Conclusion

The fact that no appreciable temperature effect was observed in the infrared experiments leads us to conclude that the local orientational correlations between neighboring chain segments in *cis*-1,4-polyisoprene exhibit an entropic character.

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An AM1 Computational Study of the Cationic Polymerization Mechanism of Cyclic Acetals

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Introduction

A long standing problem in cationic polymerization of cyclic acetals is identification of the propagation mechanism and active species.[1] The complexity of polymerization systems has prevented direct study of active species by spectroscopic techniques. However, Penczek and co-workers have used model compounds and "nonpolymerization" conditions to make a detailed study of 1,3-dioxolane polymerization.[2] They propose nucleophilic ring opening of cyclic oxonium ions (**1**, eq 1) as the main propagation pathway. Two of us have recently suggested that the alternative pathway involving an α-oxycarbenium ion (**3**) is important in polymerization of the 2-substituted acetals 2-butyl-1,3-dioxepane (**4**, eq 2),[3] and 2-butyl-1,3,6-trioxocane.[4]

For complex chemical processes where the choice between mechanistic pathways cannot be made unambiguously based on experimental results, computational chemistry may be useful to help clarify matters. Although the inherent approximations in computational modeling render such models imprecise for obtaining *absolute* answers for real reactions, the level of experimental concordance with recent computational algorithms makes computation a practically useful tool for comparison of relative trends in a variety of cases. As a complement to Penzcek's model experimental data, we have applied the AM1 semiempirical molecular orbital method of Dewar and co-workers[5] toward examining whether cyclic acetal polymerization under cationic conditions occurs *via* simple S_N2-type attack or by ring opening of the complexed acetal followed by addition. We report below the results of this study.

Computational Methods

In all computations herein, the QCPE program AMPAC[6] was used, as adapted for the University of Massachusetts chemistry department Celerity 1260-D UNIX computer. For all molecules, the AM1 parameterization[5] was used for optimization of both energy minimum and transition-state structures, using restricted Hartree–Fock (RHF) closed-shell wave functions. The transition states were obtained by using the SADDLE routine in AMPAC[6] and were verified in each case by finding a single imaginary vibrational mode at the AM1-RHF level. Geometry punch files in typical AM1-RHF Z-matrix format are listed in supplementary material for energy minimum and transition-state structures discussed in this paper. Readers are referred to this material for complete computational structural information.

Before considering our results, it is worth recalling the assumptions of the computational model used. All energies computed are theoretical gas-phase enthalpies of formation based upon semiempirical parameterization and so do not explicitly include effects of entropy or substrate solvation. Such effects would certainly affect absolute numbers obtained in our study. However, comparison of relative trends ought not to be so greatly affected as to obviate their usefulness, hence we approach the interpretation of our results in a manner to emphasize such trends between similar processes. The success of such comparisons in past semiempirical reaction studies is,[7] in our opinion, sufficient justification for use of this approach.

Results

We initially studied the energetics of cyclic oxonium cations versus their ring-opened counterparts (the quasi-cyclic carbenium forms), using different ring sizes and different substitution patterns at the 2-carbon (vide infra). The transition state for unsubstituted and 2-methyl-substituted 1,3-dioxolane ring opening was also found, from which the indicated activation barriers E_a were computed[8] by using heats of formation and structures obtained directly from the AMPAC program. Figure 1 sumarizes these results.

Since the effect of ring size on the thermodynamics of ring opening is small at the AM1-RHF level of theory, we carried out our study on reactions modeling eq 1 versus eq 2 for the simplest, dioxolane case only, compound

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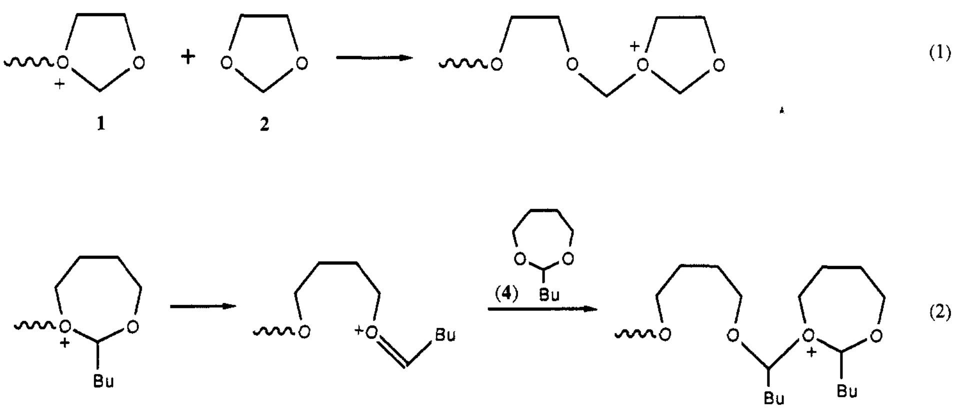
Scheme I



2. Mechanisms I and II show the model reaction mechanisms. Figures 2 and 3 show reaction coordinates along the paths of mechanisms I and II, respectively, using AM1-RHF energies computed at a variety of points along the C_2–O_1 coordinate where the nucleophilic oxygen of the attacking ring 2 is approaching[9,10] the 2-carbon of the complexed ring in its oxonium and carbenium forms, 5 and 6, respectively. Figure 4 shows three-dimensional representations of the transition-state geometries 17 and 18 found with the SADDLE routine in AMPAC for each mechanism.[6]

Discussion

The results summarized in Figure 1 indicate that, at the AM1 level of theory, the ring opening of the oxonium form of cyclic acetals is expected to be a kinetically facile process that does not involve large enthalpy changes. Despite quantitative caveats described earlier (vide supra), given that the size of the molecules remains similar and that the species are of the same charge type, it seems reasonable to accept these computed heats of reaction as useful relative numbers for comparison on a qualitative basis.

Our results show that increasing ring size does not appreciably affect the thermodynamics of ring opening. However, 2-alkyl substitution—as in 5, 9, and 13 versus 7, 11, and 15—substantially lowers the energy of the carbenium form relative to the oxonium form. The effect of 2-alkyl substitution is understandable, since the oxonium form has only one low-energy resonance structure available, while the carbenium form has two (see below). The resonance structure bearing positively charged carbon would obviously be stabilized by change of R′ from H to alkyl. Qualitatively, 2-alkyl substitution actually may reverse the slight preference in the unsubstituted cases for the oxonium form of the complexed acetal, implying that 2-alkyl substitution in cyclic acetal polymerization might profoundly affect the reaction course.

The activation barriers E_a computed for the opening of oxonium to carbenium form in the 1,3-dioxolanes are small, 5 kcal/mol for the unsubstituted case and 1 kcal/mol for the 2-methyl case. It seems unlikely that solvation would so greatly affect these numbers, as to change the conclusion that ring opening of the 1,3-dioxolane at least should be a facile process at typical polymerization reaction temperatures. Our calculations for the related pair of ions 5 and 7 (Scheme III and Figure 1 ($R = H$)) give a ΔH value of 4 kcal/mol in favor of the cyclic oxonium ion. Assuming the same holds true for similar cyclic acetals, this implies that one ought to consider the potential for the carbenium form of the complexed acetal to be present in cationic polymerization conditions. This point has been made earlier by Kucera[11] and Penczek.[2] For instance, it has been shown experimentally[2] that cyclic oxonium ion 19 is only about 2 kcal/mol *less stable* (ΔG) than the open carbenium cation 20, based upon studies in SO_2 at −70 °C. Indeed, Penczek and Szymanski[2] have demonstrated that for model cations in SO_2 at −70 °C, oxonium and carbenium cations are in *rapid* equilibrium. It is also worth noting that related work[2] indicates oxonium ion 21 to be 4.3 kcal/mol *more stable* (ΔG) than the open carbenium form 20, quite similar to our gas-phase computational prediction that the enthalpy gap (ignoring entropy considerations) between the related species 13 and 14 should be 4.8 kcal/mol favoring oxonium species 13.

Besides showing the thermodynamic and kinetic acceptability of the carbenium form, one must evaluate the ease of attack of another molecule of acetal upon oxonium versus carbenium model systems, to evaluate the relative kinetics of propagation in the two intermediates if they are formed. The reaction coordinates for both reactions (Figures 2 and 3) show energy minima as the nucleophilic ring approaches the charged species from an infinite distance and becomes complexed. We take as the definition of E_a for each process the energy difference between the energy minimum of the complex and the energy maximum at the transition state.[12] This corresponds to the energy needed for the attacking molecule to overcome the desire to remain passive as a solvating species that stabilizes the positive charge on the attacked species, and so to attack the 2-carbon.

Mechanism I shows a sharply rising barrier as the attacking oxygen approaches within 2.1 Å of the 2-carbon, with an overall E_a of ~4.9 kcal/mol at a transition state C_2–$O_{1'}$ distance of 2.34 Å, with the final product C–O bond formed having a length of 1.533 Å. Mechanism II, on the other hand, has a fairly flat potential coordinate, with a gradual rise to an E_a of ~1.3 kcal/mol at a transition state C_2–$O_{1'}$ distance of 2.28 Å, leading to the same final product geometry and energy as mechanism I. The structures 17 and 18 for mechanisms I and II were characterized by imaginary negative vibrational frequencies for the C_2–$O_{1'}$ reaction coordinate of −305 and −107 cm^{-1}, respectively, showing 17 and 18 to be transition-state structures. Therefore, our results indicate that addition of monomeric 2 to the carbenium form should proceed with a lower activation enthalpy than nucleophilic ring-opening substitution upon the 2-carbon of the oxonium form.

These semiquantitative results are quite reasonable. Addition to the carbenium ion (mechanism II) involves attack upon an sp^2 carbocation center with little steric hindrance, whereas substitution upon the 2-carbon (mechanism I) involves the usual steric inhibitions inherent in

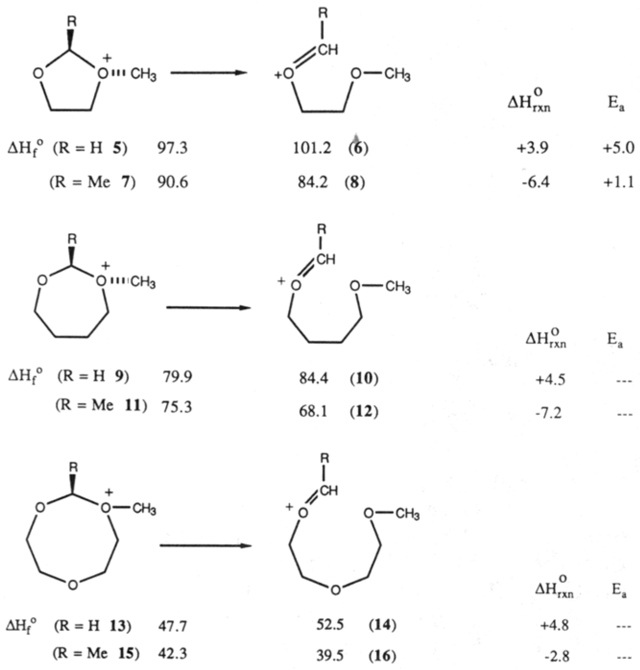


Figure 1. Heats of formation for oxonium and carbenium forms of selected complexed cyclic acetals. All heats of formation in kilocalories per mole from AM1. Full structural data are included in supplementary material. Transition state structures for **5** → **6** and **7** → **8** were characterized by vibrational analysis as described in the text.

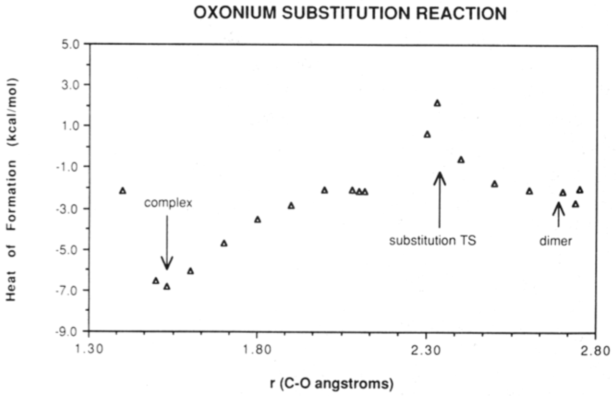
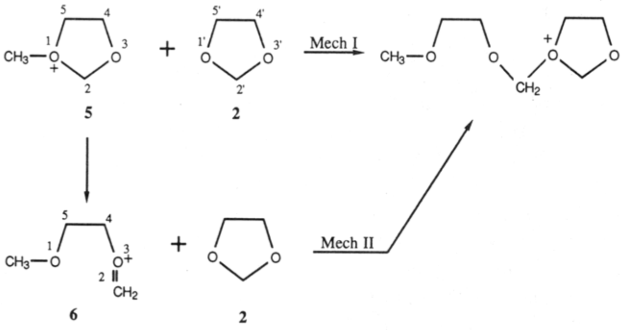


Figure 2. Reaction coordinate for oxonium mechanism I. All heats of formation in kilocalories per mole from AM1; all structures fully described in supplementary material. The energy minimum association complex between dioxolane **2** and the oxonium ion **5** is denoted "complex".

Scheme II



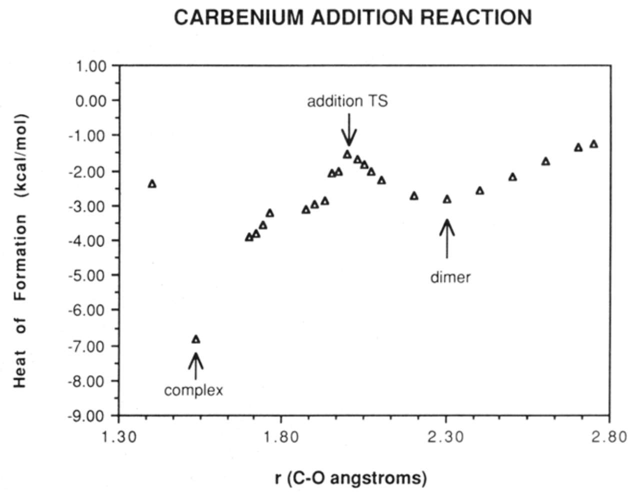
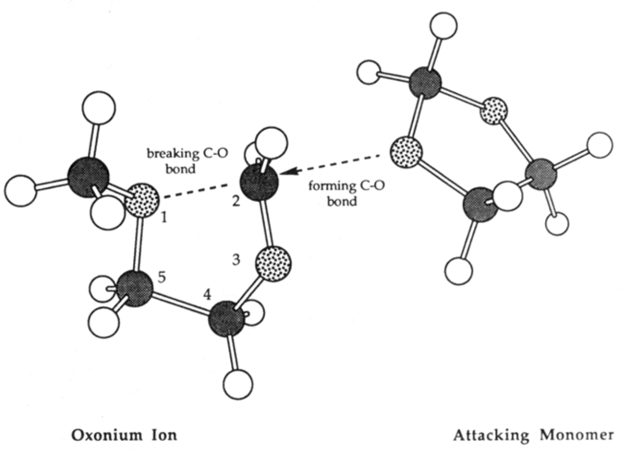
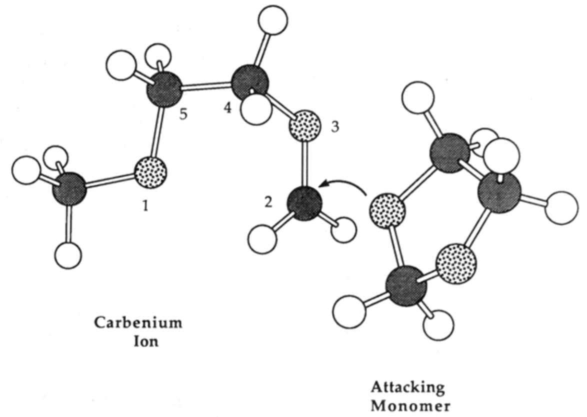


Figure 3. Reaction coordinate for carbenium mechanism II. All heats of formation in kilocalories per mole from AM1; all structures fully described in supplementary material. The energy minimum association complex between dioxolane **2** and the carbenium ion **6** is denoted "complex".


OXONIUM ION SUBSTITUTION RING-OPENING AM1 TRANSITION STATE

17

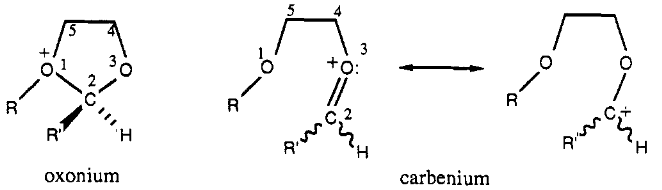

CARBENIUM ION ADDITION AM1 TRANSITION STATE

18

Figure 4. Transition-state structures for mechanisms I and II. Complete structural coordinates are given in supplementary material. Circles represent hydrogen atoms, shaded circles represent carbons, and stippled circles represent oxygens.

S_N2-type displacements. By implication, our results indicate that so long as an open carbenium intermediate may be formed to some reasonable extent in equilibrium with the closed oxonium form, the former intermediate will be faster to react with monomeric uncomplexed acetal and hence potentially to be the major chain carrying intermediate. Presumably this tendency might be particularly plausible in 2-alkyl-substituted systems, where steric

Scheme III

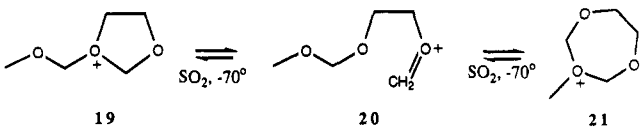


constraints greatly hinder mechanism I but should not greatly slow mechanism II.

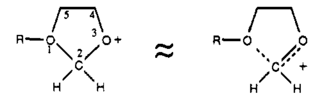
Given the rationale just stated, further discussion of the factors involved in the ring-opening process described earlier is in order. Our computations upon the complexed acetals indicate that formation of the oxonium ion 1 weakens and lengthens the O_1–C_2 bond greatly relative to the typical O–C bond in dioxolane 2 (1.53–1.60 Å *in the cyclic oxonium* examples of Figure 2 versus 1.42 Å in **2**; see supplementary material for the further data). At the same time, the C_2–O_3 bond is shortened substantially. These geometric factors are consistent with weakening of O_1–C_2 and production of some double bond character in C_2–O_3 of 1 (see Scheme V). In short, the facility of ring opening for the oxonium to the carbenium cation in the cyclic acetals is due to the great resemblance of the oxonium to the carbenium form (for complete comparisons see structural material). The AM1 oxonium structure is essentially a carbenium structure with a very strong internal complexation of O_1 to the strongly electropositive C_2. The AM1 Mulliken charge distributions in the oxonium forms of the acetals bear out this view, with the charge on C_2 ranging from +0.1 to +0.2. Indeed, the charge on O_2 in the oxonium structure is typically −0.25, showing this position to be charged negatively. The carbenium like structure of the oxonium form is also suggested by the qualitative effect of 2-methyl substitution, which for the examples in Figure 1 causes an increase in the O_1–C_2 bond length by 0.03–0.04 Å and an increase in the positive charge borne by C_2, despite the expected electron-donating effect of the methyl group. This increase in positive charge especially is counterintuitive for the oxonium resonance structure but is consistent if such substitution makes the carbenium character of the oxonium form more pronounced. Only a small amount of stretching of the weak O_1–C_2 bond is needed to turn the oxonium into the carbenium form, since the lowest energy (gas-phase) conformations of the carbenium ions of Figure 2 leave the former oxonium O_1 atoms complexed in the open form to carbenium sp^2 carbons at distances of ~2.2–2.8 Å. As a result, it seems prudent to allow for the potential presence of the carbenium form of the complexed acetal in cationic polymerizations where the oxonium form may be generated.

Some data for comparison to experimental analogues are available. Penczek and co-workers[5] have studied both nucleophilic and addition mechanisms, shown in eqs 3 and 4, respectively. Under the conditions of these studies (SO_2 solvent at −70 °C), the free energy of activation ($\Delta G^{\ddagger}$) for each process is as shown. Although the absolute values of these barriers are somewhat higher than the activation barriers for our computed models (again ignoring entropic effects and computationally using the approximation $\Delta G = \Delta H$), the difference in experimental free energy barriers, 7.7 − 5.8 = 1.9 kcal/mol, is similar to the computed 3.5 kcal/mol difference in AM1 enthalpies of activation, with the preference in speed being for the addition mechanism in both experiment and theory. It is encouraging to note that both the experimental qualitative trend and general magnitudes of the activation barriers in favoring an addition mechanism are reproduced by theory.

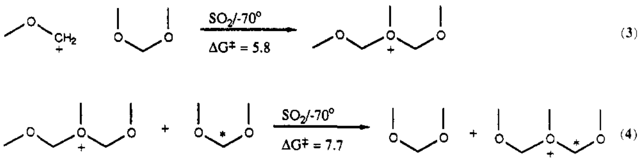
Scheme IV



Scheme V



Scheme VI



In a semiempirical study such as this, a number of factors could render more difficult interpretation of our computational findings. The factors discussed earlier must be recalled in judging any given enthalpy. Also, inadequacy of parameterization as applied to this particular problem is always a possibility. However, AM1 is one of the most recent developments of the MINDO/MNDO/AM1 series of semiempirical MO hamiltonians and has shown a substantial improvement over other related models in several types of computation.[5,13] Although the ambiguities of parameterization could be in principle eliminated by use of ab initio computations at an enormous increase in expense and computer CPU time, the difficulty of accounting for differential solvent effects would remain. Hence we feel that our choice of AM1 computations for the study of this problem is appropriate in view of the usefulness of the method to aid understanding of other chemical processes, and in view of the qualitative nature of the questions we wished to investigate.

Conclusions

From the results of our AM1-RHF computational model studies, the following conclusions may be drawn.

1. Ring opening of the complexed cyclic acetal (oxonium form) to the open-chain carbocation (carbenium form) is expected computationally not to have a large enthalpic barrier and hence may be presumed to be facile. This is in accord with experimental work.[2] The ease of ring opening is attributable to the high degree of carbenium electronic structural nature in the cyclic oxonium form. Alkyl substitution at C_2 can affect the relative computational stability of the oxonium and carbenium ions by ~8–10 kcal/mol (enthalpy) favoring the carbenium ion.

2. Relative equilibrium concentrations of cyclic oxonium and open carbenium ions will be a major determinant of mechanism. Owing to the rapid equilibration of these two cation forms and the expectation based on experiment and calculation that the chain growth step for mechanism II will be at least as fast as that for mechanism I, equal concentrations of oxonium and carbenium chain ends should result in preponderant propagation by mechanism II. Alkyl substitution at C_2 clearly favors ring opening as in mechanism II, with the subsequent addition being

sterically more permissive than the analogous S_N2 attack of mechanism I.

Our calculations give results that are in complete accord with Penczek and Szymanski's conclusion that polymerization of 1,3-dioxolane (**2**) proceeds predominantly via mechanism I.[1,2] They also are in accord with a change to propagation via open carbenium chain ends (mechanism II) for polymerization of 2-alkylated cyclic acetals as some of us have suggested.[3,4] Since the critical energy differences are small, it appears that individual cases require consideration in detail.

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Supplementary Material Available: Extra data includes copies of AM1 Z-matrix format files for all structures and transition states shown in Figures 2–4 as well as vibrational modes for transition-state structures (24 pages). Ordering information is given on any current masthead page.

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(7) Cf. for example a summary of uses for MNDO and MINDO/3 semiempirical methods in: Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985; Chapter 4.

(8) The default tolerances for normalized gradients in AMPAC were used as computed, with a check for presence of a single imaginary vibrational mode in transition-state structures using the LET option in the program.

(9) Backside nucleophilic attack in such reactions has been shown—cf. for instance a review in: Okada, M.; Sumitomo, H. *Makromol. Chem.* **1985,** *Suppl. 14,* 29.

(10) Besides the backside attack discussed in the paper, a reaction coordinate cooresponding to frontside attack was also found. Due to the extremely high energy of the transition state in this reaction coordinate, the computational nature of this process was not further explored, save to note the result by comparison to the work in ref 9.

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Registry No. 1,3-Dioxolane, 646-06-0.

Dependence of the Mutual Diffusion Coefficient on the Dye Concentration in the Polymer/Dye System

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Introduction

In recent years, the holographic grating relaxation (or forced Rayleigh scattering) technique has been proven to be very valuable in measuring the slow translational diffusion coefficient of photoreactive organic dye molecules dissolved in amorphous solid-state polymer hosts.[1–7] In the vicinity of the glass transition temperatures of amorphous polymers, diffusion coefficients are on the order of 10^{-12}–10^{-15} cm^2/s, depending on the nature of the polymers being studied. When the polymer contains monomers not removed or additives intentionally added in as plasticizers, the translational diffusion coefficient of the photoreactive dye is significantly increased.[4] Thus, in reporting the diffusion data, the state of the polymer host must be clearly characterized and defined in order to facilitate comparison. When the concentration of dye molecules is very small, the translational diffusion coefficient is found to be determined only by the size of the dye molecule and the properties of the polymer that serves as a host.[1] In the low concentration limit, the dye molecules serve as tracers. Temperature-dependence studies of the tracer diffusion coefficient in the polymer host above T_g display a non-Arrhenius behavior and are found to follow the form of the Williams–Landel–Ferry (WLF) equation,[1–6] consistent with the free-volume theory proposed for the polymer/plasticizer system originally by Fujita[8] and further elaborated by Vrentas and Duda.[9–11]

The translational diffusion coefficient measured in the polymer/dye system is strictly a mutual diffusion coefficient, and, as such, its value will depend on the concentration of the photoreactive dye molecules that are present in the polymer. Mutual diffusion is concerned with the rate at which concentration gradients approach equilibrium; on the other hand, self-diffusion deals with the mobility of the molecule in a chemically uniform environment. At vanishing dye concentration, the mutual diffusion coefficient is the self-diffusion coefficient of the dye molecules in the polymer environment. In this limit, the self-diffusion coefficient of the dye molecules is entirely dictated by the density fluctuation of the amorphous polymer matrix; hence, the mutual diffusion coefficient in the limit of vanishing concentration of dye molecules can be used as a probe for studying the dynamics of polymer chains above and below the glass transition temperature when other techniques become inadequate due to very slow polymer dynamics involved. While in the literature there is an abundance of diffusion data for polymers in solvents of small molecules, concentration-dependence data for diffusion of small molecules in polymer hosts are quite scarce. In this communication, we report the results of the mutual diffusion coefficient (D) measurement on the poly(methyl methacrylate) (PMMA)/camphorquinone (CQ) system as a function of the CQ concentration. Our object is to show that D varies greatly with the concentration of CQ. A very small concentra-

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