\alpha = \frac{1}{bs}(1 - e^{-bsL})[e^{2(bs+b's')L} + R_\infty{}'e^{2bsL} - R_\infty e^{(2b's'+bs)L} - R_\infty R_\infty{}'e^{bsL}] - \frac{1}{bs + b's'}(1 - e^{-(bs+b's')L})[e^{2(bs+b's')L} - R_\infty R_\infty{}'e^{(bs+b's')L}] - \frac{1}{bs - b's'}[(e^{2bsL} - e^{(bs+b's')L} - e^{2b's'L})] \quad (2c)$$

In deriving eq 2, we have neglected the scattering and reabsorption of reemitted fluorescence by acceptors excited by absorbing the donor fluorescence. Equation 2 is applicable only when emission is measured in a front-face geometry and when excitation and emission path lengths are equal.

The use of Kubelka theory in this calculation requires a random distribution of fluorescent species throughout the medium. This assumption is not valid when the donor and acceptor are partitioned into separated phases as a result of the materials' multiphase structure. Accounting rigorously for the influence of chromophore partitioning would require a detailed knowledge of the phase morphology. For example, a lamellar structure oriented perpendicular to the incident exitation would behave quite differently than one oriented in the parallel direction.

Within certain limits, however, eq 2 can serve as a useful approximation for estimating the effects of scattering and radiative energy transfer in nonradiative energy-transfer experiments. Specifically, the use of eq 2 is reasonable when the phase dimensions are much smaller than the overall optical path length and when the phase morphology is globally isotropic. Under these conditions, the probabilities for radiative and nonradiative energy transfer may be considered independent, and the local acceptor and donor concentrations in a differential layer of thickness, dx, are equal to the macroscopic values. It should be realized, however, that the applicability of any conclusions reached from the following discussion are limited by these conditions.

Case I: Relative Acceptor–Donor Emission in the Absence of Scattering of both the Incident and Emitted Radiation

If there is no scattering of the incident and emitted radiation, or $s = s' = s'' \to 0$, we have $R_\infty = R_\infty{}' = R_\infty{}'' \to 0$, $bs \to k$, $b's' \to k'$, and $b''s'' \to k''$. With $k'' = 0$ and $k' = k_a{}'$, eq 2 reduces to

$$\frac{F_a}{F_d} = \rho\left(\frac{k + k'}{k}\right)\left(\frac{1 - e^{-kL}}{1 - e^{-(k+k')L}}\right) + q_s\left[\left(\frac{k + k'}{k}\right)\frac{(1 - e^{-kL})}{(1 - e^{-(k+k')L})} - 1\right] \quad (3)$$

where

$$\rho = \frac{q_a}{q_d}\frac{(k_a + k_dE)}{k_d(1 - E)}$$

For small kL (i.e., weak absorbance or dilute chromophore conditions) this becomes

$$\frac{F_a}{F_d} = \rho = \frac{q_a}{q_d}\frac{(k_s + k_dE)}{k_d(1 - E)} \quad (4)$$

From this relation, it is apparent that, for a transparent film with either very low optical density or optical path length, the relative acceptor and donor emission intensity is unaffected by radiative energy transfer, and any increase in the relative emission intensity ratio is due to an increase in the efficiency of nonradiative energy transfer.

For large kL value (i.e., strong absorbance), eq 3 reduces to

$$\frac{F_a}{F_d} = \frac{q_a(k_a + k_dE)}{q_dk_d(1 - E)}\left(1 + \frac{k'}{k_a + k_d}\right) + q_a\frac{k'}{k_a + k_d} \quad (5)$$

The effect of radiative energy transfer under this condition can be calculated by evaluating eq 5 for a particular set of parameters: $q_a/q_d = 1$, $k'/k = 0.4$, $q_a = 0.5$, and $k_a/k_d = 0.04$. F_a/F_d values as a function of E are shown in Table I. Two observations can be made from this calculation: (1) radiative energy transfer makes an important contribution to the relative acceptor and donor emission intensity, and this contribution is about 30% even

Table I
Relative Acceptor and Donor Emission Intensity as a Function of E

E	F_a/F_d[a]	F_a/F_d[b]
0	0.26	0.04
0.05	0.33	0.09
0.1	0.42	0.16
0.2	0.62	0.30
0.3	0.88	0.48
0.4	1.23	0.73
0.5	1.71	1.08
0.6	2.44	1.60
0.7	3.66	2.47
0.8	6.08	4.20
0.9	13.36	9.4

[a] Relative acceptor and donor emission intensity in the presence of radiative energy transfer. [b] Relative acceptor and donor emission intensity after correcting for contributions from radiative energy transfer.

Table II
Predicted Effect of Radiative Energy Transfer on Relative AMM and CEMA Emission Intensity as a Function of AMM Concentration

concn C, $\times 10^{-3}$ M	f[a]	$(I_a/I_d)_{obs}$[b]	$(I_a/I_d)_{calc}$[c]
0.05	1.59	0.2	0.037
0.5	1.74	0.27	0.06
0.15	1.76	0.37	0.10
0.20	1.77	0.49	0.17
0.25	1.77	0.56	0.22
0.30	1.77	0.69	0.29
0.40	1.77	1.30	0.64
0.60	1.77	2.50	1.31
0.80	1.77	3.60	1.94
1.0	1.77	5.47	2.99
1.2	1.77	6.63	3.65

[a] Radiative energy transfer factor given by eq 6a. [b] Observed relative AMM and CEMA emission intensity in ref 4. [c] Corrected relative emission intensity using eq 6.

when $E = 0.9$ for the particular set of parameters adopted; (2) The amount of the radiative energy transfer decreases with an increase in the efficiency of nonradiative energy transfer. This is understandable since an increase in E will decrease the probability for radiative energy transfer.

Equation 3 is generally valid for finite kL values. When the path length for excitation and emission is different, an equation can be derived for the following geometry. Let us assume that the incident beam is at 30° from the normal and that the emission intensity is measured at 60° from the normal, so that for a path length $x/\cos 30°$ of the exciting beam within the sample, the path length of the emitted beam is $x/\cos 60° = 2x$, where x is the distance from the sample surface. F_a/F_d under these conditions can be shown to be

$$\frac{F_a}{F_d} = \frac{q_a}{q_d}\frac{(k_a + k_d E)}{k_d(1 - E)}f + q_a(f - 1) \tag{6}$$

where

$$f = \left[1 + \frac{2k_a'}{1.15(k_a + k_d)}\right]\left[\frac{[1 - e^{-1.15(k_a+k_d)L}]}{[1 - e^{-[1.15(k_a+k_d)+2k_a']L}]}\right] \tag{6a}$$

Equation 6 is very similar to that used by Jachowicz and Morawetz[11] for estimating the contribution of radiative energy transfer to the measured relative emission intensity for very thick films (they did not consider the reemission of fluorescence from acceptors excited by absorbing the donor emission). It can be used for correcting the effect of radiative energy transfer on the fluorescence behavior for solutions containing 2-(*N*-carbazolyl)ethyl methacrylate (CEMA) donors and 9-anthrylmethyl methacrylate (AMM) acceptors used by Horsky and Morawetz.[4] For this donor–acceptor pair, $k_a = 2.302\epsilon_a C_a$, $k_d = 2.302\epsilon_d C_d$, and $k_a' = 2.302\epsilon'_a C_a$. Using $\epsilon_d = 15\,400$ M^{-1} cm^{-1}, $\epsilon_a = 600$ M^{-1} cm^{-1} at 294 nm (excitation wavelength), $\epsilon_a' = 7080$ M^{-1} cm^{-1} at 360 nm (emission maximum of CEMA), $q_a/q_d = 0.95$,[10] $L = 1$ cm, and $C_a = C_d = C$, we have

$$\frac{F_a}{F_d} = 0.95\left(\frac{600 + 15400E}{15400(1 - E)}\right)f + q_a(f - 1) \tag{7}$$

where

$$f = 1.769\frac{[1 - e^{-42357C}]}{[1 - e^{-77495C}]}$$

The results are shown in Table II, where the q_a value was obtained by assuming that, at $C = 5 \times 10^{-5}$ M, there is no contribution from nonradiative energy transfer. We see that radiative energy transfer accounts for 60–80% of the value of their recorded acceptor and donor emission intensity ratio over the concentration range from 1×10^{-4} to 3×10^{-4} M.

Case II: Relative Acceptor and Donor Emission Intensity in the Presence of Scattering of both the Incident and Emitted Radiation

In the case where scattering of both the incident and emitted radiation is significant, eq 2 becomes for a thick film

$$\frac{F_a}{F_d} = \rho\frac{(1 + R_\infty'')(bs + b's')}{(1 + R_\infty')(bs + b''s'')} + q_a\frac{k'}{k}\frac{1}{(1 + 2s/k)^{1/2}} \tag{8}$$

Several interesting observations can be made from this equation:

(a) With $k' = k'' = 0$, or in the absence of absorption of emitted photons, $F_a/F_d = \rho$. Light scattering makes no contribution to the fluorescence behavior of the donor and acceptor under these conditions. This result has also been demonstrated by Allen.[10] His result shows that, in the absence of absorption of the emitted fluorescence, the scattering of the emitted radiation does not affect the measured fluorescence intensity ratio. The effect of scattering of the exciting beam on the relative emission intensity for the donor and the acceptor is canceled out, so that the experimentally measured emission intensity can be related directly to the efficiency of nonradiative energy transfer.

(b) With $k'' = 0$ and $s' = s'' = 0$ but $k' \neq 0$, in other words, when absorption of the acceptor emission is weak and when scattering of the emitted beam is weak compared to that of the incident beam, we have

$$\frac{F_a}{F_d} = \rho\left(1 + \frac{k'}{(k^2 + 2ks)^{1/2}}\right) + q_a\frac{k'}{k}\frac{1}{(1 + 2s/k)^{1/2}} \tag{9}$$

Scattering of the exciting radiation tends to attenuate the contribution from radiative energy transfer to the measured emission intensity ratio at a constant optical density value. It also indicates that, at constant s, an increase in the optical density increases the contribution from radiative energy transfer. Nevertheless, radiative energy transfer is less efficient for a scattering medium than for a transparent medium.

Table III
Predicted Effect of Scattering and Radiative Energy Transfer on the Relative Acceptor and Donor Emission Intensity as a Function of s/k

s/k	F_a/F_d[a]	s/k	F_a/F_d[a]
0.1	2.8	0.8	2.3
0.2	2.7	1.0	2.2
0.4	2.5	2.0	2.1
0.6	2.4	10.0	1.7

[a] Calculated by using eq 12.

(c) With $k'' = 0$, we have

$$\frac{F_a}{F_d} = \rho\frac{2}{(1+R_\infty')}\left(\frac{bs+b's'}{bs}\right) + q_a\frac{k'}{k}\frac{1}{(1+2s/k)^{1/2}} \quad (10)$$

This equation corresponds to the case of strong scattering of the acceptor fluorescence without absorption. Substituting R_∞', b, and b' into eq 10, we have

$$\frac{F_a}{F_d} = 2\rho\left\{\frac{s'+k'+(k'^2+2k's')^{1/2}}{2s'+k'+(k'^2+2k's')^{1/2}}\right\}\times \left(1+\frac{(k'^2+2k's')^{1/2}}{(k^2+2ks)^{1/2}}\right) + q_a\frac{k'}{k}\frac{1}{(1+2s/k)^{1/2}} \quad (11)$$

It can be rearranged to

$$\frac{F_a}{F_d} = 2\rho\left\{\frac{1+\frac{s'/k}{k'/k}+\left(1+2\frac{s'/k}{k'/k}\right)^{1/2}}{1+2\frac{s'/k}{k'/k}+\left(1+2\frac{s'/k}{k'/k}\right)^{1/2}}\right\}\times \left(1+\frac{k'}{k}\left(\frac{1+2\frac{s'/k}{k'/k}}{1+2s/k}\right)^{1/2}\right) + q_a\frac{k'}{k}\frac{1}{(1+2s/k)^{1/2}}$$

For a two-phase medium in the Rayleigh–Gans–Debye limit, the scattering coefficient may be written as $s \propto (r^3/\lambda^4)(n_1 - n_2)^2$, where r is the average size of the scattering particle, λ is the wavelength, and $n_1 - n_2$ is the difference in the refractive indices for the two phases. If it is assumed that $(n_1 - n_2)^2$ changes very slowly with wavelength, we find $s \propto 1/\lambda^4$. Again taking carbazole and anthracene as an example, the wavelength of the excitation is about 294 nm and that of the fluorescence of the donor can be taken at 360 nm, so that $s'/s = 0.421$. Assuming $k'/k = 0.443$, $q_a = 0.23$, and $C_a = C_d$ as in the previous example, we have

$$\frac{F_a}{F_d} = 2\rho\left(\frac{1+0.95s/k+(1+1.9s/k)^{1/2}}{1+1.9s/k+(1+1.9s/k)^{1/2}}\right)\times \left(1+0.443\left(\frac{1+1.9s/k}{1+2s/k}\right)^{1/2}\right) + \frac{0.1}{(1+2s/k)^{1/2}} \quad (12)$$

When the last term is neglected, the calculated F_a'/F_d' values are shown as a function of s/k in Table III.

Both eq 12 and the results in Table III indicate that radiative energy transfer and scattering influence substantially the measured relative acceptor and donor emission intensity. Since these results correspond to a complete scattering of the acceptor emission flux, the data for $s/k = 0$ at $k \neq 0$ is meaningless since one cannot assume here that there is no scattering contribution. Thus, imperfect scattering of the donor fluorescence due to the presence of radiative energy transfer always makes a contribution to the relative emission intensity by a factor larger than the radiative energy transfer for transparent films. It also indicates that for finite s, an increase in the absorption power increases the contribution from scattering and radiative energy transfer to the relative emission intensity.

Even though scattering and radiative energy transfer affect the fluorescence behavior of media containing both donors and acceptors, an interpretation of relative donor and acceptor emission intensity in terms of miscibility for labeled binary polymer mixtures is still justified under conditions such as used by Amrani et al.[6] for the following reasons: the relative acceptor and donor emission intensity values from their measurements vary from 1 to 5 (see Figure 6 in ref 6), depending on the acrylonitrile contents. These values are too large to be accounted for by only scattering and radiative energy transfer. When the correction factor 2.8 in Table III is used for $s/k = 0.1$, the relative emission intensity after this correction would change from 0.36 to 1.8. Since the optical density of the film remained constant for their sample, an increase in the scattering power from $s/k = 0.1$ to $s/k = 10$ (i.e., correction factor 1.7) decreases the range of this variation to a range from 0.59 to 2.94, which is significant enough to be interpreted as a change in the polymer compatibility. Yet, the film thickness is not infinite for the samples they used, so that the contribution from scattering and radiative energy transfer should become smaller, since this contribution increases as L increases.

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Appendix

The fluorescence of the donor and acceptor in the layer dx of the film are given by

$$\mathrm{d}F_d = k_d q_d (1-E)\, I(x)\, u''(x)\, \mathrm{d}x \quad (A1)$$

$$\mathrm{d}F_a = q_a (k_a + k_d E)\, I(x)\, u'(x)\, \mathrm{d}x \quad (A2)$$

where $u'(x)$ and $u''(x)$ account for scattering and absorption of the donor and acceptor fluorescence, respectively. They can be obtained by using eq 1 as

$$u'(x) = \frac{1}{2}(1+R_\infty')e^{b's'x}(e^{2b's'(L-x)} - R_\infty')/(e^{2b's'L} - R_\infty'^2) \quad (A3)$$

$$u''(x) = \frac{1}{2}(1+R_\infty'')e^{b''s''x}(e^{2b''s''(L-x)} - R_\infty'')/(e^{2b''s''L} - R_\infty''^2) \quad (A4)$$

Using eq 1 and integrating eqs A1 and A2 over the thickness L, we obtain

$$F_d = \frac{k_d q_d (1-E) I_0 (1+R_\infty)(1+R_\infty')}{2(e^{2bsL} - R_\infty^2)(e^{2b's'L} - R_\infty'^2)}\times \left\{\frac{[e^{(bs+b's')L} + R_\infty R_\infty' e^{-(bs+b's')L}][e^{(bs+b's')L} - 1]}{bs+b's'} - \frac{[1 - e^{(b's'-bs)L}][R_\infty e^{2bsL} + R_\infty' e^{2b's'L}]}{bs-b's'}\right\} \quad (A5)$$

$$F_a = \frac{q_a (k_a + k_d E)(1+R_\infty)(1+R_\infty'')}{2(e^{2bsL} - R_\infty^2)(e^{2b''s''L} - R_\infty''^2)}\times \left\{\frac{[e^{(bs+b''s'')L} + R_\infty R_\infty'' e^{-(bs+b''s'')L}][e^{(bs+b''s'')L} - 1]}{bs+b''s''} - \frac{[1 - e^{(b''s''-bs)L}][R_\infty e^{2bsL} + R_\infty'' e^{2b''s''L}]}{bs-b''s''}\right\} \quad (A6)$$

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The relative acceptor and donor emission intensity is then given by

$$\frac{F_a}{F_d} = \frac{q_a}{q_d}\frac{(k_a + k_d E)}{k_d(1-E)}\frac{(1+R_\infty'')(e^{2b's'L} - R_\infty'^2)f_A}{(1+R_\infty')(e^{2b''s''L} - R_\infty''^2)f_D} \qquad (A7)$$

where f_A and f_D are given by eqs 2b and 2a, respectively.

The acceptors excited by absorbing the donor fluorescence can reemit fluorescence to return to their ground states. In the absence of scattering and absorption of the reemitted fluorescence, the contribution to the observed acceptor fluorescence due to this radiative energy transfer in layer dx is

$$\mathrm{d}P_A = \frac{\mathrm{d}F_d}{2} q_a k_a' \int_0^x \frac{(1+R_\infty')[e^{b's'(2L-y)} - R_\infty' e^{b's'y}]}{[e^{2b's'L} - R_\infty'^2]}\,\mathrm{d}y \qquad (A8)$$

Using eqs 1 and A1 and integrating over the thickness L, we found

$$P_A = I_o q_a k'_a (1-E)(1+R_\infty) \times (1+R_\infty')\frac{\alpha}{2b's'(e^{2bsL} - R_\infty^2)(e^{2b's'L} - R_\infty'^2)} \qquad (A9)$$

where α is given by eq 2c. Equation A7 is thus modified to give eq 2.

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Degradation of Polymer Solutions in Extensional Flows

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ABSTRACT: Elongational flow techniques are applied to the examination of flow-induced chain scission of macromolecules in solution. An opposed-jets apparatus is used both to produce mechanical scission and to monitor the molecular weight distribution of the scission products. We have explored the combined effects of elongational flow and elevated temperatures upon degradation of almost monodisperse atactic polystyrene solutions. Between 25 and 150 °C degradation occurs as closely central scission of the molecules beyond a critical strain rate ($\dot\epsilon_f$). $\dot\epsilon_f$ is found to be a decreasing function of temperature. At 150 °C we present also results for thermal degradation alone. These results correlate well with predictions based upon a thermally activated barrier to scission (TABS) model. We also present results on the strain-rate dependence of the scission rate beyond $\dot\epsilon_f$ at room temperature. These results clearly indicate that in dilute solution only those molecules that are virtually fully stretched can undergo central scission. Degradation in real flow situations (for instance, flow through GPC columns) seems to parallel our idealized experiments. Our results have serious implications for the latest theories of polymer dynamics. Finally, we speculate that, contrary to common belief, simple laminar shear flows may be almost incapable of degrading polymer solutions and that degradation is only encountered when the flow contains an appreciable elongational component, commonly arising as a result of flow instabilities or turbulence.

1. Introduction

Stress-induced scission of polymers in solution is a subject of major theoretical and technological interest. The thermochemical nature of mechanically induced scission of polymers has attracted the attention of many theorists since the pioneering works of Kuhn and Frenkel.[1,2] These authors over 40 years ago pointed out that long-chain molecules can be stretched out and broken if the stress applied exceeds the breaking stress of the fundamental chemical bonds. Technologically, the use of polymer solutions for flow modifications (in drag reduction or viscosity enhancement for example) is limited mostly by mechanically and/or thermally induced scission of the chains.

The breakage of chains in dilute solution can be studied by elongational flow.[3-8] Stagnation-point extensional flow fields can effectively apply a controlled stress to the isolated molecule. Simultaneously, the conformation of the molecule can be monitored by a variety of optical techniques. Using elongational flow techniques, one can vary both the stress and the temperature applied to the molecules in order to study their vital influence in the flow-induced scission process.

In an elongational flow field an isolated flexible-chain molecule is expected to undergo a coil-stretch transition at a critical strain rate, $\dot\epsilon_c$. This is a prediction from theoretical considerations,[9-11] being due to the hysteresis of molecular relaxation time with chain extension. The critical strain rate is related to the longest relaxation time of the molecule (τ) as

$$\dot\epsilon_c \tau \approx 1 \qquad (1)$$

Extensional flow fields have been realized experimentally by a number of devices, cross slots, opposed jets,

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