Quenching of Carbonyl n–π* Excited Triplets by Macromolecules

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ABSTRACT: Quenching rates of biacetyl, benzil, and benzophenone triplets by several polymers in solution have been measured. The quenching processes considered comprise different mechanisms: charge transfer (CT), photoreduction, and energy transfer. The relationship between the quenching rate of the polymer and that of a model compound depends strongly upon the quenching mechanism and the quenching rate. For slow reactions, the polymer can be a better quencher (i.e., in processes that occur by a CT mechanism) or a poorer one (i.e., in hydrogen abstraction). For diffusion-controlled processes, the polymer quenches triplets at a considerably slower rate that depends both upon the polymer molecular weight and the characteristics of the solvent media.

Introduction

The quenching of small excited molecules by macromolecules in solution has only been studied in a small number of systems. Heskins and Guillet[1] and Somersall and Guillet[2] have measured the rate of quenching of naphthalene excited singlet by ethylene–CO copolymers and by poly(methyl vinyl ketone). These authors concluded that while the collisional efficiency for the energy exchange process with the copolymer was similar to that of the corresponding model compounds, quenching (per monomer unit) by the homopolymers was between 2 and 3 times less efficient. Horie and Mita[3] have measured the rate of energy transfer from the triplet of benzil to an anthracene moiety located at the end of a polystyrene (PS) molecule. The quenching rate obtained was a factor of 2 smaller than that measured employing 9-methylanthracene as quencher and varied by less than 30% when the degree of polymerization was changed from 25 to 740. Recently, Horie et al. extended this work by employing different solvents, longer PS chains, and polymers with anthryl groups located at the center of the PS chain.[4] It was found that the larger macromolecules were somewhat less efficient quenchers. This effect was more noticeable when the anthryl group was located at the center of the macromolecule and was attributed to the obstructive effect of polymer segments on the diffusion of excited benzil molecules through the polymer coil. Webber et al.[5] have measured the quenching of biphenyl triplets by poly(2-vinylnaphthalene) (P2VN). The quenching rate constant, expressed in terms of the concentration of naphthalene groups, was up to 90 times smaller than that of naphthalene and changed by more than a factor of 4 when the degree of polymerization varied from 109 to 2690. Consideration of these studies shows that all the systems investigated involved exothermic energy transfer and that the rate of the process is limited by diffusion. In order to improve our understanding of the "polymer effect" in small-molecule–polymer interactions, we have measured the rate of biacetyl, benzil, and benzophenone triplet quenching by several polymers and suitable model compounds. The systems considered involve different quenching mechanisms (charge transfer complexes, photoreduction, and energy transfer) and cover a wide range of quenching rate constant values. This type of data, besides providing insight regarding the "polymer effect" in chemical reactions, is needed for a quantitative evaluation of the transformations[6] and/or degradations[7] that can take place in the macromolecule in the presence of sensitizers.

Experimental Section

Materials. Poly(4-methoxystyrene), poly(4-bromostyrene), poly(2-vinylnaphthalene), and poly(*cis*-1,3-butadiene) were commercial (Aldrich Chemical Co.) products. Poly(α-methylstyrene) was prepared by cationic polymerization in toluene at −78 °C, employing boron trifluoride diethyl etherate as catalyst. All other polymers were prepared by thermal free radical polymerization under high-vacuum conditions. All polymers were purified by repeated precipitations from benzene solutions with methanol. They were dried under vacuum at room temperature. Viscosity-average molecular weights were evaluated from the intrinsic viscosities. K and a constants were taken from the literature.[8]

Benzil (Fluka) and benzophenone (Fluka) were recrystallized from ethanol. Biacetyl (Fluka, puriss) was used as received. Their absorption and emission spectra were in agreement with those reported in the literature. Solvents employed were fluorescence spectroscopy grade (Merck).

Determination of Quenching Rate Constants. Quenching rate constants were determined by measuring the change in phosphorescence yield of the carbonyl compounds as a function of the quencher concentration. Measurements were carried out in a Perkin-Elmer 204-S spectrofluorimeter at room temperature. Solutions were deaerated by nitrogen bubbling or by several freeze–thaw cycles under high-vacuum conditions. In all the systems considered, the added polymers modified neither the absorption nor the emission spectral distribution of the carbonyl compounds.

Results and Discussion

Quenching rate constants have been obtained by using the relationship

$$I^0/I = 1 + k_Q \tau_T Q \qquad (1)$$

where I is the phosphorescence intensity, τ_T is the mean lifetime of the triplet state, and Q is the molar concentration of quenching units. When a polymer is employed, this concentration can measure either the concentration of quenching groups or the concentration of macromolecules. Depending on this choice, the value of k_Q will be given in terms of the concentration of monomeric units, $(k_Q)_m$, or polymer molecules, $(k_Q)_p$. With these definitions

$$\bar{n}(k_Q)_m = (k_Q)_p$$

where $\bar{n}$ is the average degree of polymerization. Typical plots of I^0/I against the quencher concentration are given in Figure 1. The values of $(k_Q)_m$ obtained from this type of plot are given in Tables I–III. The τ_T values were obtained from a Stern–Volmer plot employing triethylamine as quencher and the k_Q values for this compound given in the literature.[9] Given the sensibility of the triplet lifetimes to the experimental conditions employed (solvent

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Table I
Quenching Rate Constants for Non-Diffusion-Controlled Processes[a]

quencher		donor		
polymer	model	biacetyl	benzil	benzophenone
poly(α-methylstyrene)		5.0	0.14	230
	tert-butylbenzene	6.0	0.22	32
polystyrene		17	1.3	190
	toluene	0.13	0.01	50
	cumene	16	1.1	370
poly(*p*-methylstyrene)		16	1.3	380
	p-xylene	3.8	0.03	310
	p-cymene	22	2.2	290
poly(*p*-bromostyrene)		33	5.1	810
poly(*p*-chlorostyrene)		19	0.6	260
	p-chlorotoluene	0.2	0.04	23
poly(*p*-methoxystyrene)		70	4.6	3700
	p-methoxytoluene	3.9	0.6	2400
poly(4-vinylbiphenyl)			58	
	biphenyl		18	
poly(*cis*-1,3-butadiene)		75	3.8	2500
	1,5-cyclooctadiene	210	3.3	8000
poly(cyclohexyl methacrylate)				18
	cyclohexyl acetate			68

[a] Rate constants given in 10^4 M^{-1} s^{-1}. Estimated error in the relative k_Q values is approximately 10%. Absolute error could be larger due to the error in the triplet lifetime. Benzene as solvent; quenching rate constants for the polymers given in monomeric base units $(k_Q)_m$.

Table II
Solvent Effect in Quenching of Benzil Triplets

polymer	solvent	$(k_Q)_m/(k_Q)_{model}$[a]
polystyrene	benzene	1.2
	4:6 benzene-hexane[b]	0.4
poly(*p*-methylstyrene)	benzene	0.61
	2:8 benzene-hexane[b]	0.34

[a] Cumene and *p*-cymene employed as model compounds for polystyrene and poly(*p*-methylstyrene), respectively. [b] Nearly Θ solvent.

Table III
Triplet Quenching Rate Constants by Polymers Containing Naphthyl Groups

quencher[a]	10^{-3}MW	$(k_Q)_m$[b]	$(k_Q)_{model}/(k_Q)_m$[c]
	Benzil		
P2VN	19	0.002	0.5
	Benzophenone		
P2NMA	650	0.48	130
P2NMA	270	0.64	98
P2NMA	115	0.70	90
P1NMA		0.91	88
P2VN	19	3.6	12

[a] P2VN = poly(2-vinylnaphthalene); P2NMA = poly(2-naphthyl methacrylate); P1NMA = poly(1-naphthyl methacrylate). [b] In 10^8 M^{-1} s^{-1}. Benzene as solvent. [c] 2-Methylnaphthalene employed as model compound for P2VN; 2-naphthyl acetate and 1-naphthyl acetate employed as model compounds for P2NMA and P1NMA, respectively.

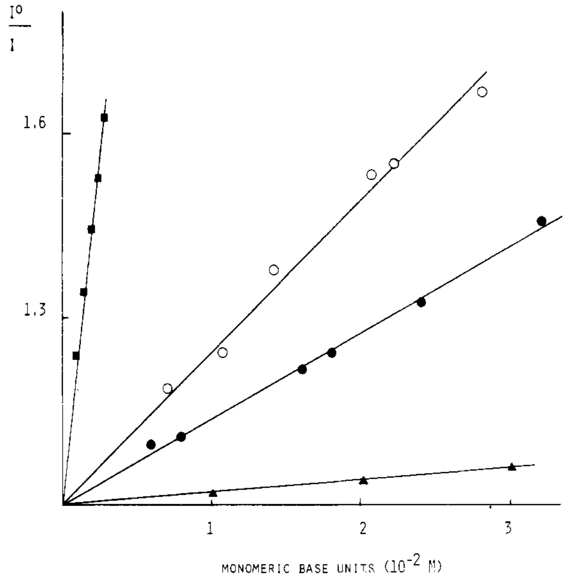

Figure 1. Change in phosphorescence intensity of benzophenone as a function of quencher concentration: (○) poly(*p*-methylstyrene); (■) poly(*p*-methoxystyrene); (●) polystyrene; (▲) poly(cyclohexyl methacrylate).

purity, residual oxygen concentration), this method is considered more reliable than one employing τ_T values obtained from the literature.

Prior to a discussion of the results given in Tables I–III, it is necessary to consider possible quenching by impurities incorporated in the macromolecules and hence not removed in the polymer purification. This effect cannot be conclusively disregarded in all systems considered but it is unlikely to be significant in most of the systems employed. For example, for PS, a commercial sample (Hewlett-Packard standard sample) and several polymers prepared under different experimental conditions and employing different batches of monomer gave essentially the same results. Furthermore, poly(methyl methacrylate) prepared under conditions similar to those employed for the other polymers did not show any measurable quenching capacity.

Non-Diffusion-Controlled Quenching Processes. Table I gives the results obtained in the quenching of biacetyl, benzil, and benzophenone triplets by polystyrene and polystyrene derivatives in benzene. In this table are also given the quenching rate constants of several related small molecules.

Aromatic compounds can quench benzophenone triplets by a charge transfer mechanism.[10] Most of the results given in Table I, both for the model compounds and the polymers, can also be explained by a quenching mechanism involving charge transfer interactions. In particular, the fact that a *p*-methoxy group increases the quenching rate considerably could be explained in terms of the lower ionization potential (IP) of these compounds. Nevertheless, the fact that cumene quenches the excited triplets faster than *tert*-butylbenzene implies that the hydrogen transfer step can be, in some systems, rate controlling. A possible mechanism to explain the present results is given in Scheme I:

Scheme I

$$D^* + Q \xrightarrow{k_2} D^{\delta-}Q^{\delta+} \tag{2}$$

$$D^{\delta-}Q^{\delta+} \xrightarrow{k_3} D^* + Q \tag{3}$$

$$\xrightarrow{k_4} D + Q \tag{4}$$

$$\xrightarrow{k_5} DH + Q(-H) \tag{5}$$

Scheme I leads to

$$k_Q = k_2\left(\frac{k_4 + k_5}{k_3 + k_4 + k_5}\right) \tag{6}$$

The quenching rate constant would then be dependent upon both the rate of formation of the charge transfer complex (and hence on the IP of the quencher) and the rate of hydrogen transfer within the complex. The number of factors involved makes a quantitative discussion of the $(k_Q)_{\mathrm{model}}/(k_Q)_{\mathrm{m}}$ ratios difficult. Nevertheless, the data given in Table I show that in most systems considered the quenching rate by the polymers is similar to (and even larger than) that of the corresponding model compounds. There is not a significant decrease in the rate associated with the presence of the polymer chains, as observed in other systems involving energy transfer or chemical reaction.[5,11,12] Furthermore, it is also interesting to note that, contrary to the results found in other systems,[5] there are no significant changes in $(k_Q)_{\mathrm{m}}$ in the quenching of benzophenone triplets by PS when the molecular weight of the polymer is increased from 2.8×10^4 to 1.2×10^6. In order to explain these differences, we must taken into account two aspects of the present systems.

First, the processes are not diffusion controlled, and therefore they will not be affected by an obstructive effect of the polymer segments toward the diffusion of the small molecule. Therefore any "macromolecular effect" must arise from differences in the free energies of the activated complexes. These differences have been found to be relatively small when the reactive center is located in the pendant group.[12] Furthermore, it is interesting to note that no "polymer effect" has been observed in the equilibrium constants for the ion pair formation between dimethylbenzylamine and 2,6-dinitro-4-(benzoyloxy)phenol groups when one of the groups is attached to a PS chain.[13]

The second point to be considered is that the rate of the process is strongly dependent upon the IP of the acceptor. Since it can be expected that the IP's of the polymers are lower than those of the model compounds considered, a small "polymer effect" could be masked by the differences in ionization potential.

In the present work the results obtained in the quenching of benzophenone triplets by poly(α-methylstyrene) are not in agreement with those reported by Ikeda et al.[14] in a study of the photosensitized degradation of the polymer. The considerably smaller value of k_Q given by these authors (9×10^3 M^{-1} s^{-1}) could be partly due to the assumption that the quantum yield of cleavage under conditions of total quenching equals one. For example, if it is assumed that this yield is 3×10^{-2} (a value compatible with the reported experimental results) and that the triplet lifetime is that employed in the present work, the resulting value of k_Q is 5×10^5 M^{-1} s^{-1}.

The effect of the solvent in polymer processes is difficult to interpret due to the number of factors involved: dependence of the rate upon the solvent polarity, polymer effect upon the solvent micropolarity, change in macromolecular shape, and preferential absorption of the excited donor. Table II shows the data obtained for the quenching of benzil triplets in benzene and benzene/*n*-hexane mixtures. These data show that quenching by the polymer is relatively slower in the Θ mixtures than in benzene. This difference can be attributed to an increase in the steric hindrance associated with the increase in the degree of coiling.[15]

The effect of the solvent polarity upon the quenching rate of benzil by poly(*p*-methylstyrene) was evaluated by measuring the quenching rates in two Θ solvent mixtures of different polarities (2:8 benzene–hexane and 1:1 benzene–acetonitrile). It was found that, in agreement with the behavior expected for a charge transfer process, the quenching rate was nearly 4 times faster in the more polar mixture.[16]

Results obtained in the quenching by poly(*cis*-1,3-butadiene) and poly(cyclohexyl methacrylate) are summarized in Table I. Quenching of carbonyl triplets by diolefins is an example of a photochemical reaction that involves as a first step the formation of a charge transfer complex. This can, afterward, react by hydrogen abstraction and/or double-bond addition.[17] The data of Table I show that the reactivity of poly(*cis*-1,3-butadiene) toward excited carbonyl triplets is similar to that of 1,5-cyclooctadiene, a small molecule that also contains 1,4 unconjugated double bonds.

Quenching by poly(cyclohexyl methacrylate) can be considered to take place by hydrogen abstraction from the cyclohexyl group. This assumption is based on the lack of quenching by poly(methyl methacrylate) observed under similar conditions. The value of k_Q obtained for the polymer and the model compound is compatible with the reactivity observed for alkanes toward benzophenone triplets.[18] The data of Table I show that the reactivity of the polymer is nearly 3 times smaller than that of the model compound. A similar result has been obtained with *tert*-butoxy radicals.[12] The difference can be related to a polymer effect arising as a consequence of increased steric hindrance in the macromolecular system.

The quenching rate constants obtained for the quenching of benzil triplets by P2VN and its model compound 2-methylnaphthalene are given in Table III. The results obtained indicate that both compounds show similar quenching efficiencies. The quenching mechanism in this case can involve a charge transfer complex (the IP of 2-methylnaphthalene is 7.9 eV) or an endothermic energy transfer. In this regard, it is interesting to note that the triplet of 2-methylnaphthalene lies approximately 6.5 kcal higher than the benzil triplet. The expected quenching rate by an energy transfer mechanism is then of the order 10^5 M^{-1} s^{-1}, which is of the same order of magnitude as that determined experimentally.

Diffusion-Controlled Processes. Benzophenone triplets are quenched by the model compounds 1-naphthyl acetate, 2-naphthyl acetate, and 2-methylnaphthalene with rate constants very near the diffusional limit (see Table III), a result compatible with the exothermicity of the energy transfer process. Table III shows that the polymers are, in terms of molar concentration of naphthalene units, considerably less efficient and that the efficiency depends upon molecular weight of the polymer. Similar results have been reported by Webber et al. for the quenching of biphenyl triplets by P2VN.[5] These results cannot be due to a decrease in diffusion rate due to the added polymer since the microviscosity (i.e., the diffusion of the excited donor) will be practically the same as it is in the pure solvent.[19]

The low values of $(k_Q)_m$ obtained for the quenching of triplet benzophenone by polymers containing naphthyl groups can be explained in terms of the inhomogeneous distribution of the quencher units. Since the polymer concentration under these conditions was lower than 0.02%, the solution can be considered inhomogeneous at the microscopic level, comprising zones of "pure" solvent and "polymer coils" with a high concentration of quenching units. If it is assumed that at the low polymer concentration employed the proportion of donor molecules that are excited inside a polymer coil can be disregarded, the quenching rate constant, on the basis of polymer molecular concentration, can be evaluated by employing the classical Smoluchowski equation

$$(k_Q)_p = 4\pi N' r_p D_D p \qquad (7)$$

where, due to the large excited lifetime of the donor, the time-dependent term is not included.[20] Furthermore, due to the large difference in size between donor and quencher, only the diffusion coefficient of the donor (D_D) and the "equivalent radius" of the polymer coil (r_p) have been included. This equivalent radius of the polymer coil is defined as the radius of an equivalent sphere that in contact with any excited molecule gives a unity probability of quenching prior to emission (hence p in eq 7 is equal to 1). Given the rather large concentration of naphthyl groups "inside" a polymer coil, the volume of the sphere defined above will be closely related to the coil volume. Equation 7 shows that $(k_Q)_p$ for a given donor–polymer pair will depend upon r_p and hence on the polymer molecular weight. Furthermore, if it is assumed that D_D is approximately equal to the diffusion coefficient of the polymer model compound, then

$$(k_Q)_p/(k_Q)_{\text{model}} = \frac{1}{2p}\,\frac{r_p}{r_{(\text{D-M})}} \qquad (8)$$

where p is the probability of quenching in an encounter of the donor and the model compound. The fact that $(k_Q)_p/(k_Q)_{\text{model}}$ values are considerably larger than 1 is compatible with values expected from eq 8. Furthermore, since $r_p/\bar{n}r_{(\text{D-M})}$ can be expected to be smaller than 1 and to decrease with $\bar{n}$, the smaller values of $(k_Q)_m$ and its dependence on $\bar{n}$ can be easily explained.

The dependence of r_p on $\bar{n}$ can be obtained by plotting log $(k_Q)_p$ against log $(\bar{n})$. This plot is shown in Figure 2 for the data obtained in the present work and that previously reported by Webber et al.[5] From this figure the following relationships can be obtained:

$$(k_Q)_p \propto \bar{n}^{0.55} \qquad (9)$$

for P2VN and

$$(k_Q)_p \propto \bar{n}^{0.5} \qquad (10)$$

for P2NMA. Comparison of these relationships leads to

$$r_p \propto \bar{n}^{0.55} \qquad (11)$$

for P2VN and

$$r_p \propto \bar{n}^{0.5} \qquad (12)$$

for P2NMA. The radius of the hydrodynamically equivalent sphere is related to the chain length by

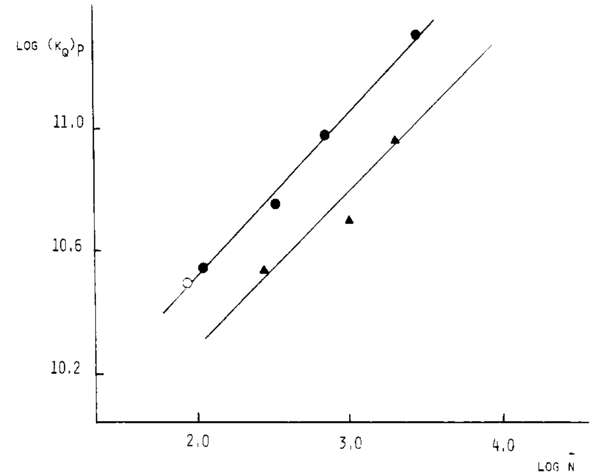

Figure 2. Dependence of quenching rate constant $(k_Q)_p$ with degree of polymerization in benzene at 20 °C: (▲) benzophenone–poly(2-naphthyl methacrylate); (●) biphenyl–poly(2-vinylnaphthalene;[5] (○) benzophenone–poly(2-vinylnaphthalene).

$$r \propto \bar{n}^{\beta} \qquad (13)$$

where β is a constant related to the a parameter of the Mark–Houwink–Sakurada equation by

$$\beta = (a + 1)/3 \qquad (14)$$

Since the values of a in benzene are 0.72 and 0.57 for P2VN and P2NMA, respectively, the β values are 0.57 and 0.52, respectively, which are very close to the exponents of eq 11 and 12. We can conclude then that the equivalent sphere defined in the present work shows the same dependence on the average length of the polymer chain as the hydrodynamically equivalent sphere. A similar dependence of the rate constant on the polymer chain length has been reported by Behzadi et al.[21] for the reaction of OH radicals with various polymers and was also explained in terms of the diffusional rate toward the polymer coils.[22]

The effect of polymer coil shape upon the quenching rate constant was evaluated by measuring the quenching of P2NMA (M_w = 6.5 × 10^5) and 2-naphthyl acetate in benzene and in a near-Θ solvent of the polymer (56:44 benzene–acetonitrile). The values of $(k_Q)_m/(k_Q)_{\text{model}}$ obtained were 7.7 × 10^{-3} and 2.5 × 10^{-3}, respectively. The decrease in rate observed in the Θ solvent can then be related to the diminution of the size of the polymer coil and affords a direct measure of the expansion of the macromolecule in a good solvent.

In conclusion, the results obtained in the present work show that quenching by polymers in dilute solution is similar to that of model compounds for slow processes, but it is considerably slower for diffusion-controlled reactions. In this case, the results can be explained in terms of an inhomogeneous distribution of quenching units.

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Self-Diffusion of 1,3-Dimethyladamantane Dissolved in Hexafluorobenzene and in Polybutadiene

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ABSTRACT: We report self-diffusion measurements on both components of the systems 1,3-dimethyladamantane (1,3-DMA) dissolved in C_6F_6 and 1,3-DMA dissolved in polybutadiene. The concentration and temperature dependences of diffusion and the nonideal solution behavior follow free-volume models, permitting the deduction of free-volume and collision parameters for 1,3-DMA.

I. Introduction

The study of binary liquid solutions and solutions of liquids and rubbery polymers has been considerably furthered by measurements of transport properties, about which self-diffusion can yield detailed information.[1] Consequently, self-diffusion measurements of both components in a solution as functions of concentration and temperature can provide a detailed characterization of certain molecular attributes of one species if those of the other species are known. Self-diffusion in liquid or polymer systems is extremely sensitive to free-volume availability and to the dynamics of the collisions among molecules.[2] The parameters to be determined thus are those entering the free-volume theories suitably augmented by collision dynamic considerations.[3–5]

The molecule of interest in this work is 1,3-dimethyladamantane, not well-known until recently and to our knowledge not yet characterized in these terms. This molecule is relatively rigid and compact; its intermediate size makes it a suitable candidate to investigate the onset of dynamic anomalies that are known to be present in larger molecules such as 5α-cholestane and cholesta-3,5-diene[6] but that are absent in smaller molecules[4] and even in segmentally mobile *n*-paraffins.[7,8] In the process, an improved understanding of the diffusion process may be achieved.

The pulsed-gradient spin-echo method[9] is ideally suited for measuring self-diffusion in multicomponent systems at equilibrium concentration. The different components can be observed via NMR of mutually exclusive nuclides or by relying on differences in chemical shift. The samples may be reused indefinitely, making it convenient to measure the temperature dependence of diffusion and minimizing the consumption of expensive ingredients.

A preliminary report of this work has been given.[10]

II. Theory

It will be useful to collect here the theoretical expressions used in the analysis of the data. The fractional free volume f of a polymeric or other liquid of species i is given approximately by[11]

$$f_i = f_{g_i} + \Delta\alpha_i(T - T_{g_i}) \qquad (1)$$

This relation holds above the liquid's glass transition temperature T_g, where f reduces to $f_g = 0.025$. The free-volume expansivity $\Delta\alpha$ can be estimated from the difference in expansivity above and below T_g. In a binary mixture of liquids (i = 1, 2) the diffusion coefficients D_1 and D_2 depend on the weight fraction w_1 of the first species in a way described by Vrentas and Duda:[4,5]

$$\ln D_1 = \ln D_1^0 + B_1 w_1 S_1/(1 + w_1 f_2 S) \qquad (2)$$

$$\ln D_2 = \ln D_2^0 + B_2 w_1 S_2/(1 + w_1 f_2 S) \qquad (3)$$

where[6]

$$S = (\rho_2 f_1/\rho_1 - f_2)/f_2^2 \qquad (4)$$

$$S_1 = (\rho_2 M_1 f_1/\rho_1 M_2 - f_2)/f_2^2 \qquad (5)$$

$$S_2 = S_1 M_2/M_1 \qquad (6)$$

and

$$B_i = g\hat{V}_i^*/\hat{V}_2^0 \qquad (7)$$

Here ρ_i and M_i denote, respectively, the mass density and molecular or segmental mass of species i. The ratio M_1/M_2 in liquid systems may depart substantially from the molecular weight ratio when the species are dissimilar; in the general case, M_1/M_2 characterizes the collision dynamics