the internal pores is determined by flow.[1] In that case, however, the transport through the pores would be determined by flow even for lower molecular mass samples. The measurement of the permeation dispersion at that column, however, did not indicate convective transport for these samples.[6]

Because of the still approximate character of the theoretical calculations for hydrodynamic chromatography, the possibility of the action of hydrodynamic fractionation of the high molecular mass samples studied cannot be totally ruled out, but it seems more probable that the effect found at that column is based on the deformation of the macromolecules in the interstitial volume.

In the case of the VITX column the samples reinjected at the slower flow rate showed a higher elution volume than the freshly injected ones. That means that at the higher flow rate a degradation of the samples had taken place on the column. The fact that the injection volume of the reinjected sample is still less than the elution volume of a fresh injected sample at the high flow rate points to an additional effect, probably based on the reversible deformation of the macromolecules.

The distinct behavior of the samples at both materials investigated might be based on the fact that the macromolecules are subject to higher local shearing and stretching stresses at the edged VITX particles and are therefore more easily degraded than at the spherical TSK particles.

The effects found should show up especially in the case of high-speed SEC and for samples of extremely high molecular mass. Here there are only but a few investigations published. While several investigators found an increase of the elution volume with increasing flow rate,[8–11] Kato and co-workers[12] could separate PS samples of molecular masses ranging from $10^6$ to $10^7$ at a flow rate of 0.5 mL/min at the material TSK G6000H8 (particle diameter about 8 μm) without any problems. The reason for this might be the solvent used by the authors, methyl ethyl ketone. MEK is nearly a Θ solvent for PS, while $CHCl_3$ and THF are good solvents. A decrease of the coil dimensions brings about a decrease of the forces acting at the molecule and an increase of the stability of the coil.

SEC materials can thus fail in the region of high molecular mass in spite of sufficiently large internal pores. Working in this region, one has to consider the possibility that deformation or degradation effects demand a decrease of the flow rate or a change of the solvent, respectively, on the column.

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# Rates of Intramolecular Collision between Terminal Groups of α,ω-Dianthrylpolystyrene in Benzene and Cyclohexane Solutions As Studied by Triplet–Triplet Absorption Measurements

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ABSTRACT: Rate constants of intramolecular end-to-end collisions, $k_{intra}$, in α,ω-dianthrylpolystyrene have been measured in benzene and cyclohexane solutions by following the rate of decay of triplet-excited anthryl groups. Polymer solutions were irradiated with 25-ns flashes of 347-nm light produced by a ruby laser. The decay of the triplet–triplet absorption after the flash was recorded as a function of time. In order to minimize intermolecular interactions, very dilute polymer solutions ($1 \times 10^{-5}$–$3 \times 10^{-6}$ mol/L) were used. The values of $k_{intra}$ were in the range $2 \times 10^5$–$1 \times 10^3$ $s^{-1}$. In the case of benzene solutions at 22 °C, $k_{intra}$ decreased with increasing degree of polymerization, $N$, according to $k_{intra} = (\mathrm{const})N^{-n}$, with $n = 1.0 \pm 0.06$ for $N$ covering the range 110–3000. In the case of cyclohexane solutions at 34 °C (Θ condition), a more complicated function holds for the decrease of $k_{intra}$ with increasing $N$. The dependence can be approximately described by $k_{intra} = (\mathrm{const})N^{-n}$, with $n = 1.5$ for $N \leq 300$ and with $n = 1.0$ for $N \geq 300$. A theoretical treatment taking into account the short-time fluctuation of chain segments is presented which explains the dependence of $k_{intra}$ on $N$ in the present case as well as in other cases reported previously in the literature.

## I. Introduction

Time-resolved luminescence and absorption spectroscopy is a powerful tool for the study of structure, mobility, and kinetics of reactions of both synthetic and biological macromolecules.[1] If intramolecular reactions between the terminal groups of a polymer molecule occur as diffusion-controlled reactions, the rate constant of these reactions may be considered as a measure of the conformational mobility of the polymer chains. Photophysical processes[2–6] as well as electron-transfer processes in connection with ESR measurements[7] have proved suitable as probes for the study of intramolecular end-to-end collisions

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Table I
Characterization of A-PS-A

| polymer | $\overline{M}_n$ | $\overline{M}_w/\overline{M}_n$ | $N$ | % anthryl groups at chain ends |
|---|---|---|---|---|
| APS110A | $1.12 \times 10^4$ | 2.11 | 107 | 100 |
| APS135A | $1.40 \times 10^4$ | 1.56 | 134 | 100 |
| APS280A | $2.95 \times 10^4$ | 1.59 | 280 | 100 |
| APS300A | $3.11 \times 10^4$ | 1.84 | 296 | 92 |
| APS640A | $6.68 \times 10^4$ | 1.45 | 639 | 100 |
| APS940A | $9.78 \times 10^4$ | 1.38 | 937 | 100 |
| APS1300A | $1.35 \times 10^5$ | 1.42 | 1290 | 100 |
| APS1500A | $1.58 \times 10^5$ | 1.28 | 1520 | 100 |
| APS2600A | $2.78 \times 10^5$ | 1.19 | 2670 | 78 |
| APS3000A | $3.09 \times 10^5$ | 1.24 | 2970 | 91 |
| PS400A[a] | $4.20 \times 10^4$ | 1.28 | 404 | 51 |

[a] Reference polymer with an anthryl group at one chain end only.[14]

of chain molecules, but most of these studies concerned rather short-chain molecules, containing less than 30 atoms in the main chain. Rate constants of intramolecular collisions between terminal groups of end-labeled polystyrene chains have been recently obtained by some of the present authors[2] by measuring the rate of triplet–triplet annihilation (delayed fluorescence) and by Winnik et al.[3] by measuring the rate of excimer formation (excimer prompt fluorescence). As far as the dependence of the rate constant of intramolecular end-to-end collision, $k_{\text{intra}}$, on the degree of polymerization, $N$, is concerned, the former results were at variance with the theories[8–11] on the dynamics of end-to-end collisions in flexible linear macromolecules.

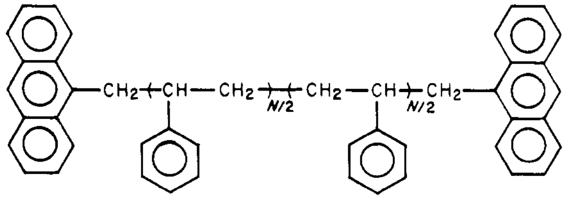
In both cases mentioned above[2,3] experimentally well-established techniques were applied. Moreover, the polystyrene samples possessing anthryl or pyrenyl end groups at both chain ends had very narrow molecular weight distributions. However, the former measurements,[2] which were carried out in benzene solution with polymers of $N$ ranging from 280 to 3000, were somewhat hampered by the rather low output power of the nitrogen laser ($8 \times 10^{14}$ photons/pulse). Although the triplet lifetime of the anthryl groups was sufficiently long (0.2–1.0 ms), the polymer concentrations for the cases of large $N$ could not be kept low enough in order to avoid the interference of intermolecular with the intramolecular collisions. Additional problems arose because of the intense prompt-fluorescence signal, whose interference with the delayed fluorescence limited the accuracy of the determination of decay rates of delayed fluorescence at times shorter than 20 μs. In the other case,[3] the short lifetime of pyrene excimers ($\simeq$200 ns) restricted the measurements of $k_{\text{intra}}$ to polymers with rather small $N$ (30–260), though the measurements could be carried out at sufficiently low polymer concentrations ($\simeq 1 \times 10^{-6}$ M).

In the present work, transient absorption measurements served to obtain values of $k_{\text{intra}}$, the rate constant of triplet–triplet annihilation between terminal groups of α,ω-dianthrylpolystyrene (A-PS-A) with $N$ ranging from 110 to 3000, in benzene at 22 °C (good solvent) and in cyclohexane at 34 °C (Θ solvent) at polymer concentrations of the order of $10^{-6}$ mol/L (lower than 1 g/L).

The characteristic features of the present absorption experiments as compared with the previous delayed fluorescence measurements[2] are the following: (i) The higher intensity of the frequency-doubled ruby laser pulse in the Hahn-Meitner-Institut in Berlin ($\simeq 5 \times 10^{16}$ photons/pulse) enabled most of the anthryl groups in A-PS-A to become excited during a single flash. (ii) Absorption measurements yielded the time dependence of the absolute optical density of the triplet anthryl groups. Thus, we could obtain decay curves covering the time range from 10 ns to 10 ms from several oscilloscope traces obtained with the same solution using different time scales. (iii) The very low concentration of A-PS-A in the present experiments eliminates the superposition of intra- and intermolecular collisions. Consequently $k_{\text{intra}}$ for A-PS-A could be measured not only in a good solvent but also in a Θ solvent.

## II. Experimental Section

**A. Materials.** α,ω-Dianthrylpolystyrene (A-PS-A) was synthesized in a sealed tube by the direct attack of 9-(chloromethyl)anthracene onto living polystyryl dianions prepared by anionic polymerization of styrene under high vacuum in tetrahydrofuran with sodium–naphthalene. Details of the preparation have been described.[12] The structure of A-PS-A is



The A-PS-A was purified by repeated precipitations from benzene solutions with methanol until no trace of low molecular weight impurities was observable by gel permeation chromatography (GPC) with a 350-nm absorption detector. Number-average molecular weights, $\overline{M}_n$, and molecular weight distributions of A-PS-A were measured with a TSK HLC-802UR type GPC apparatus. The molecular weight distribution was evaluated according to Pierce et al.[13] The content of terminal anthryl groups (A) was determined with a Shimadzu MPS-5000 type spectrophotometer. The characteristics of A-PS-A samples are shown in Table I.

Uvasol-grade benzene (BZ) was purified by shaking with $H_2SO_4$, dried over $CaCl_2$ and sodium, and distilled over a fractionation column (Fischer, Bonn). The Uvasol-grade cyclohexane (CH) was dried over sodium and distilled over a fractionaion column.

**B. Apparatus.** About 3 cm$^3$ of sample solution in a cylindrical Pyrex cell with a polymer concentration of $3 \times 10^{-6}$–$1 \times 10^{-5}$ M was deaerated by several freeze–pump–thaw cycles at $10^{-5}$ torr and sealed under vacuum. The sample solutions were irradiated with single 347-nm light flashes of half-width 25 ns from a frequency-doubled ruby laser (Korad K1QS2).[15] For measuring changes in the optical absorption, the light beam of a xenon lamp (Osram, XBO 450W) was directed through the cell perpendicular to the photolyzing ruby laser beam and was focused on the entrance slit of a high-intensity monochromator (33-86-76, Bausch and Lomb). The output of the photomultiplier (RCA, 1P28) was fed into a 7A13 or 7A22 plug-in (Tektronix) and displayed on a storage oscilloscope (Tektronix, 7633).

**C. Transient Absorption Measurements.** In the case of benzene solutions the measurements were carried out at room temperature (22 °C). In the case of cyclohexane solutions the sample cell was set in a water jacket (34 °C) regulated by a water-circulating thermostat (Haake).

The optical density, $E$, was calculated according to

$$E = -\log\,(1 - \Delta U/U_0) \qquad (1)$$

where $\Delta U$ is the photomultiplier output voltage corresponding to the absorption and $U_0$ is that without absorption.

Transient absorption spectra of triplet anthryl groups in A-PS-A observed immediately after the flash are shown in Figure 1. Absorption peaks were located at 435 nm (A-PS-A in benzene) and at 430 nm (A-PS-A in cyclohexane). These values indicate small red shifts due to alkyl substitution relative to $\lambda_{\max}$ 430 nm for anthracene in benzene and $\lambda_{\max}$ 420 nm for anthracene in cyclohexane.[16] Thus the decay curves for triplet absorption of A-PS-A were measured mostly at 435 nm in the case of benzene solution and at 430 nm in the case of cyclohexane solution.

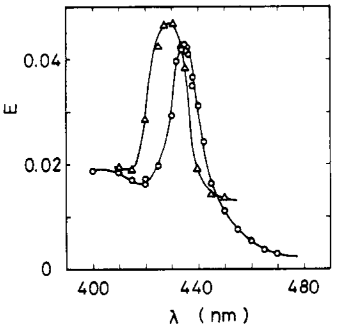


**Figure 1.** Transient absorption spectra of APS110A in benzene (○) and in cyclohexane (△) at the end of a 25-ns flash. [A] = 1.9 × $10^{-5}$ M in benzene, [A] = 1.6 × $10^{-5}$ M in cyclohexane.

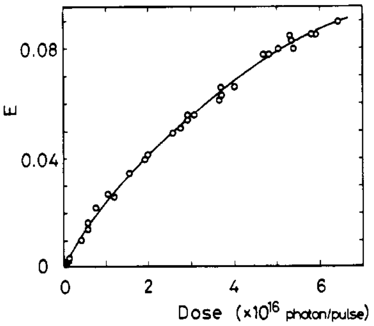


**Figure 2.** Dependence of the optical density, $E$, at $\lambda$ = 435 nm measured at the end of a 25-ns flash on the exposure dose, $D$, for APS135A in benzene (9.6 × $10^{-6}$ M).

For the kinetic treatment of triplet decay, several oscilloscope traces obtained for various time regions were normalized with respect to the absorbed dose per flash. The typical dependence of the initial optical density on the exposure dose is shown in Figure 2. The curvature is due to saturation, i.e., to the fact that at high exposure doses a significant fraction of anthryl groups is transferred to the triplet state.

**D. Actinometry.** The exposure dose, $D$, i.e., the number of photons incident upon the solution, was determined with benzophenone (0.001–0.002 M)–naphthalene (0.1 M) actinometer in benzene.[17] A plot of $D$, calculated from the transient absorption of naphthalene triplets ($\epsilon_{425}$ 2.3 × $10^4$ $M^{-1}$ $cm^{-1}$), vs. the photocell output monitoring the intensity of the laser pulse gave a straight line over the whole intensity range (2 × $10^{15}$–6 × $10^{16}$ photons/flash). An exposure dose of 6 × $10^{16}$ photons/flash corresponds to an absorbed dose of 1.1 × $10^{-4}$ einstein/(L·flash) at 30% absorption.

## III. Kinetics for the Decay of Triplet Anthryl Groups

We have shown[12] that in the case of $\alpha$-anthrylpolystyrene the triplet anthryl groups, A*, decay not only via radiationless transitions (rate constant $k_d^T$), concentration quenching ($k_{cq}$), and intermolecular triplet–triplet (T–T) annihilation ($k_{TT}^{inter}$) but also via intra- and intermolecular quenching by polystyrene chains ($k_{St}^{intra}$ and $k_{St}^{inter}$). The decay rate is expressed by

$$-d[A^*]/dt = k_1[A^*] + 2k_{TT}^{inter}[A^*]^2 \quad (2)$$

$$k_1 = k_d^T + k_{St}^{intra} + k_{cq}[A] + k_{St}^{inter}[St] \quad (3)$$

where [A] is the concentration of anthryl groups, [St] is the concentration of polystyrene in (base mol/L), and $k_1$ is the apparent first-order rate constant with respect to [A*].

When anthryl groups are attached to both ends of a chain, electronic excitation during the laser pulse produces two species: singly and doubly excited molecules, denoted by A*-A and A*-A*. In the case of A-PS-A, the kinetic scheme of the decay of both species is depicted by reactions 4a–f, where the rate of each reaction is also shown and

$$A^*\text{-}A^* \rightarrow A^*\text{-}A \qquad 2k_1[A^*\text{-}A^*] \quad (4a)$$

$$A^*\text{-}A^* \rightarrow A\text{-}A \qquad k_{TT}^{intra}[A^*\text{-}A^*] \quad (4b)$$

$$A^*\text{-}A^* + A^*\text{-}A^* \rightarrow A^*\text{-}A + A^*\text{-}A \qquad 4k_{TT}^{inter}[A^*\text{-}A^*]^2 \quad (4c)$$

$$A^*\text{-}A^* + A^*\text{-}A \rightarrow A^*\text{-}A + A\text{-}A \qquad 2k_{TT}^{inter}[A^*\text{-}A^*][A^*\text{-}A] \quad (4d)$$

$$A^*\text{-}A \rightarrow A\text{-}A \qquad k_1[A^*\text{-}A] \quad (4e)$$

$$A^*\text{-}A + A^*\text{-}A \rightarrow A\text{-}A + A\text{-}A \qquad k_{TT}^{inter}[A^*\text{-}A]^2 \quad (4f)$$

$k_{TT}^{intra}$ and $k_{TT}^{inter}$ are the rate constants of the intra- and intermolecular T–T annihilations. The rate of disappearance of each species can be expressed by eq 5 and 6.

$$-d[A^*\text{-}A]/dt = k_1[A^*\text{-}A] + 2k_{TT}^{inter}[A^*\text{-}A]^2 - 2k_1[A^*\text{-}A^*] - 8k_{TT}^{inter}[A^*\text{-}A^*]^2 \quad (5)$$

$$-d[A^*\text{-}A^*]/dt = k_{TT}^{intra}[A^*\text{-}A^*] + 2k_1[A^*\text{-}A^*] + 2k_{TT}^{inter}[A^*\text{-}A^*][A^*\text{-}A] + 8k_{TT}^{inter}[A^*\text{-}A^*]^2 \quad (6)$$

$$[A^*] = 2[A^*\text{-}A^*] + [A^*\text{-}A] \quad (7)$$

Here it should be noted that two molecules of A*-A disappear or appear for each reaction of (4f) or (4c). As the intramolecular quenching by the moieties of the polystyrene chain ($k_{St}^{intra}$) occurs much faster than the intramolecular concentration quenching by A ($k_{cq}^{intra}$),[12,18] we can assume that $k_1$ in eq 2, 4a, and 4e has the same value.

It should be recalled here that the aim of the present investigation is the determination of $k_{TT}^{intra}$. In the following, we will show that the second-order terms containing [A*-A*] in eq 5 and 6 can be neglected under the present experimental conditions. The value of $k_1$ can be calculated from eq 3, since we have already determined all the rate constants constituting $k_1$ for $\alpha$-anthrylpolystyrene in benzene and cyclohexane.[12,18] Moreover, we obtain $k_1$ quite easily from the slope of the linear part of the curves in Figure 4, as will be discussed in the next section. The rate constant $k_{TT}^{inter}$ is supposed to have a value similar to that for the quenching of polystyrylbenzil phosphorescence by $\alpha$-anthrylpolystyrene,[14,19] both being rate constants of diffusion-controlled polymer–polymer reactions between terminal triplet-excited groups. The initial concentrations of A*-A and A*-A* can be estimated from the concentration of anthryl groups [A], the exposure dose, the molar extinction coefficient of anthryl groups, $\epsilon_{347}$ 3.1 × $10^3$ $M^{-1}$ $cm^{-1}$, and the anthryl triplet quantum yield $\phi$ = 0.72. The introduction of these values together with the previously reported value[2] for $k_{TT}^{intra}$ leads to the conclusion that the fourth term in eq 5 and the third and fourth terms in eq 6 are negligibly small, even in the initial stages of the triplet deactivation process. For example, in the case of APS300A in benzene with [APSA] = 9 × $10^{-6}$ M and an exposure dose of 3 × $10^{16}$ photons/pulse, about 50% of the anthryl groups were excited to $^1A^*$, and the following values were obtained: $k_1[A^*\text{-}A]_0 = 1.2 \times 10^{-2}$ M $s^{-1}$, $2k_{TT}^{inter}[A^*\text{-}A]_0^2 = 1.6 \times 10^{-2}$ M $s^{-1}$, $k_{TT}^{intra}[A^*\text{-}A^*]_0 = 5.0 \times 10^{-2}$ M $s^{-1}$, $2k_1[A^*\text{-}A^*]_0 = 6.0 \times 10^{-3}$ M $s^{-1}$, $8k_{TT}^{inter}[A^*\text{-}A^*]_0^2 = 4.0 \times 10^{-3}$ M $s^{-1}$, and $2k_{TT}^{inter} \cdot [A^*\text{-}A^*]_0[A^*\text{-}A]_0 = 4.0 \times 10^{-3}$ M $s^{-1}$. As the values of the second-order terms containing [A*-A*] in eq 5 and 6 decrease much more rapidly with time than those of the other terms, eq 5 and 6 reduce to

$$-d[A^*\text{-}A]/dt = k_1[A^*\text{-}A] + 2k_{TT}^{inter}[A^*\text{-}A]^2 - 2k_1[A^*\text{-}A^*] \quad (8)$$

$$-d[A^*\text{-}A^*]/dt = k_{TT}^{intra}[A^*\text{-}A^*] + 2k_1[A^*\text{-}A^*] \quad (9)$$

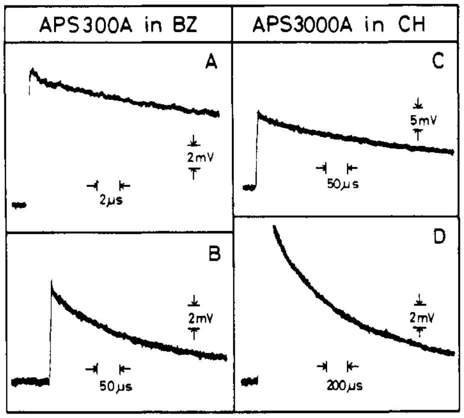


**Figure 3.** Oscilloscope traces obtained with APS300A in benzene (A, B) and APS3000A in cyclohexane (C, D): (A) $U_0$ = 242 mV, $D = 3.0 \times 10^{16}$ photons/flash; (B) $U_0$ = 164 mV, $D = 5.2 \times 10^{16}$ photons/flash; (C) $U_0$ = 363 mV, $D = 2.1 \times 10^{16}$ photons/flash; (D) $U_0$ = 406 mV, $D = 4.5 \times 10^{16}$ photons/flash.

By solving these differential equations, using the substitutions $x$ = [A*-A*], $y$ = [A*-A], $k_2 = k_{\mathrm{TT}}{}^{\mathrm{inter}}$, and $k_3 = k_{\mathrm{TT}}{}^{\mathrm{intra}}$, we obtain

$$[\mathrm{A}^*] = 2x + y = \{2x_0 - 2k_1x_0(1+f)^{-1}(k_1+k_3)^{-1}\}\exp\{-(k_3 + 2k_1)t\} + (1+f)^{-1}\{y_0 + 2k_1x_0(k_1+k_3)^{-1}\}\exp(-k_1t) \quad (10)$$

where

$$f = k_2k_1^{-1}B\{1 - \exp(-k_1t)\} \quad (11)$$

and

$$B = y_0 + 2k_1x_0(k_1+k_3)^{-1}[1 - \exp\{-(k_1+k_3)t\}] \quad (12)$$

As the optical density, $E$, is proportional to [A*], we get finally

$$E = Z_1\exp\{-(k_{\mathrm{TT}}{}^{\mathrm{intra}} + 2k_1)t\} + Z_2\exp(-k_1t) \quad (13)$$

with

$$Z_1 = 2[\mathrm{A^*\text{-}A^*}]_0 - 2k_1[\mathrm{A^*\text{-}A^*}]_0/\{(1+f)(k_1 + k_{\mathrm{TT}}{}^{\mathrm{intra}})\} \quad (14)$$

$$Z_2 = \{[\mathrm{A^*\text{-}A}]_0 + 2k_1[\mathrm{A^*\text{-}A^*}]_0/(k_1 + k_{\mathrm{TT}}{}^{\mathrm{intra}})\}/(1+f) \quad (15)$$

Possible changes in $Z_1$ and $Z_2$ with time, $t$, are supposed to be negligibly small.

## IV. Results

**A. Analysis of the Decay of Triplet–Triplet Absorption of A-PS-A in Solution.** Typical oscilloscope traces depicting the decay of the T–T absorption after the flash are shown in Figure 3. As has been described in the Experimental Section, the decay could be followed over a broad time range extending from 100 ns up to several milliseconds. Figure 4 shows typical semilogarithmic plots of the normalized optical density, $E'$, against the time after the flash. For the systems APS300A/benzene and APS3000A/cyclohexane the plots exhibit initial curvatures in contrast to the system PS400A/benzene, where a straight line covering the whole time range was obtained. PS400A is a α-anthrylpolystyrene and intramolecular triplet–triplet deactivation is not possible in this case. From a comparison of the results shown in Figure 4, it is therefore concluded that the initial curvature observed with the α,ω-dianthryl polymers is caused by intramolecular triplet–triplet deactivation. From the slopes of the linear portions of the plots in Figure 4, the values of $k_1$ were determined. For analysis of the initial decay of the optical density, we referred to eq 13. Applying least-squares treatment, we extrapolated the linear portion toward $t$ = 0 and plotted the logarithm of the difference $(E' - E'_{\mathrm{ext}})$ vs. time. Typical plots are also shown in Figure 4 (designated by (c)). According to eq 13 the slopes of the straight lines thus obtained correspond to $k_{\mathrm{TT}}{}^{\mathrm{intra}} + 2k_1$. The values of $k_1$ and $k_{\mathrm{TT}}{}^{\mathrm{intra}}$ obtained with A-PS-A in benzene and cyclohexane in the present work are summarized in Tables II and III, respectively.

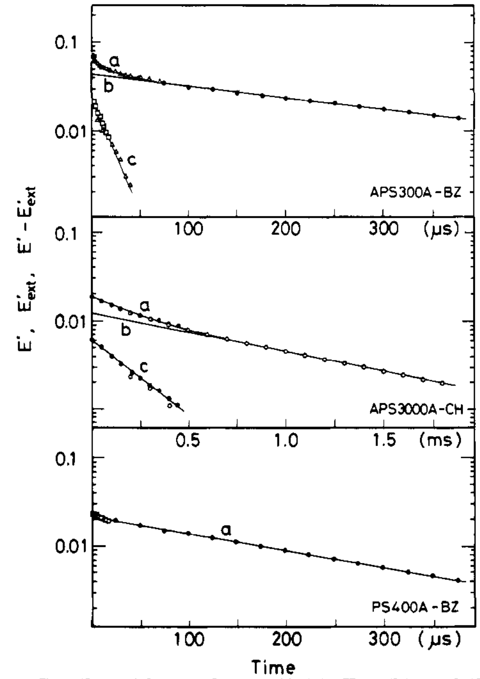


**Figure 4.** Semilogarithmic plots of $E'$ (a), $E'_{\mathrm{ext}}$ (b), and $(E' - E'_{\mathrm{ext}})$ (c) against time, $t$, for APS300A in benzene, APS3000A in cyclohexane, and PS400A in benzene. The time scales of the oscilloscope traces used for the construction of the graphs were 500 ns/division (×), 2 μs/division (□), 10 μs/division (△), 50 μs/division (●), and 200 μs/division (○).

At time zero the ratio $(E' - E'_{\mathrm{ext}})/E'$ is equal to $Z_1/(Z_1 + Z_2)$, which corresponds approximately to the fraction of excited anthryl groups that contribute to intramolecular T–T annihilation. Values ranging from 0.2 to 0.5 were estimated for this fraction.

**B. Rates of Collision between Terminal Anthryl Groups in A-PS-A.** The rate constants $k_{\mathrm{intra}} \equiv k_{\mathrm{TT}}{}^{\mathrm{intra}}$ obtained for A-PS-A in benzene and in cyclohexane are plotted in Figure 5 as a function of $N$, the average number of styrene moieties per macromolecule. It can be seen from Figure 5 that the measured values cover the range from $2 \times 10^5$ to $1 \times 10^3$ s$^{-1}$ and that $k_{\mathrm{intra}}$ decreases with increasing $N$ both in benzene and in cyclohexane. In benzene, the dependence of $k_{\mathrm{intra}}$ on $N$ follows the relationship

$$k_{\mathrm{intra}} = (\mathrm{const})N^{-n} \quad (16)$$

with $n = 1.0 \pm 0.06$. In cyclohexane solution $k_{\mathrm{intra}}$ is 2–4 times smaller than in benzene solution. Moreover, the dependence of $k_{\mathrm{intra}}$ on $N$ cannot be described by a simple relationship such as given in eq 16.

The values of $k_{\mathrm{intra}}$ obtained in benzene solution are at variance with values obtained previously with the aid of the delayed fluorescence technique,[2] as far as the range of $N$ between 940 and 3000 is concerned. In that case the exponent $n$ was determined as 0.53, while for lower values of $N$ (280–780) the same results were obtained as in the

Table II
Rate Constants $k_1$ and $k_{TT}^{intra}$ Obtained with A-PS-A in Benzene at 22 °C

| polymer | polymer concn | | $10^{-3}k_1$, $s^{-1}$ | $10^{-3}(k_{TT}^{intra} + 2k_1)$, $s^{-1}$ | $k_{TT}^{intra}$, $s^{-1}$ |
|---|---|---|---|---|---|
| | in $10^{-6}$ M | in g/L | | | |
| APS110A | 9.8 | 0.11 | 4.2 | 155 | $1.5 \times 10^5$ |
| APS135A | 8.3 | 0.12 | 3.0 | 110 | $1.0 \times 10^5$ |
| APS280A | 10.8 | 0.32 | 4.6 | 67.4 | $5.8 \times 10^4$ |
| APS300A | 9.0 | 0.30 | 2.9 | 71.5 | $6.6 \times 10^4$ |
| APS640A | 10.4 | 0.70 | 1.7 | 31.5 | $2.8 \times 10^4$ |
| APS940A | 5.2 | 0.51 | 1.3 | 17.6 | $1.5 \times 10^4$ |
| APS1300A | 5.0 | 0.68 | 1.2 | 15.8 | $1.3 \times 10^4$ |
| APS1500A | 5.5 | 0.87 | 3.2 | 14.7 | $8.2 \times 10^3$ |
| APS2600A | 2.8 | 0.98 | 1.3 | 8.3 | $5.7 \times 10^3$ |
| | 10.0 | 3.56 | 1.7 | 8.5 | $5.0 \times 10^3$ |
| APS3000A | 2.9 | 0.98 | 1.3 | 9.6 | $7.0 \times 10^3$ |
| PS400A | 10.4 | 0.86 | 3.9 | | |

Table III
Rate Constants $k_1$ and $k_{TT}^{intra}$ Obtained with A-PS-A in Cyclohexane at 34 °C

| polymer | polymer concn | | $10^{-3}k_1$, $s^{-1}$ | $10^{-3}(k_{TT}^{intra} + 2k_1)$, $s^{-1}$ | $k_{TT}^{intra}$, $s^{-1}$ |
|---|---|---|---|---|---|
| | in $10^{-6}$ M | in g/L | | | |
| APS110A | 8.2 | 0.09 | 3.4 | 87.4 | $8.1 \times 10^4$ |
| APS135A | 9.1 | 0.13 | 3.3 | 57.2 | $5.1 \times 10^4$ |
| APS280A | 10.2 | 0.30 | 2.5 | 26.2 | $2.1 \times 10^4$ |
| APS300A | 9.7 | 0.33 | 2.9 | 18.1 | $1.2 \times 10^4$ |
| APS640A | 8.8 | 0.59 | 1.0 | 6.9 | $4.8 \times 10^3$ |
| APS940A | 4.9 | 0.48 | 1.2 | 7.6 | $5.2 \times 10^3$ |
| APS1300A | 4.7 | 0.64 | 1.3 | 7.4 | $4.8 \times 10^3$ |
| APS1500A | 5.3 | 0.84 | 1.4 | 5.9 | $3.1 \times 10^3$ |
| APS2600A | 2.8 | 0.98 | 0.62 | 3.8 | $2.6 \times 10^3$ |
| APS3000A | 2.9 | 0.98 | 0.95 | 3.4 | $1.5 \times 10^3$ |

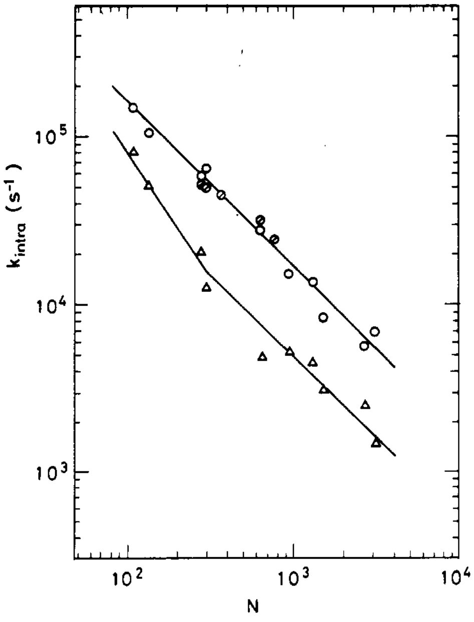


**Figure 5.** Dependence of $k_{intra}$ for end-to-end collision on the degree of polymerization, $N$, of A-PS-A in benzene (○) and in cyclohexane (△). Previous results[2] (⊘) obtained for A-PS-A in benzene by delayed fluorescence measurements ($N$ = 280–780, [APSA] ≃ $3 \times 10^{-5}$ M) are also shown.

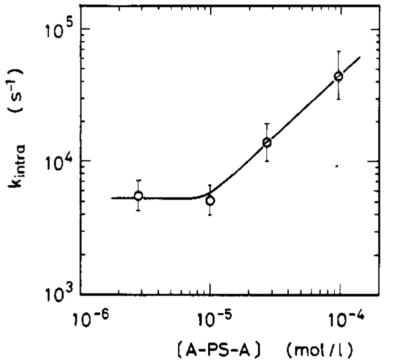


**Figure 6.** Dependence of $k_{intra}$ on polymer concentration. APS2600A in benzene. (○) Results of T–T absorption measurements. (⊘) Results of delayed fluorescence measurements.

present work. The discrepancy can be explained in terms of a polymer concentration effect. Figure 6 shows a plot of $k_{intra}$ vs. the polymer concentration. The values were obtained with APS2600A in benzene by the present technique at [A-PS-A] ≤ $1 \times 10^{-5}$ mol/L and by delayed fluorescence measurements at [A-PS-A] ≥ $2.7 \times 10^{-5}$ mol/L. It is seen that $k_{intra}$ is independent of the concentration only at [A-PS-A] ≤ $1 \times 10^{-5}$ mol/L. It is important to point out that this critical concentration is well below $C^*$, the overlap concentration of polymer coils (30 g/L or $1.1 \times 10^{-4}$ mol/L for APS2600A in benzene).[20] The critical concentration becomes higher with decreasing $N$ because the coil diameter decreases with decreasing N. It is, therefore, concluded that during the previous studies the polymer concentrations applied were not always low enough in order to prevent intermolecular T–T deactivation to compete with intramolecular interaction. This does not pertain to the experiments with relatively low values of $N$ but to those with $N \geq 940$, where a polymer concentration of $3 \times 10^{-5}$ mol/L (3–9 g/L) had been used. It is interesting to note the $k_{intra}$ values determined during the present work for $N \leq 280$ are about 2–3 times smaller than the values reported by Winnik et al.[3] for a similar range of $N$.

## V. Discussion

The present work presents the chain length dependence of the rate constant for intramolecular collision of terminal groups in polystyrene molecules dissolved in benzene and in cyclohexane. A comparison of relevant results, obtained with other polymers by various authors,[3,6,7] with the results

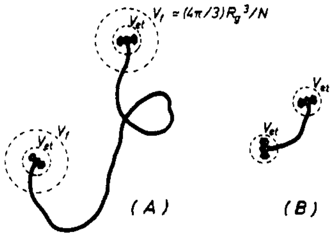


**Figure 7.** Schematic picture of the model for diffusion-controlled intramolecular end-to-end reaction of A-PS-A. (A) The case for large $N$: Reaction volume ($V_r$) = fluctuation volume ($V_f$) > volume for triplet energy transfer ($V_{et}$). (B) The case for small N: $V_r = V_{et}$.

of this work leads to the conclusion that a simple relationship with a constant exponent, such as that given in eq 16, does not hold for a very broad range of $N$, including oligomers.

In the following we try to eludicate this aspect from a theoretical point of view.

On the basis of the microreversibility of conformational change, Sisido and Shimada[11] have shown that the rate of an intramolecular diffusion-controlled reacion of a reversible type is related to the equilibrium distribution of end-to-end distance $W(r)$, and the rate constant $k_{\text{intra,rev}}$ is given by

$$k_{\text{intra,rev}} = (1/2)W(r \le r_0)/\langle\tau\rangle_1 \qquad (17)$$

where $W(r \le r_0)$ is the probability for the end-to-end distance $r$ being smaller than or equal to the reaction distance $r_0$, and $\langle\tau\rangle_1$ is the mean lifetime of the cyclic conformations favorable to the reaction. They[11] have also suggested that eq 17 serves as a good approximation for the rate of a diffusion-controlled reaction of an irreversible type, after changing the reaction probability from $^1/_2$ to 1.

In order to evaluate $W(r \le r_0)$ for large values of $N$, a concept developed by Doi[9] will be applied here, according to which the magnitude of the reaction volume, $V_r$, is strongly affected by the short-time behavior of the segmental motion. A chain end of long-chain polymer fluctuates very rapidly in a certain fluctuation sphere around its averaged position for the short period. The diffusion-controlled end-to-end reaction takes place if $r$ becomes smaller than the fluctuation diameter, $r_f$, of the chain end because the motion of the chain end is very rapid and free inside the fluctuation sphere. Thus the terms fluctuation volume, $V_f$, and reaction volume, $V_r$, become synonymous in this case. A schematic picture of the model is given in Figure 7.

By using the above-mentioned suggestion[11] together with the concept of fluctuation volume, we write the rate constant, $k_{\text{intra}}$, for a diffusion-controlled irreversible reaction by

$$k_{\text{intra}} = W_f(r \le r_f)/\langle\tau\rangle_1 \qquad (18)$$

$$W_f(r \le r_f) = V_f/(4\pi/3)R_g^3 \qquad (19)$$

where $W_f(r \le r_f)$ is the probability for $r$ being $r \le r_f$ and $R_g$ is the radius of gyration of the polymer. It is not unreasonable to assume that the fluctuation volume, $V_f$, is roughly equal to the reciprocal of segment density, $(4\pi/3)R_g^3/N$, inside the polymer coil. Then we obtain

$$k_{\text{intra}} = \frac{V_f}{(4\pi/3)R_g^3\langle\tau\rangle_1} \simeq \frac{1}{N\langle\tau\rangle_1} \propto N^{-1.0} \qquad (20)$$

Equation 20 is in accordance with the experimental results obtained in benzene solution for $N$ covering the range between 110 and 3000 (see Figure 5). $\langle\tau\rangle_1$ is supposed to be independent of $N$ and to be of the order of $10^{-8}$ s.

The concept of fluctuation volume no longer appplies at low values of $N$ since $V_f$ decreases with decreasing $N$ and becomes smaller than the intrinsic reaction volume. In the present case, where triplet–triplet annihilation occurs, $V_r$ is determined by the critical distance for energy transfer. Consequently $V_r$ has a constant value and the diameter of a respective sphere would be about 10 Å. On this basis it can be estimated that $k_{\text{intra}}$ will depend on $N$ as $k_{\text{intra}} \propto N^{-1.5}$. This can be seen from the following consideration: with $V_r$ = const, one obtains eq 21 in place of eq 20. Here it is taken into account that $R_g \propto N^{0.5}$ in this case.

$$k_{\text{intra}} = \frac{V_r}{(4\pi/3)R_g^3\langle\tau\rangle_1} \propto R_g^{-3} \propto N^{-1.5} \qquad (21)$$

Equations 20 and 21 hold for extreme cases, i.e., for rather high and very low values of $N$, respectively. The value of $N$ where both models predict the same value of $k_{\text{intra}}$ will not be larger than 110 for polystyrene in benzene since eq 20 agrees with the results of $N$ = 110–3000. As benzene is a "good" solvent for polystyrene, intramolecular segment–segment interaction should not affect remarkably the fluctuation of chain ends. However, if the solvent quality is worsened, the number of intramolecular contact pairs is increased.[21] Thus, the concept elaborated above for high values of $N$ can no longer be applied without restrictions. This might explain the differences becoming evident upon a comparison of the dependence $k_{\text{intra}} = f(N)$ found experimentally for polystyrene in benzene (good solvent) and in cyclohexane ($\Theta$ solvent). The value of $N$ for the crossover from eq 20 to eq 21 was found to be about 300 for cyclohexane solutions (see Figure 5).

It is inferred from Figure 5 that $k_{\text{intra}}$ is lower in cyclohexane than in benzene solution. This might be explained on the basis that $\langle\tau\rangle_1$ is larger in cyclohexane than in benzene because the microviscosity (viscosity of the solvent) of cyclohexane is higher than that of benzene.

In conclusion, it may be stated that on the basis of eq 20 and 21 all reported experimental data concerning the chain length dependence of rate constants of intramolecular terminal collisions of linear macromolecules can be explained.

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# Diffusion and Reaction Rates of End-Labeled Polystyrenes in Semidilute Solution Studied with Luminescent Triplet Probe

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ABSTRACT: The diffusion-controlled quenching rate constants, $k_q$, between two end-labeled macromolecules (polystyrylbenzil and polystyrylanthracene) in the presence of inert polystyrene in benzene or cyclohexane have been measured for polymer concentrations, $C$, up to 0.30 kg/dm$^3$ with a luminescent triplet probe method. The $k_q$ in benzene increases with increasing $C$ until $C$ reaches about 0.05 kg/dm$^3$, while $k_q$ in cyclohexane decreases monotonously with increasing $C$. The $k_q$ in benzene begins to decrease with further increases in $C$ at the point corresponding to the crossover from the dilute to the semidilute region. In the semidilute region, $k_q$ in benzene is proportional to $C^{-\alpha}$, with $\alpha = 1.7$–$1.9$. This value of $\alpha$ coincides with the prediction of $D_{\mathrm{self}} \propto C^{-1.75}$ by de Gennes' dynamic scaling theory with a reptation model. The importance of probing distance, $d$, regulated by the time scale of the measurements, for the interpretation of diffusion data is emphasized. The present results suggest that the onset of the gel effect in radical polymerization corresponds to the point where molecular diffusion of the reacting species becomes restricted to reptation.

Luminescence spectroscopy is a powerful research tool in the study of structure, mobility, and reaction of both synthetic and biological macromolecules.[1] In comparison with fluorescence spectroscopy, information from excited triplet-state probes detected by phosphorescence, delayed fluorescence, or triplet-triplet absorption is of special importance, since much longer lifetimes of excited triplet states compared with fluorescence lifetime allow study of mobility and reactions reflecting the large-scale motions of the whole polymer chain in solution[2–5] and slow motions in solid state.[6]

In previous papers,[2,3] quenching rates of phosphorescence of the benzil group at a chain end of polystyrene (PS-B) by the anthryl group at a chain end of another polystyrene (PS-A) were measured in dilute benzene, butanone, or cyclohexane solution. The effects of molecular weight and solvent power on the intermacromolecular quenching rates have been discussed. In the present paper, the measurements of the quenching rates are extended to the reactions in the semidilute region, i.e., in benzene and cyclohexane solutions with polymer concentration $C$ = 0.05–0.30 kg/dm$^3$, by using a 10-ns nitrogen laser pulse.

The measurements of quenching rate constants between two end-labeled monodisperse polymers in the semidilute region are supposed to provide valuable information concerning two recent topics in polymer chemistry and physics.

The first is about dynamics of polymer chains in semidilute and gellike solutions. The dynamic scaling theory and reptation model proposed by de Gennes[7–9] have predicted the concentration and molecular weight dependences of two different modes of diffusion: cooperative diffusion of the pseudogel ($D_{\mathrm{coop}}$) and macroscopic self-diffusion of one labeled chain ($D_s$). Over the past several years, Adam and Delsanti[10] have revealed that $D_{\mathrm{coop}}$ is proportional to $C^{0.67}$ and independent of the number of monomer units, $N$, by using quasielastic light scattering. Klein[11] and Hervet et al.[12] have ascertained the de Gennes prediction of $D_s \propto N^{-2}C^{-1.75}$ by measuring the molecular weight dependence of macroscopic self-diffusion of deuterated polyethylene and by measuring the concentration dependence of self-diffusion of end-labeled polystyrene with a forced Rayleigh light scattering technique, respectively. The $N$ dependence of the mutual diffusion coefficient in polymer melt has been studied for the poly(vinyl chloride)/poly($\epsilon$-caprolactone) system.[13] The triplet probe technique also provides another experimental approach for studying self-diffusion and large-scale intramolecular relaxation in the time scale up to 10 ms in semidilute solution. The former is discussed in the present paper.

The second topic related to the present paper is the onset of the gel effect in free-radical polymerization. The sudden increase in the rate of polymerization observed at the intermediate or later stage of polymerization is called the gel effect and has been shown by many investigators to be due to the diffusion control of the termination process caused by the increasing viscosity of the system.[14] With the passage of time this termination process between two polymeric radicals has become widely recognized to be a diffusion-controlled process even in the initial stage of polymerization, in other words, even before the onset of the gel effect.[15] Thus the onset of the gel effect has been studied again recently by several investigators who relate it to the close packing of macromolecules with unperturbed dimensions,[16] to the formation of chain entanglements,[17,18] to a change in the rate-determining step from segmental diffusion to translational diffusion,[19] to the free volume concept,[20,21] and to the onset of reptative motion.[22] The present results with the triplet probe give a general picture for the molecular weight, concentration, and solvent power dependences of the diffusion-controlled rate constants between two end-labeled monodisperse polymers.

## Experimental Procedures

**Materials.** Benzil or anthracene was attached to the chain end of anionically prepared polystyrene as previously reported.[2] Molecular weights and molecular weight distributions of poly-

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