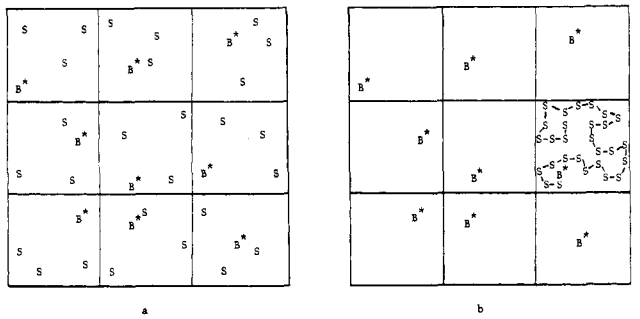

Figure 4. Pictorial representation of the reaction between B* and S when individual S units are free in solution (a) and connected to form a polymer chain (b). If this reaction is sufficiently slow that the B* molecules equilibrate between the boxes before the reaction occurs, both "solutions" will show the same macroscopic kinetics. This will no longer be true in the case of a diffusion-controlled reaction.

In the case where the segments are joined into a polymer, the concentration of S in the jth compartment is $[S_j]$. For a fixed sufficiently dilute solution, $[S_j]$ will be zero in most compartments. The number of compartments having nonzero values of $[S_j]$ and the magnitude of $[S_j]$ will depend upon the degree of polymerization. From a macroscopic point of view, the observed rate will be the average rate of reaction over all J compartments.

$$-\frac{d[B^*]}{dt} = \frac{1}{J}\sum_{j=1}^{J} k_2'[B^*][S_j] \qquad (4)$$

$[B^*]$ is uniform in solution, and k_2' is independent of chain length. The two reaction rates are the same since $(1/J)\sum[S_j] = [S]$.

This point is easily illustrated in terms of the nine-box grid shown in Figure 4. In Figure 4a the reactants B* and S are uniformly distributed. Their reaction rate is described by eq 3. In Figure 4b, all the S molecules are located in one box. In that box, B* reacts nine times as fast. The macroscopic rate is the average rate in all nine boxes and is identical with that in Figure 4a.

For a chemical reaction to show this behavior, k_2' or k_2 must be smaller than the diffusion limit. Otherwise, the concentration of B* in the compartments containing polymer would diminish faster than in other compartments. The assumption of uniform distribution presumes fast exchange between compartments and is substantiated experimentally by the observation of single exponential decays for excited benzophenone at all alkane concentrations.

The straight line in Figure 2 suggests that the second-order molar rate constant for the reaction increases without limit for high polymers. Alkanes are not the best substrates for testing this prediction because of their poor solubility. Whether such behavior continues for chains of 100 or 10^4 atoms would be very interesting to establish.

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Substituent Effects on Hydrocarbon Chain Cyclization Probed by an Intramolecular Photochemical Reaction

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ABSTRACT: The molecules benzophenone-4-$CO_2(CH_2)_nCH_3$(IV) undergo an intramolecular hydrogen abstraction reaction. So, too, do the molecules benzophenone-4-CO_2-X'-$O_2C(CH_2)_{12}CH_3$, where the substituents (I, X' = $-CH_2CH_2-$, II, X' = *trans*-1,2-cyclohexyl, and III, X' = 1,2-benzenyl) impose conformational constraints on the chain which are predicted to increase the cyclization probability of the chain. Flash photolysis measurements indicate that cyclization is enhanced by factors of 2.5, 6, and 9 for I, II, and III, respectively, over the 17-carbon ester of IV.

Introducing a substituent into a flexible chain molecule affects the conformation of the chain.[1] In hydrocarbon chains, a small substituent might affect only the gauche/trans rotational populations of nearly C–C bonds. Larger substituents can cause rotational angle distortion and other effects which are extremely difficult to describe, much less to quantify. Since the overall problem is complex, individual examples where the effect of a single substituent on the conformation of a hydrocarbon chain can be assessed serve as a valuable guide to our understanding of substituent effects on chain properties.

The molecules I, II, and III[2] contain substituents on sites corresponding to the 1, 2, 3, and 4 positions (see Scheme I) of the hydrocarbon chain of the parent molecule IV-17.

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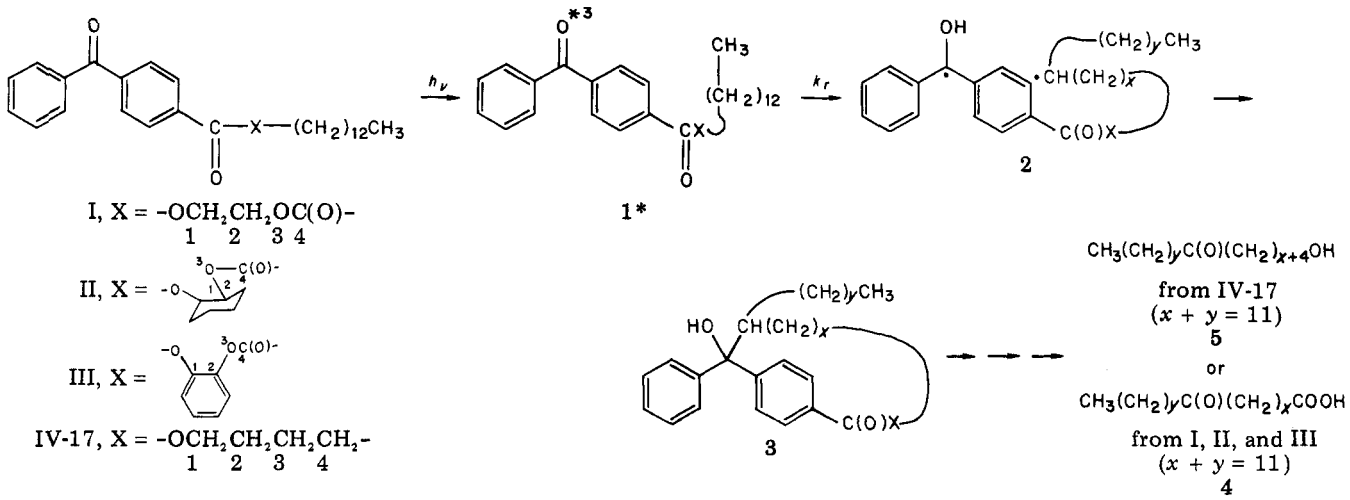
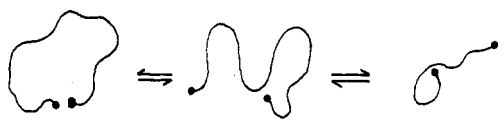
Scheme I



One might expect that the average conformations of I, II, and III differ from that of IV and that these differences are due to the presence of the substituents. Cyclization probability is one measure of the conformation of a polymer.[3,4] Photochemical means can be used to obtain experimental values for the cyclization probability in IV.[5-7] Since the same type of experiments can be carried out on I–III, a method is available for assessing quantitatively the effect of their respective substituents on chain cyclization.

Our photochemical studies on I–IV measure the rate of an intramolecular hydrogen abstraction reaction. The rate constant for this process is a measure of the chain cyclization probability. This cyclization probability is not of the end-to-end cyclization type but rather of the "self-avoiding walk" to "tadpole" type.[8] The transition



state for hydrogen abstractions has the topology of a tadpole graph. Since hydrogen abstraction can occur from any accessible CH_2 group, the rate constant obtained reflects the sum of all tadpole cyclization probabilities in each molecule. Our results provide a measure of the effect of substituents at the 2, 3, 4, and 5 position of the chain in IV on the rate constant for intramolecular hydrogen abstraction and consequently on the probability of achieving a tadpole geometry.

In each case[2,5,7] (see Scheme I), excitation gives the benzophenone excited singlet state which forms its triplet state with unit efficiency. This long-lived state abstracts a hydrogen from among the CH_2 groups that can reach it, to give a mixture of biradical intermediates **2**. Of these, most disproportionate to give ground state starting material. Some biradicals couple to form macrocyclic lactones **3**. For IV in carbon tetrachloride, the fraction of **2** which couples to form **3** is 16%.[5] The chemical yield of **3** is 25 to 50%.[2,5,7] Chemical degradation of **3** yields the keto esters which can be hydrolyzed to yield keto acids (I, II, and III) or keto alcohols (IV), which in turn can be analyzed to determine the distribution of products.[2,7]

Two aspects of these reactions give information about the conformation of the chains. (i) The rate constant k_r measures the sum of probabilities that a CH_2 group in the chain achieves a reactive conformation. This is proportional to the probability of cyclizing to a tadpole conformation. (ii) The product distribution is sensitive to the relative probability that each CH_2 group in the chain has a reactive conformation. The product distribution, as a function of solvent, has been reported for I, II, III, and IV.[2,7]

In IV, these experimental results have been compared with the results of conformational calculations based upon a rotational isomeric state (RIS) model.[5] The model has been elaborated in some detail and makes certain predictions about how cyclization probability depends upon the rotational states of certain bonds in the chain.[9] These calculations suggest that gauche rotamers near the ester group are important for a reactive conformation because they help to overcome bond correlation effects (described by the "persistence vector") which oppose cyclization. While long chains seem to have the same fraction of gauche bonds in cyclized conformers as in the total ensemble of conformations, short chains ($n < 20$) must be rich in trans rotamers. A minimum of three gauche rotamers is necessary for cyclization; for sufficiently short chains to react, the C(1)–C(2) bond must be gauche.[9]

The substituents in I, II, and III affect the rotational populations corresponding to the C(1)–C(2), C(3)–C(4), and C(4)–C(5) bonds of the alkyl chain in IV. In addition, they affect certain bond angles and the rotational angle adjacent to C=O which replaces C(4). Comparison of the rate constants k_r for intramolecular hydrogen abstraction for these compounds with those for IV ought, when compared with the predictions of the conformational calculations, to lead to a deeper understanding of the factors involved in cyclization of chain molecules.

Experimental Section

The preparations of I, II, and III have been reported previously.[2] Solutions of each were prepared at concentrations of 1×10^{-4} to 5×10^{-3} M, degassed by five successive freeze–pump–thaw cycles, and sealed into Pyrex tubes. Carbon tetrachloride (Burdick and Jackson, spectro grade) was further purified by the method of Schuster.[10] Acetonitrile (Burdick and Jackson, spectro grade) was used as received. Water was purified by refluxing deionized water over potassium permanganate and distilling twice.

Lifetimes, τ, were measured at 22 °C by the flash photolysis method described in the accompanying paper.[11]

Lifetimes extrapolated to infinite dilution, τ^0, were obtained by extrapolating reciprocal lifetimes measured at various concentrations according to the equation

$$\frac{1}{\tau} = \frac{1}{\tau^0} + k_{sq}[1] \qquad (1)$$

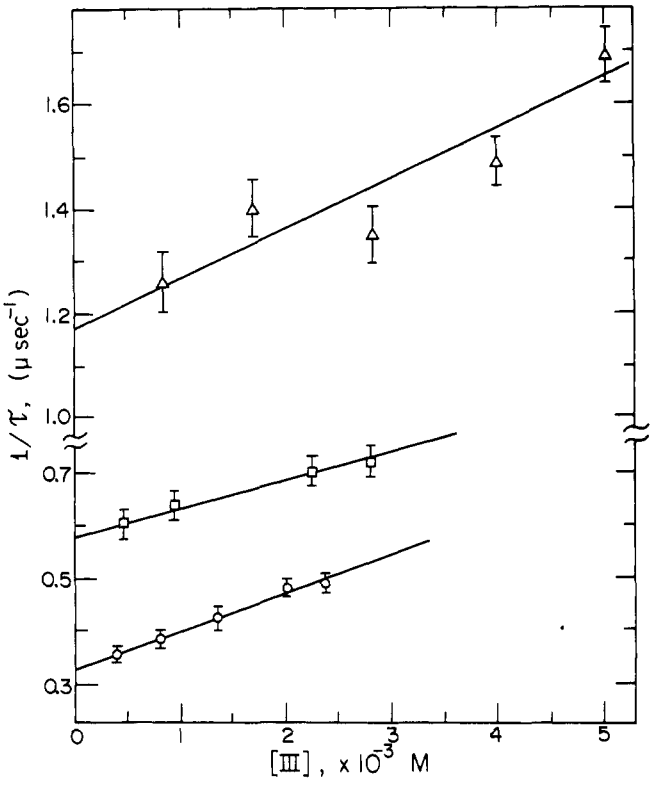


Figure 1. Stern-Volmer plot of $1/\tau$ vs. concentration for III in (○) CCl_4, (□) CH_3CN, and (△) CH_3CN/H_2O, 4/1 (v/v). Error bars represent one standard deviation in the measurement of τ.

The slopes of the plots according to eq 1 for III give the bimolecular rate constants for self-quenching, k_{sq}. Studies of I and II showed a small concentration dependence of the lifetimes for concentrations above 1×10^{-3} M. This apparent self-quenching is probably due to trace levels of impurities in I and II. Their contribution to τ is less than 5% at 1×10^{-3} M and becomes negligible at lower concentrations.

Results and Discussion

For I, II, and IV, bimolecular reactions between the excited state of one benzophenone and the chain of another molecule are sufficiently slow that one can work at a concentration where these reactions are unimportant. Measured phosphorescence lifetimes are virtually independent of concentration. This is not true for III. In III, a relatively slow intramolecular hydrogen abstraction reaction competes with a rapid and efficient bimolecular reaction between the electron-rich catechol ring on one molecule and the excited benzophenone on another. Geometrical considerations prevent the aromatic ring from achieving a reactive configuration intramolecularly.

This result is important from the point of view of understanding the reactivity of the benzophenone *p*-carboxylate chromophore. The magnitude of the bimolecular rate constant, $k_{sq} = 7 \times 10^7$ M^{-1} s^{-1}, its weak dependence on solvent polarity (Figure 1), and the absence of intramolecular reaction comment on the nature of charge-transfer quenching of the excited chromophore by electron donors.

Phosphorescence lifetimes of I and II and extrapolated lifetimes τ^0 for III are collected in Table I. Also included are lifetimes of the corresponding methyl esters IV-1 of benzophenone-4-carboxylic acid. For each compound, the lifetimes decrease in the order carbon tetrachloride > acetonitrile > aqueous acetonitrile. This order may simply reflect the purity of each solvent.

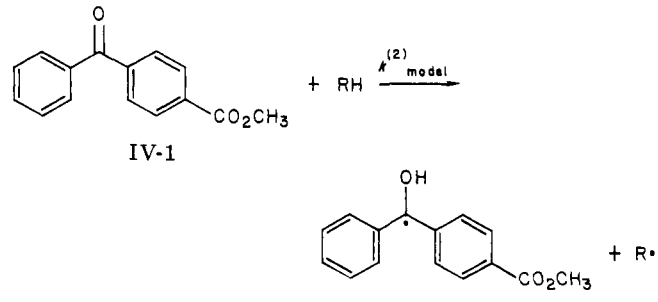
The meaningful measure of reactivity is the rate constant for intramolecular hydrogen abstraction, obtained from the lifetime data by means of the expression

$$\frac{1}{\tau_l} - \frac{1}{\tau_1} = k_r; \qquad l = \text{I, II, III} \qquad (2)$$

where τ_l is the lifetime of I, II, or III, and τ_1 is the lifetime of the methyl ester IV-1. Values of k_r are collected in Table II. These values may be compared with values of k_r obtained for the heptadecyl ester IV of benzophenone-4-carboxylic acid in each solvent. While these values have not been calculated from measurements on IV-17, they can be inferred by interpolating k_r values available for IV-*n* for many values of $n \leq 23$.[5]

From Table II, one sees that increasing solvent polarity causes marked increases in the magnitude of k_r for all four molecules. The increase is about a factor of 2 between CCl_4 and CH_3CN and about a factor of 3 to 4 between CCl_4 and $CH_3CN{\cdot}H_2O$ (4/1, v/v). Because the reactivity of the excited benzophenone carboxylate chromophore itself is sensitive to solvent polarity,[5] these increases do not necessarily indicate an effect of solvent on the probability of the chain assuming a reactive conformation.

To obtain this information, one must separate solvent effects on chromophore reactivity from those on chain shape. This may be done by choosing a model substance for the reactive portion of the alkane chain and obtaining the bimolecular rate constant $k^{(2)}_{model}$ for its reaction with



IV-1

Table I
Phosphorescence Lifetimes in Solutions

solvent	lifetime,[a] μs			
	$\tau_{IV\text{-}1}$[b]	τ_I	τ_{II}	τ°_{III}
CCl_4	106	10.2 ± 0.4	3.8 ± 0.15	3.08 ± 0.09
CH_3CN	65	4.08 ± 0.08	1.80 ± 0.03	1.72 ± 0.10
CH_3CN/H_2O, 4/1 (v/v)	53.5	2.53 ± 0.07	1.41 ± 0.03	0.85 ± 0.20

[a] Average of three flashes of one sample. Error analysis (one standard deviation) is taken from the computer fit. [b] Methyl ester of IV; average of several measurements; standard error ca. ±5%; values of k_r are not sensitive to errors in this value.

Table II
Rate Constants for Intramolecular Hydrogen Abstraction

solvent	$10^{-4}k_r$, s^{-1}			
	IV-17	I	II	III
CCl_4	3.2 (0.062)[a]	8.9 (0.17)	25 (0.49)	32 (0.62)
CH_3CN	8.6 (0.12)	23 (0.31)	54 (0.73)	56 (0.76)
CH_3CN/H_2O, 4/1 (v/v)	12 (0.21)	38 (0.65)	69 (1.18)	110 (1.88)

[a] Values of $(k_r/k^{(2)})$ where $k^{(2)}$ is the second-order rate constant for reaction of IV-1 with *n*-hexane in each solvent. The $k^{(2)}$ values are taken from ref 6 except for CH_3CN/H_2O, 4/1 (v/v), where we have determined the value of $k^{(2)} = 5.84 \times 10^5$ M^{-1} s^{-1}. Values in parentheses have units of mol/L.

Table III
Enhancement Factors[a] for Intramolecular Reactivity of I, II, and III over That of IV

solvent	I	II	III
CCl_4	2.8	7.8	9.9
CH_3CN	2.7	6.3	6.6
CH_3CN/H_2O, 4/1 (v/v)	3.0	5.6	9.3

[a] Obtained from $k_r(l)/k_r(IV\text{-}17)$, l = I, II, III.

the chromophore. By making the assumption that all solvent effects on the reactivity of the chromophore appear in values of $k^{(2)}_{model}$ measured in each solvent, one can separate solvent effects from conformational effects by normalizing each k_r value by its corresponding $k^{(2)}$ value. We have chosen *n*-hexane as our model alkane. Values of $(k_r/k^{(2)}_{hexane})$ are presented in Table II.

From the data in Table II, one sees that there are small solvent effects on the probability that the chain achieves a reactive conformation. Polar solvents cause increases of a factor of 2 for the completely flexible species I and IV and much smaller increases (25%) for the chains substituted by rigid substituents II and III.

Conformational calculations[9] on IV indicate that for chains of less than 20 carbons to achieve a reactive conformation, the C(1)–C(2) bond should be gauche and that a majority of the subsequent bonds should be trans. These calculations also indicate that a minimum of 3 gauche bonds, appropriately placed, are necessary for reaction and that C(11) should be the first carbon in the chain susceptible to reaction. Because the model treats RIS chains embedded in a diamond lattice, model chains are somewhat more rigid than real chains; consequently the finding that C(10) in IV is capable of reacting is not surprising.

In I, one can estimate that the oxygen in place of C(3) has the effect of making the gauche rotamer at the C(1)–C(2) bond nearly 0.5 kcal/mol more stable than the trans rotamer.[12] In II, the cyclohexane ring freezes the C(1)–C(2) in the gauche rotational state, and in III the rotational angle about this bond is now that of the eclipsed cis conformation. There are small changes in bond lengths at C(3) and C(4) because of the presence of the ester group in the chain and bond angle changes. The benzene ring in III causes the ∠OCC bond angles to open to 120° compared to ca. 105° in I and II. The ester group has a similar effect on the ∠COC(2) and ∠C(5)CO bond angles compared with those of IV. The carbonyl group of the ester group affects the rotational angle about the C(4)–C(5) bond, but more important, it imposes a trans orientation about the C(3)–C(4) bond.

According to the model,[9] the two most important effects should be the increased gauche rotamer population of the C(2)–C(3) bond and the enforced trans orientation of the ester group replacing the C(4)–C(5) bond of the alkyl chain. Both effects should lead to enhancement of cyclization probability. Enhancement factors $[k_r(I,II,III)/k_r(IV\text{-}17)]$ in each solvent are collected in Table III. The qualitative predictions of the model are substantiated by the finding of a 2.5-fold increase in the cyclization probability in I, which is flexible at C(2)–C(3), and an eight- to ten-fold increase in cyclization probability in II and III, which are held rigidly in the gauche and cis configurations, respectively, at that bond.

Additional information about chain conformation is available from analysis of the reaction products—the distribution of products of oxidation at each site describing, in principle, the relative cyclization probability of each CH_2 group in the chain. We emphasize the proviso "in principle" because factors intervene which make it possible that the product ratios may not truly reflect the distribution of hydrogen abstraction sites in the initial photochemical step: the biradical **2** forms products with low quantum efficiency; product yields **2** are not quantitative; and each successive chemical transformation leading to the product analysis may discriminate among products in the mixture. Nonetheless, it is reasonable to assume that these factors do not affect the general features of the cyclization process inferred from product analysis, particularly if one compares two molecules reacting in the same solvent.

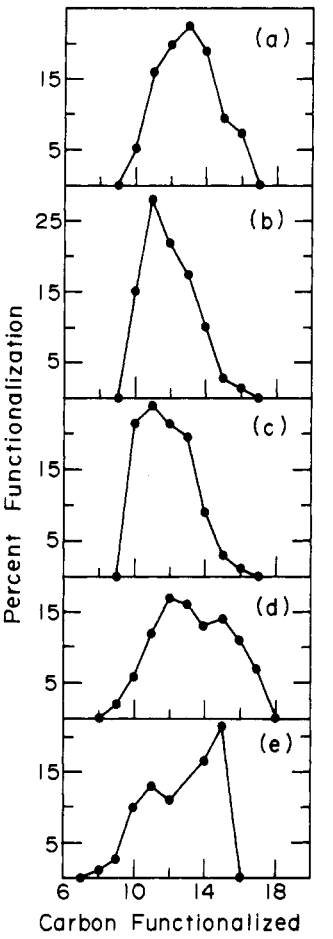


Figure 2. Percent functionalization at each carbon in the hydrocarbon chain for (a) I, (b) II, and (c) III in CCl_4, data from ref 2; (d) IV-18 in CCl_4, data from ref 7a; (e) IV-16 in CCl_4, data from ref 7b. The numbering scheme for the carbons is explained in the text.

Exact comparison between product distributions from I, II, and III with that of IV-17 cannot be made because its photochemistry has not been reported. Nonetheless, general comparisons are possible because Breslow[7] has published product analyses from corresponding studies with IV-16 and IV-18. In Figure 2 we have plotted percent functionalization at each carbon in the chain. In order to compare the various molecules, we have assigned C(1) to the carbon attached to the benzoate ester oxygen as indicated in the Scheme I so that the terminal methyl group is C(17) in I, II, and III and C(16) and C(18) respectively in IV-16 and IV-18. It can be seen that the structural changes imposed by the substituents do not affect the onset of reaction at C-10. When compared with IV-16, the substituents appear to affect the distribution of reactive sites in that the maximum is reached earlier and a rapid decay follows. This behavior is that to be expected if the substituent had the effect of pointing the initial bonds of the chain in the direction of the reactive carbonyl oxygen.

The comparison with IV-18 does not show as pronounced an effect.

The effects of the solvent are complex and difficult to interpret. Solvent effects on the rate enhancements in Table III are conformational in origin, since in each solvent the chemical reactions of I, II, III, and IV are the same: This means that the probability of a CH_2 group being in the reactive volume adjacent to the ketone oxygen of the chromophore is sensitive to solvent. Many factors can affect this probability. Among them are the interaction of the ester dipoles with the solvent dipoles and favorable interactions in poor solvents between CH_2 groups of the chain with the aromatic rings of the benzophenone. Intramolecular interactions between CH_2 groups in the chain are unlikely to play an important role because, for chains as short as 17 carbons, the pentane effect makes nonbonded interactions between remote CH_2 groups extremely improbable.

Solvent effects on product distribution are even more difficult to interpret because a major component of that effect could be solvent influences on the partitioning of the biradical **2** to starting ketone and to product.

Conclusion

Molecules I, II, and III possess flexible chains containing substituents which perturb the population of rotational states corresponding to the C(1)–C(2) and C(3)–C(4) bonds of the alkyl chain in IV. In addition, the substituents make small changes in bond and rotational angles. Rotational isomeric state model calculations suggest that the former effects should increase the cyclization probability and hence the rate constant for intramolecular reaction. Flash photolysis measurements indicate that I, II, and III undergo intramolecular reactions respectively 2.5, 6, and 9 times more readily than the molecule IV with the same length alkyl chain.

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A Determination of Polymer Number-Averaged and Weight-Averaged Molecular Weight Using Photon Correlation Spectroscopy

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ABSTRACT: A method is developed whereby the autocorrelation spectra of light scattered inelastically from dilute polymer solutions can be used to determine polymer number-averaged and weight-averaged molecular weights. The method is based on transforming the polymer z-averaged diffusion coefficient and its relative dispersion, extracted from a cumulants analysis of the spectra, into number-averaged and weight-averaged molecular weights. To do this, experimentally determined constants from diffusion coefficient versus molecular weight studies are employed. The range of validity in the resulting transform expressions is subject to certain restrictions in the width and in the magnitudes of higher moments of the polymer molecular weight distribution. The expressions derived have particular potential usefulness in the determination of $\bar{M}_n$ and $\bar{M}_w$ for rodlike polymers. $\bar{M}_n$ and $\bar{M}_w$ values determined using these expressions to analyze narrow and intermediate molecular weight polystyrene samples are in good agreement with both the manufacturers data and gel permeation chromatographic analyses.

The characterization of polymer molecular weight distributions using time-average or so-called "elastic" light-scattering techniques continues to merit investigation.[1,2] During the past decade, though, inelastic (or quasielastic) light-scattering techniques have also been successfully applied to this endeavor.[3] In inelastic scattering, an analysis is made of phase fluctuations in the scattered light using either the power spectral density or

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