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Influence of Solvent on the Ultrafast Kinetics of Electron Photoejection

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Abstract: Picosecond spectroscopy revealed that sodium salt of tetraphenylethylene dianion (T^{2-},$2Na^+$) is bleached by a 530-nm pulse whether dissolved in dioxane or tetrahydrofuran (THF). It was established that in either solvent T^{2-},$2Na^+$, and not T^{2-},Na^+, is the photolyzed species. The original absorbance returns within about 10 psec when dioxane solution is photolyzed, but the bleached state persists for at least a nanosecond when the reaction occurs in THF. The different structure of the aggregate, tighter in dioxane and looser in THF, is reflected in the different behavior of the excited state. The absorbance of $T\cdot^-$ radical anion (λ_{max} = 660 nm) is not observed in either system within the time scale of our experiments. Although electron ejection follows the photolysis of T^{2-},$2Na^+$ in THF, either only a small fraction of excited aggregates undergoes autoionization (making the detection of $T\cdot^-$ hardly possible) or the resulting $T\cdot^-$ retains the geometry of T^{2-} for at least 60 psec (the long time of our observations) and the distorted radical anion apparently does not absorb in the expected region. To differentiate between these alternatives, sodium salt of tetracene dianion was flash photolyzed in dioxane and in THF. Bleaching and the appearance of tetracene radical anion was observed in both solvents. It is probable, therefore, that the substantially different shapes of T^{2-} and of $T\cdot^-$ prevent the observation of $T\cdot^-$ formation in dioxane.

Flash photolysis of sodium salt of tetraphenylethylene dianions, T^{2-},$2Na^+$, in tetrahydrofuran (THF) leads to electron photoejection[2]

$$T^{2-},2Na^+ \xrightarrow{h\nu} T^{-}\cdot,2Na^+ + e^- \longrightarrow T^{-}\cdot,Na^+ + e^- + Na^+$$

The reaction is manifested by bleaching of the 480-nm absorption band of the dianion and by the simultaneous appearance of a 660-nm transient arising from the formation of the tetraphenylethylene radical anion, $T\cdot^-$,Na^+. The latter is produced by two processes: (1) by the primary photolytic act, and (2) through capture of the ejected electron by tetraphenylethylene, T

$$T + e^- \text{ (or } e^-, Na^+) \longrightarrow T^{-}\cdot \text{ (or } T^{-}\cdot, Na^+)$$

The latter reaction was rapid since the concentration of tetraphenylethylene in the photolyzed system was relatively large. In the following dark period, the disproportionation regenerated the dianions

$$2T^{-}\cdot, Na^+ \longrightarrow T^{2-}, 2Na^+ + T$$

and the systems returned every time precisely to its initial state.

The above experiments were preformed with visible light (λ >420 nm), the radiation of shorter wavelength being quantitatively absorbed by suitable filters. In a typical flash, about 20% of the 480-nm absorption had been bleached and the degree of bleaching had not been affected by the addition of even a large excess of sodium tetraphenylboride, the presence of which greatly reduced the concentration of T^{2-},Na^+. One concludes therefore that the photolysis involves the T^{2-},$2Na^+$ aggregate and *not* the half-dissociated T^{2-},Na^+.

Repetition of these experiments with dioxane solution of T^{2-},$2Na^+$ led to surprising results.[2] Although the experimental conditions were basically the same as those maintained in the previous experiments, no bleaching whatsoever of the 480-nm band had been observed, even when substantially more powerful flashes were employed.

It is known that the ionic aggregates are tighter in dioxane than in tetrahydrofuran and therefore the different behavior of this salt in THF and in dioxane has to be attributed to the difference of their structures. Apparently the absorbed light excites the T^{2-},$2Na^+$ aggregate to its autoionizing state, and the excited species formed from the looser aggregate present in THF has a finite, although probably small, probability to undergo autoionization leading to electron ejection into the bulk of the liquid. Such an electron may escape the attractive field of the sodium ions and has then a chance to be trapped by T. On the other hand, the excitation of the tight aggregate present in dioxane leads not to its autoionization but probably to *intra*molecular electron transfer to a sodium cation

$$(T^{2-}, 2Na^+)^* \longrightarrow T^{-}\cdot, Na^+, Na^0 \text{ or } T^{-}\cdot, Na^+, (e^-, Na^+)$$

The reverse reaction, a kind of cage process, occurs rapidly, e.g.

$$T^{-}\cdot, Na^+, Na^0 \longrightarrow T^{2-}, 2Na^+$$

and therefore the relatively slow flash-photolysis technique is incapable of revealing the occurrence of this process. To test these ideas, the photolysis of T^{2-},$2Na^+$ in THF and in dioxane was reinvestigated by the method of picosecond absorption spectroscopy.[3]

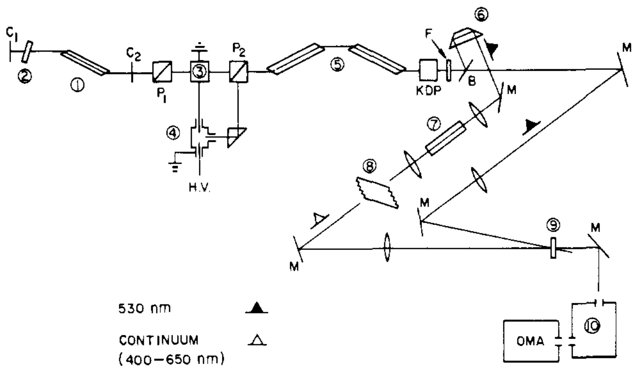

Figure 1. Diagram of apparatus used to observe the time-resolved bleaching of T^{2-},$2Na^+$ in dioxane and THF. Its components include: (1) Nd^{3+} glass oscillator with cavity mirrors C_1, C_2; (2) saturable dye absorber cell; (3) Pockels cell positioned between crossed Glan polarizers P_1, P_2; (4) spark gap; (5) Nd^{3+} glass amplifiers; (6) translatable prism used to generate variable delay; (7) broadband continuum cell containing 1-octanol; (8) stepped delay transmission echelon; (9) sample cell; (10) monochromator. Mirrors are denoted by M, beam splitter by B, optical filter by F, and optical multichannel analyzer by OMA.

Experimental Section

Mode-locked 1.06-μ pulse trains were generated in a 1.1-m oscillator cavity (Figure 1) containing a Brewster Nd^{3+} glass rod (0.5 in. diameter × 7 in. length) and a 1-cm cell containing EK No. 9860 saturable dye absorber. The pulses were monitored with an ITT FW-114 S-1 photodiode and a Tektronix 519 oscilloscope. Extraction of a single pulse was accomplished with a 0.5-in. aperture Pockels cell energized by the rejected oscillator train. Following successive amplification by Nd^{3+} glass rods (dimensions 0.75 × 12 in. and ⅝ × 7.5 in., respectively), ~10% of the transmitted single pulse was converted to the second harmonic in a 1-in. cube phase matched KDP crystal. The 530-nm single pulse with a typical energy of ~25 mJ was split approximately into two equal parts. One part generated a broadband picosecond continuum[4-6] arising from self-phase modulation of the pumping pulse and stimulated Raman emission[7] in a 20-cm 1-octanol cell; this served as an interrogating beam.[8] The remainder of the 530-nm pulse was collimated to a 2-mm diameter and served for excitation of the tetraphenylethylene dianion clusters.

The continuum pulse was split by a stepped delay transmission echelon[9] into a vertically stacked picosecond train of pulses separated by 5.5 psec. This train provided the experimental clock. The echelon image was focussed into a 2-mm diameter spot overlapping the excitation pulse in the sample cell, and imaged onto the slit of a 1-m Interactive Technology monochromator (dispersion 8 Å/mm). The image at the exit slit of the monochromator was composed of a series of lines which represented the echelon segments. Each one corresponded to an absorption measurement in succeeding time intervals of 5.5 psec. This image display of time at a specified frequency impinged upon the silicon surface of a vidicon tube. An optical multichannel analyzer (OMA) processed the vidicon signal and displayed it as an image on a monitor oscilloscope analogous to a one-dimensional microdensitometer trace of a photographically recorded echelon.[10] The data of Figures 2 and 3 are the exact copies of the curves displayed by the OMA on the monitor oscilloscope. This detection method, as pointed out previously, has many advantages over the photographic techniques, including linearity of response, wide dynamic range, and spectral sensitivity from 300 to 1100 nm.

The excitation pulse was made to coincide in time and space in the reaction cell with a preselected segment of the interrogating echelon train. This was achieved with a variable delay afforded by a translatable prism, which was eventually superseded by two orthogonally placed mirrors to minimize dispersion broadening of the pulses. The timing was confirmed (Figure 2) using a CS_2 optical shutter, which enables the time evolution of all wavelengths in the continuum to be measured simultaneously.[11]

Most experiments were conducted at ambient temperature (~20°). The concentration of T^{2-},$2Na^+$ was varied from 2.3 × 10^{-4} to 2.4 × 10^{-5} *M*, the corresponding optical densities at 530 nm being 3.0 to 0.4.

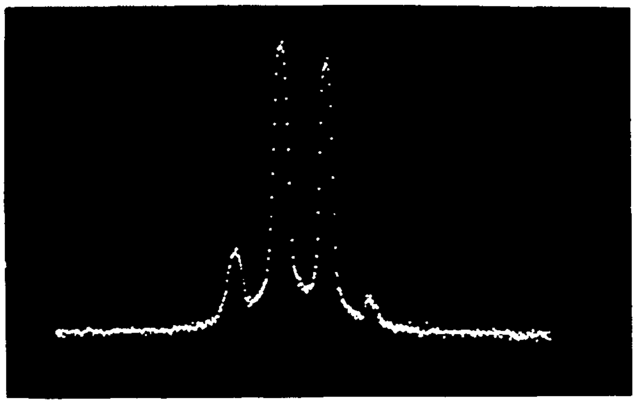

Figure 2. Typical monitor oscillope photograph of a CS_2 optical shutter timing shot detected by the optical multichannel analyzer. Each peak corresponds to a particular segment of the transmission echelon, so that the horizontal time coordinate is stepped in increments of ~5.5 psec. The CS_2 shutter was triggered by the 530-nm single pulse used as the excitation source in the absorption experiments. The intensity vs. time distribution of the transmitted 510-nm portion of the broadband interrogating continuum (see text) indicates the synchronized echelon segments (near center of figure) as well as the approximate interrogating pulse width.

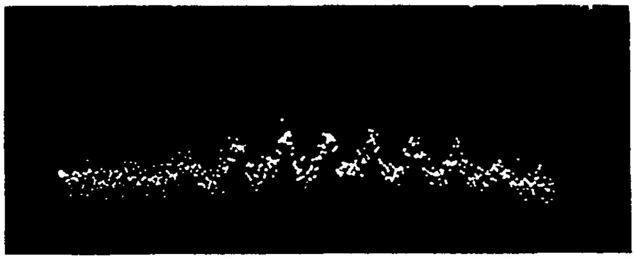

Figure 3. Monitor oscilloscope photograph of 510-nm interrogating pulse train transmitted by 1.7 × 10^{-5} *M* T^{2-},$2Na^+$ in dioxane (5-mm cell), in the absence of any 530-nm excitation pulse. Each peak corresponds to a pulse in the echelon train, each separated by ~5.5 psec with the time coordinate running from left to right.

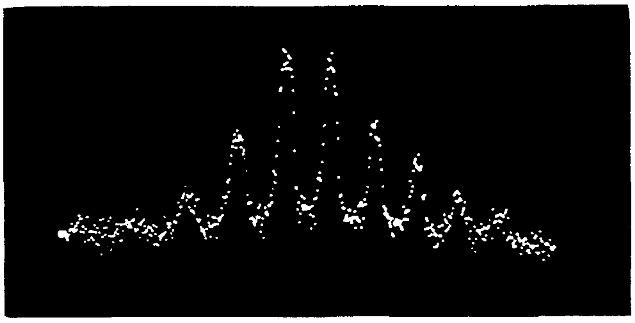

Figure 4. Monitor oscilloscope photograph of 510-nm interrogating train transmitted under identical conditions as in Figure 3 except that the excitation pulse (synchronized with the echelon segments as in Figure 2) is admitted. Bleaching commences immediately with the arrival of the 530-nm pulse, and subsides after a time interval comparable to the pulse width of ~8 psec.

The dianion salt was prepared under vacuum by reduction of tetraphenylethylene with metallic sodium. The concentration of the reduced species was ~10^{-3} *M*. This stock solution was placed in a storage bulb which was connected through a break-seal to an evacuated quartz cell (path length 2 to 5 mm). Without opening the system to the air, the sample was introduced into the optical cell by distilling the solvent and then adding a drop or two of the residual solution by simply tilting the reservoir bulb. This method, described in greater depth elsewhere,[13] made possible the adjustment of the concentration in the cell from ~3 × 10^{-2} *M* to essentially

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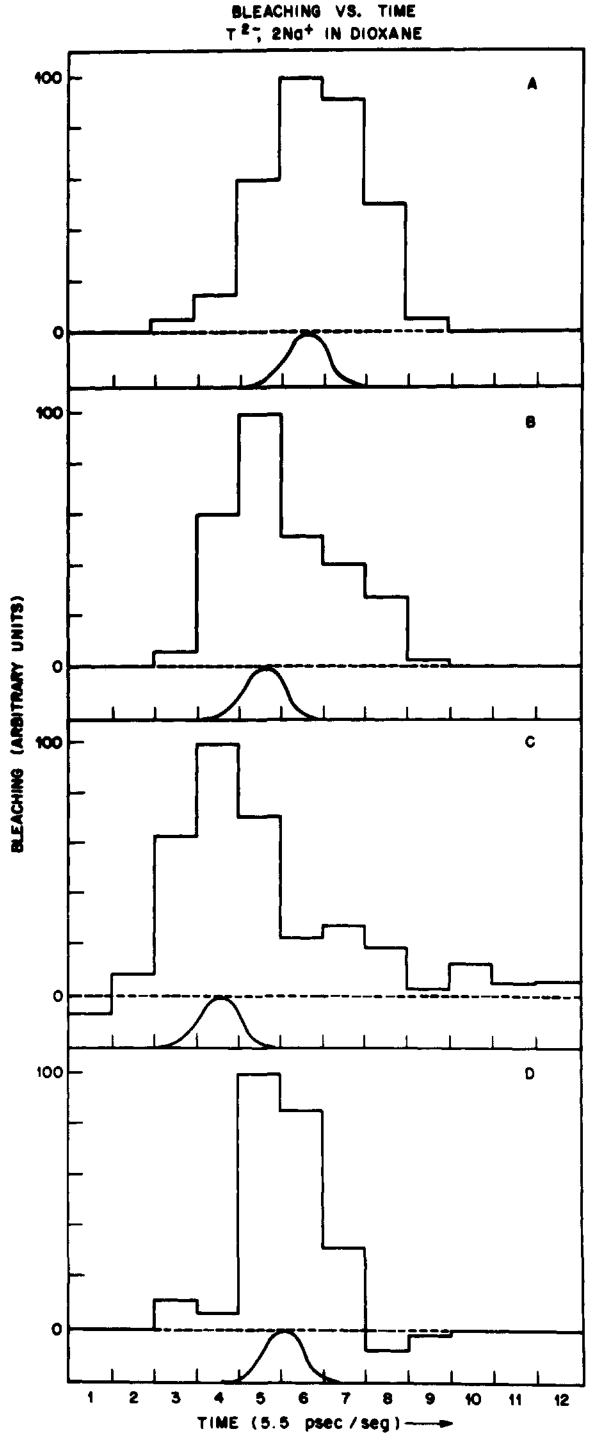

Figure 5. Time-resolved bleaching of T^{2-},2Na^{+} in dioxane at 20°: (A) 2.4 × 10^{-4} *M*, 5400-Å interrogation; (B) 4 × 10^{-5} *M*, 4900-Å interrogation; (C) 7.5 × 10^{-5} *M*, 5100-Å interrogation; (D) 1.7 × 10^{-5} *M*, 5000-Å interrogation. The gaussian-shaped curves indicate the positions of the excitation pulses. The segments proceeding the excitation were used to scale the experiments with excitation (e.g., Figure 4) to those without excitation (e.g., Figure 3). The data were then subtracted in pairs and a correction for the unequal segment heights within the echelon profile was applied. Area of each rectangle represents the average of the number of points recorded in the appropriate time segment in several independent experiments.

pure solvent without introducing any contamination. In addition, by returning the solution from the optical cell to the storage bulb after each experiment, a fresh solution could be prepared for further experiments. The concentration of the solution and its spectrum was measured in a Cary 15 spectrophotometer. Special care was taken to monitor changes at 490 and 660 nm, where T^{2-} and T$\cdot^{-}$, respectively, have absorption maxima.

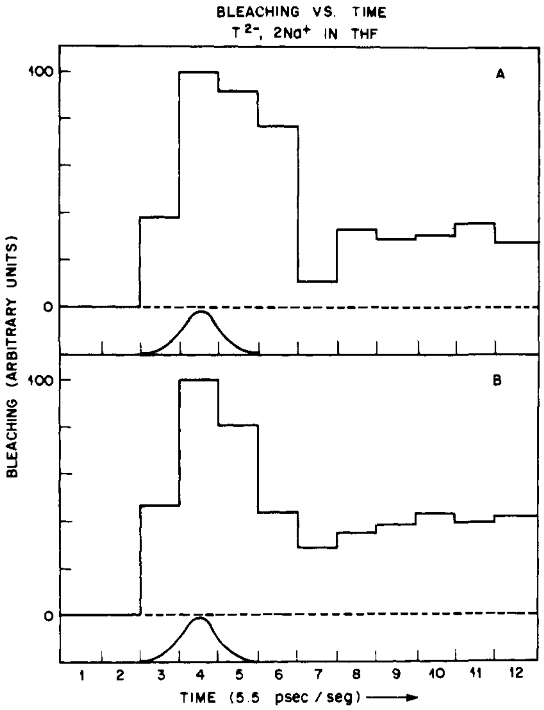

Figure 6. Time-resolved bleaching of T^{2-},2Na^{+} in THF: (A) ~1 × 10^{-4} *M*, −36°, 5100-Å interrogation; (B) 8 × 10^{-5} *M*, 20°, 5100-Å interrogation. The gaussian-shaped curves indicate the positions of the excitation pulse. Area of each rectangle represents the average of the number of points recorded in the appropriate time segment in several independent experiments.

The kinetics of the T^{2-},2Na^{+} system was followed by monitoring the time resolved changes of the dianion absorption band in the region 480–550 nm. In addition, the formation of T$\cdot^{-}$ was searched for by interrogation at its ground state absorption maximum at 660 nm ($\epsilon = 1.1 \times 10^4$).

Results and Discussion

The photolysis of dioxane solution by a 530-nm pulse bleached the 480-nm T^{2-},2Na^{+} band for a time interval of about 10 psec comparable to the duration of the pulse (see Figures 4 and 5). In contrast, as revealed by Figure 6, the system remained in a bleached state for at least a few nanoseconds when THF solution of T^{2-},2Na^{+} was irradiated. The eventual recovery of the original absorption spectrum demonstrates that the decomposition, if any, of the T^{2-},2Na^{+} salt is negligible in either solvent. The bleaching and the return of the absorbance was monitored at 490, 510, and 540 nm; the kinetic behavior of the system was similar at each of these wavelengths.

The above results imply that the dark processes occurring after the psec excitation of T^{2-},2Na^{+} are different depending on whether dioxane or THF surrounds the salt. Either the diverse structures of the aggregate or the dissimilarity of the solvent cage created around the ejected electron may account for these observations. It was shown elsewhere[13] that localization of an ejected electron in water occurs in about 4 psec. Such localization of the ejected electron could also take place in dioxane or in THF, and this in turn may affect the probability of electron return.

The bleaching of the 480-nm band does not provide yet a compelling evidence for the genuine electron photoejection, because the excitation of the aggregate to a discrete autoionizing state leads also to a decrease in the 480-nm absorption. We have to conclude, then, that either autoionization in dioxane is hindered or the return, kind of a cage reaction, described by the previously mentioned process

$$\mathrm{T}^{2-}, 2\mathrm{Na}^{+} \rightleftarrows \mathrm{T}^{-}\cdot, \mathrm{Na}^{+}, \mathrm{Na}^{0}\ (\text{or } \mathrm{T}^{-}\cdot, \mathrm{Na}^{+}, \mathrm{e}^{-}, \mathrm{Na}^{+})$$

is exceedingly fast.

The genuine expulsion of an electron from the T^{2-} ion into an adjacent solvent cage, or its capture by Na^+, should produce a $T\cdot^-$ radical ion, the formation of which could be recognized by its characteristic absorption band (λ_{max} = 660 nm). However, no absorption at 660 nm was detected in either system and the failure of observing the $T\cdot^-$ radical ion in THF may be accounted for in two ways. It has been suggested that $T\cdot^-$ and T^{2-} differ in geometry,[14] $T\cdot^-$ resembling T in its structure while T^{2-} acquires the shape of two connected $\bar{C}Ph_2$ planar groups placed in mutually perpendicular planes. Indeed, the 480-nm absorption band of the latter is identical with that of the $\bar{C}Ph_2$ chromophore in other compounds, e.g., CH_3-$\bar{C}Ph_2$. Accordingly, the excitation, even if accompanied by electron photoejection, could produce a distorted $T\cdot^-$ radical and its ground state would appear only after the $\bar{C}Ph_2$ groups had time to rotate, i.e., most likely after 60 psec, which is the long-time limit of the present experiments. No absorbance of the undistorted $T\cdot^-$ could be then observed.

The probability of autoionization of the excited T^{2-},$2Na^+$ is not too high even in THF. Our results indicate that more than half of the bleached species returned to their ground state in about 10 psec, while the return of the remaining ones was slow. The latter apparently represent the "distorted" $T\cdot^-$,Na^+ pairs, separated from the ejected electrons, which regenerate the dianions in a diffusion-controlled process. On this basis, we find the probability of electron ejection from T^{2-},$2Na^+$ in THF to be lower than 0.5.

It is interesting, therefore, to compare these results with those obtained in the photolysis of the salt of tetracene dianion, since in that system the electron photoejection is not followed by the rearrangement of the molecular framework. Flash photolysis of sodium salt of tetracene dianions in THF and in dioxane led to bleaching of the original absorption band and in both solvents the transient absorbance of the respective radical anion was recorded. It has been also established that the 530-nm picosecond pulse bleaches the absorbance band of potassium tetracene dianion ($\lambda_{max} \sim$ 630 nm) when its 2-MeTHF (2-methyltetrahydrofuran) or DME (dimethoxyethane) solutions are photolyzed; the transient corresponding to tetracene radical ion appears simultaneously with the bleaching. These results demonstrate that the probability of electron photoejection from tetracene dianion is much greater than from tetraphenylethylene dianion. They also suggest that the failure of detection of $T\cdot^-$ absorbance in the picosecond pulse photolysis of THF solution of T^{2-}, $2Na^+$ is most probably due to the substantially different shape of T^{2-} and $T\cdot^-$

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Flexibility of Molecular Chains Studied by Electron Spin Resonance Technique

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Abstract: A new experimental approach to dynamics of linear molecular chains has been developed. The method is illustrated by the following example. Hydrocarbons N-$(CH_2)_n$-N (N denoting an α-naphthyl moiety) were reduced to N-$(CH_2)_n$-$N\cdot^-$ radical anions possessing only one extra electron per chain. ESR spectra of their highly dilute solutions in HMPA or in DME were recorded at a series of temperatures. Their shape is modified by the *intra*molecular electron transfer N-$(CH_2)_n$-$N\cdot^- \rightleftarrows {}^-\cdot N$-$(CH_2)_n$-$N$, and computer simulation of such spectra allows us to determine the frequency, P, of the transfer as a function of n and temperature. It has been found empirically that $P(n+1)^{3/2}$ is independent of n, provided that n is sufficiently large. The bimolecular rate constant, k_{ex}, of an analogous *inter*molecular electron transfer involving α-n-butylnaphthalene and its radical anions was determined in solvents and at temperatures chosen for the study of the *intra*molecular transfer. The merits of static and dynamic models of *intra*molecular reactions are discussed in light of our results.

Conformations of any molecular chain in a liquid medium are continually changed. Consider, for example, a molecule such as $X\cdot(CH_2)_n\cdot X$. Due to Brownian motion its end groups, X, perform random movements restricted only by the constrictions imposed by the chain binding them. In the course of this motion they approach each other and, if inert, they separate and after a time lag come together again. This motion continues ceaselessly and the frequency of such encounters is determined by the length of the chain, the nature of the end groups, temperature and viscosity of the sol-