"Dark" Initiation of the Photosensitized Degradation of a Styrene–Methyl Isopropenyl Ketone Copolymer by Thermally Generated Acetone Triplets

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ABSTRACT: Studies have been made of the chain scission of a styrene–methyl isopropenyl ketone copolymer sensitized by acetone triplets generated by the thermal decomposition of tetramethyl-1,2-dioxetane.The technique of automatic viscometry permits accurate determination of very small changes in molecular weight. The decomposition of the dioxetane follows a first-order decay law over several decades of concentration. From the kinetics and quenching studies with *cis,cis*-1,3-cyclootadiene the rate constant k_{tr} for electronic energy exchange between acetone triplets and the ketone groups on the polymer chain is estimated to be 5×10^5 l. mol^{-1} sec^{-1}.

The recent discovery[2a] that 1,2-dioxetanes decompose thermally in solution to give relatively high yields of carbonyl compounds in their excited triplet states has made it possible to stimulate by thermal excitation a variety of photochemical and photophysical processes which normally require activation by light absorption. Usually the course of such reactions is followed by monitoring the phosphorescence[2b] or fluorescence[3] of the excited states of either the initial fragments of decomposition of the dioxetane or that of an acceptor molecule which receives its excitation by energy transfer. However, it is also possible to induce chemical reactions[2a,4,5] by energy transfer to a suitable acceptor molecule, providing that a sensitive method is available for detecting the chemical change.

We wish to report a new "dark" photochemical degradation of a ketone-containing polymer initiated by energy transfer from acetone triplets generated by the thermal decomposition of tetramethyl-1,2-dioxetane.

Experimental Section

The apparatus used for these studies is shown schematically in Figure 1. It consists of a specially constructed automatic viscometer similar to that described by Gramain and Libeyre[6] but with two lamps and two detectors instead of the single unit with prism used in the Gramain apparatus. The viscometer is connected to a thermostated cell of ~50 ml volume by 1/16 in. Teflon tubing. The automatic sampling system, operated by a small electronic programmer, removes a 5-ml sample from the cell under nitrogen pressure at periodic intervals and makes five to nine determinations of the flow time, which is recorded to the nearest millisecond and printed on a Hewlett-Packard 5055A digital printer. The sample is then returned to the cell under nitrogen pressure. The operation is repeated by the programmer at predetermined intervals. The flow time of the viscometer is about 20 sec for the solvents used and if the temperature of the viscometer is maintained constant within ±0.01° the times can be determined with a precision of ±1 msec. By averaging five determinations, the relative viscosity of a polymer solution can thus be determined to five significant figures. The remarkable precision of this device permits the accurate determination of extremely small changes in the molecular weight of a polymer in solution.

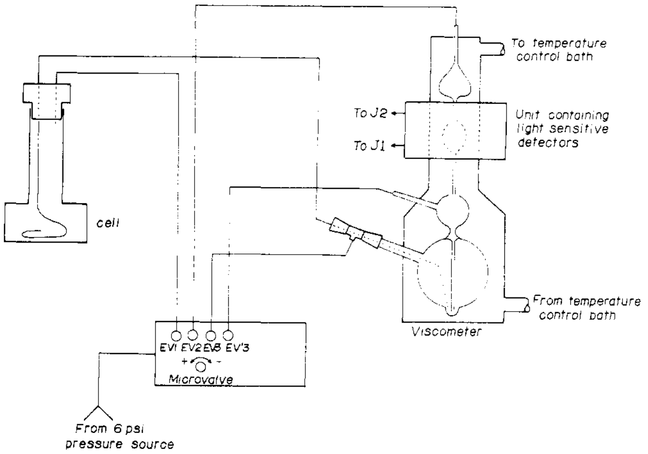
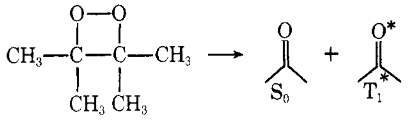


Figure 1. Schematic diagram of automatic viscometer, reaction cell, and control module.

For these studies the polymer used was a copolymer of styrene and 5 wt % methyl isoprenyl ketone prepared by suspension polymerization with a peroxide catalyst. The number average molecular weight was 83,600 as determined by osmometry in butyl acetate. The viscosity molecular weights were determined at a single concentration using literature values for K and α in the Mark–Houwinck equation. A computer program was written to correct for concentration and allow for the kinetic energy correction, which is relatively large in this case because of the short flow time of the viscometer. Most of the experiments were run at 60.2° and during a 15-hr run there is some slight solvent loss which causes the flow times to increase by as much as 20 msec. This correction was determined at the end of each run and included in the computer program. In the absence of dioxetane, the polymer was found to be completely stable and no change in flow time occurred over 15 hr. Tetramethyl-1,2-dioxetane was synthesized by the method of Kopecky.[7,8] Toluene and 1,2-dichloroethane were Baker and Adams ACS reagent grade, used without further purification. In a typical experiment a solution of polymer was made up and carefully filtered. The cell and viscometer were washed with filtered solvent. Then the solution was placed in the cell and flushed by bubbling nitrogen through for a few minutes. After thermal equilibrium was reached the dioxetane was added as a solid and the cell was flushed once more and sealed. The programming cycle was then started immediately to record the initial viscosity of the solution. The flow times were measured automatically, usually overnight or until no further change was observable.

Theory

Tetramethyl-1,2-dioxetane decomposes thermally to give two molecules of acetone, one of which is in the excited triplet state[2a]



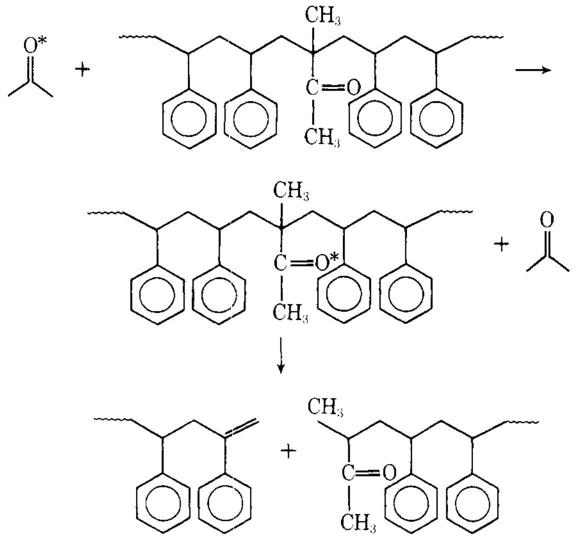
(1)

The stoichiometry can be written

$$\text{diox} \longrightarrow f\mathrm{T}_1^* + (2-f)\mathrm{S}_0 \qquad (2)$$

where f is an efficiency factor which appears to be close to unity.

In the presence of a ketone-containing polymer the acetone triplets can transfer[9] their excitation to the ketone groups in the polymer, some of which will then decompose *via* the classic Norrish type II process to cause a break in the polymer chain[10,11] and hence a decrease in the molecular weight.



(3)

(4)

In the absence of quenching molecules, the acetone triplets induce the further decomposition of dioxetane by the process

$$\text{diox} + T_1^* \longrightarrow 2S_0 + T_1^* \qquad (5)$$

The rates of the various processes can be described in a simple kinetic scheme.

If c is the concentration of dioxetane, it can be represented by the equation for a typical first-order decay

$$c = c_0 e^{-k_d t} \qquad (6)$$

where k_d is the unimolecular rate constant for decomposition. Triplet acetone will be removed by various first-order or pseudo-first-order processes if the amount of quenching molecules present is sufficient so that reaction 5 can be ignored. The composite rate constant k_r for these processes can be written

$$k_r = k_p + k_t + k_{tr}[P] + k_q[Q] \qquad (7)$$

where k_p is the rate constant for phosphorescence, k_t is the rate constant for intersystem crossing to ground state singlet, k_{tr} is the rate constant for energy transfer from acetone triplet to polymer ketone, [P] is the molar concentration of polymeric ketone groups, k_q is the rate constant for quenching with trace impurities such as oxygen or the solvent itself, and [Q] is the concentration of such quenchers.

At steady state the rate of formation of acetone triplets

$$\mathrm{dAc}^*/\mathrm{d}t = fk_d c \qquad (8)$$

will be equal to their rate of removal by all processes

$$-\mathrm{dAc}^*/\mathrm{d}t = k_r[\mathrm{Ac}^*] \qquad (9)$$

hence the steady state concentration of acetone triplets will be given by

$$[\mathrm{Ac}^*] = fk_d c/k_r = (fk_d/k_r)c_0 e^{-k_d t} \qquad (10)$$

The number of moles of chain breaks S caused by reaction 3 is given by

$$S = (W/\overline{M}_n^{\,0})[(\overline{M}_n^{\,0}/\overline{M}_n) - 1] \qquad (11)$$

As shown by Amerik and Guillet[12] this expression can be approximated by

$$S \doteq (W/\overline{M}_n^{\,0})[(\overline{M}_v^{\,0}/\overline{M}_v) - 1] \qquad (12)$$

where W is the weight of polymer in the solution and $\bar{M}_n^{\,0}$ and $\bar{M}_v^{\,0}$ are the initial and $\bar{M}_n$, $\bar{M}_v$ the final number and viscosity average molecular weights, respectively. The rate of the chain-breaking process will then be given by

$$\mathrm{d}S/\mathrm{d}t = k_{tr}\psi_{II}^{\mathrm{T}}[\mathrm{Ac}^*][\mathrm{P}] \qquad (13)$$

where ψ_{II}^{T} is the efficiency of conversion of polymer ketone triplets to chain scission by the type II process. Combining eq 10 and 13 we obtain

$$\mathrm{d}S/\mathrm{d}t = (fk_{tr}\psi_{II}^{\mathrm{T}}k_d/k_r)[\mathrm{P}]c_0 e^{-k_d t} \qquad (14)$$

Integrating this gives

$$S = f\psi_{II}^{\mathrm{T}}(k_{tr}/k_r)[\mathrm{P}]c_0[1 - e^{-k_d t}] \qquad (15)$$

or

$$S/c_0 = f\psi_{II}^{\mathrm{T}}(k_{tr}/k_r)[\mathrm{P}][1 - e^{-k_d t}] \qquad (16)$$

A plot of S/c_0 *vs.* time for various values of c_0 should fall on the same line and approach a limiting value

$$(S/c_0)^\infty = f\psi_{II}^{\mathrm{T}}(k_{tr}/k_r)[\mathrm{P}] \text{ as } t \longrightarrow \infty \qquad (17)$$

Experimental determinations indicate that f is nearly unity[2a] and from photochemical data ψ_{II}^{T} is estimated to be about 0.1.[13] Since [P] is known, k_{tr} can be estimated if k_r can be determined from triplet lifetime studies.

Similarly, the time required for the value of S/c_0 to reach one-half of the final value at $t \to \infty$ can be shown to be equal to the half-life τ of the dioxetane at the temperature of the experiment, which gives a direct measure of the rate constant k_d from the relation

$$k_d = 0.693/\tau \qquad (18)$$

If [P] and c_0 are kept constant and a triplet quencher such as *cis,cis*-1,3-cyclooctadiene (COD) is added, it is readily shown that

$$S_0^\infty/S_{\mathrm{COD}}^\infty = 1 + (k_q'/k_r)[\mathrm{COD}] \qquad (19)$$

where k_q' is the bimolecular rate constant for quenching of Ac* by [COD] and S_0^∞ and S_{COD}^∞ are the values of S as $t \to \infty$ for zero and various concentrations of COD, respectively. This is, of course, analogous to the Stern–Volmer equation and permits an independent determination of k_r if k_q' is known or can be estimated.

Similarly, eq 16 and 17 can be combined to give the following relation

$$\ln[(S^\infty - S)/S^\infty] = -k_d t \qquad (20)$$

so that if S^∞ can be determined experimentally a plot of the logarithm of $(S^\infty - S)/S^\infty$ should give a straight line, the slope of which should be equal to $-k_d$, the rate constant for dioxetane decomposition.

Results

The first experiments were run in toluene as solvent. Toluene is quite reactive to acetone triplets and hence the triplet lifetime is relatively short. The results of two experiments differing by a factor of 2 in dioxetane concentration are shown in Figure 2, plotted according to eq 16. The solid line is the theoretical line drawn utilizing only the experimental value of S^∞/c_0 and the measured value of the half-

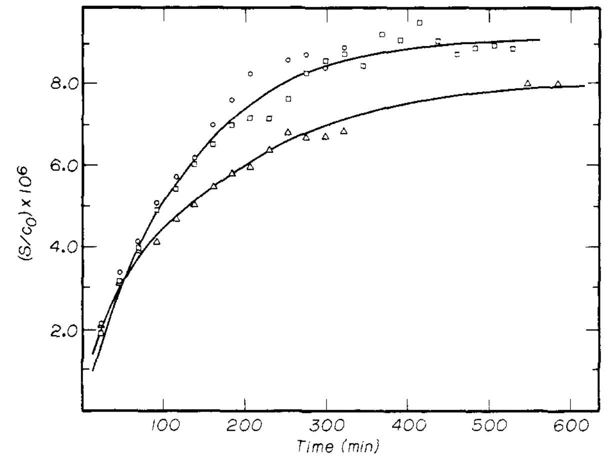


Figure 2. Degradation of PS-5% MIPK copolymer (3.14 g l.$^{-1}$) in toluene: (○) c_0 = 5.17 × 10^{-3} mol l.$^{-1}$, (□) c_0 = 10.3 × 10^{-3} mol l.$^{-1}$, (△) c_0 = 10.0 × 10^{-3} mol l.$^{-1}$, [COD] = 1.5 × 10^{-3} mol l.$^{-1}$.

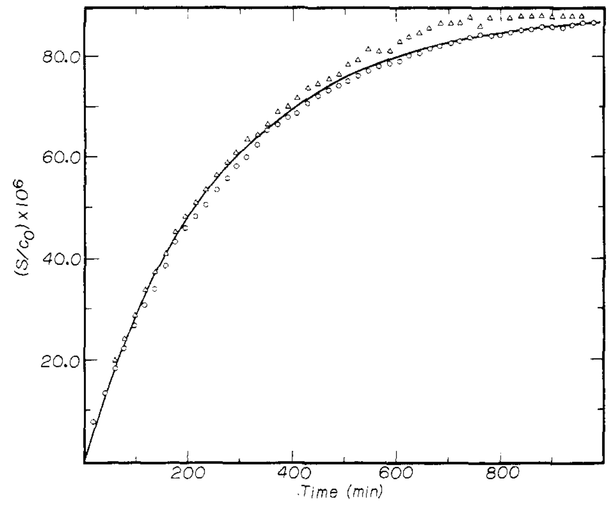


Figure 3. Degradation of PS-5% MIPK copolymer (2.99 g l.$^{-1}$) in 1,2-dichloroethane: (○) c_0 = 1.72 × 10^{-3} mol l.$^{-1}$, (△) c_0 = 0.862 × 10^{-3} mol l.$^{-1}$.

life at 60.2° (τ_{60} = 84.0 min). The total flow time difference was 74 msec at the lower concentration, so the deviation from the theoretical curve amounts to only a few milliseconds. The value of S^∞/c_0 of 9 × 10^{-6} indicates the extreme sensitivity of the method. Since c_0 is of the order of 5 × 10^{-3} mol l.$^{-1}$, the total change observed is of the order of 4 × 10^{-8} mol l.$^{-1}$. With precision of the order of 1 msec we estimate that we can detect changes of the order of 10^{-9} mol l.$^{-1}$ by this technique.

Experiments in toluene require relatively high concentrations of dioxetane (50 mg in 50 ml) so a number of other solvents were tried. The most suitable with respect to both polymer solubility and relatively long triplet lifetime was 1,2-dichloroethane. In this solvent, excellent degradation rates were obtained with as little as 5 mg of dioxetane; however, because of its lower boiling point, the correction for solvent loss was somewhat larger. Data on a typical run with 10 mg of dioxetane are shown in Table I. The results are plotted in curve 1 of Figure 3 along with those from a similar run with half the amount of dioxetane. The solid line is again the theoretical line using only the observed value of S^∞ and the measured half-life τ for dioxetane decomposition. It is clear that the data follow the exponential decay function with astonishing precision and both runs confirm the theoretical prediction within experimental error.

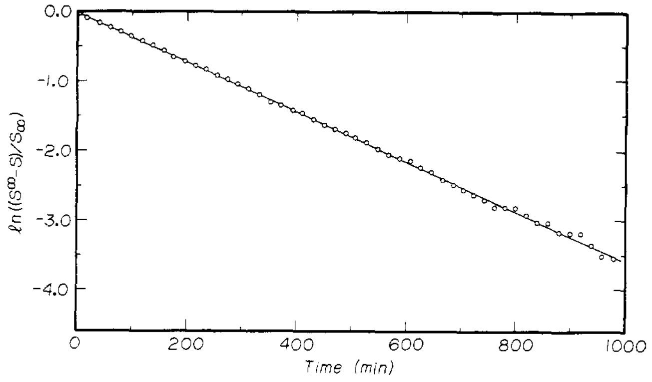


Figure 4. Degradation of PS-5% MIPK copolymer (2.99 g l.$^{-1}$) in 1,2-dichloroethane, c_0 = 1.72 × 10^{-3} mol l.$^{-1}$ plotted according to eq 20 using the best value of S^∞ obtained by the computer search program.

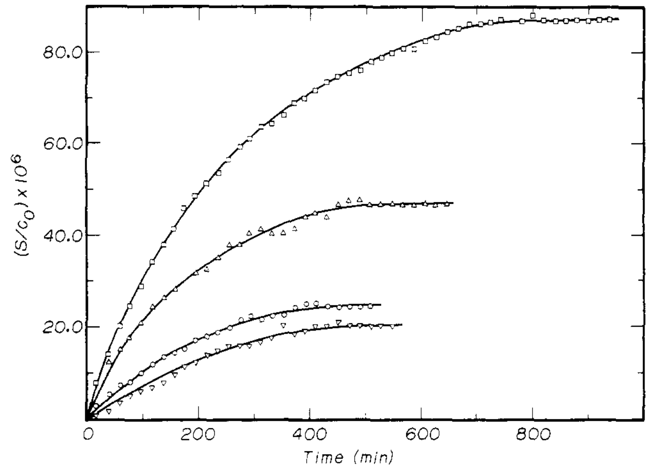


Figure 5. Degradation of PS-5% MIPK copolymer (2.99 g l.$^{-1}$ in 1,2-dichloroethane) quenched with *cis,cis*-1,3-cyclooctadiene (COD), c_0 = 0.862 × 10^{-3} mol: (□) [COD] = 0, (△) [COD] = 0.629 × 10^{-3} mol l.$^{-1}$, (○) [COD] = 1.39 × 10^{-3} mol l.$^{-1}$, (▽) [COD] = 3.03 × 10^{-3} mol l.$^{-1}$.

In order to determine the rate constant k_d with more precision it is useful to plot the data in the form of eq 20. This requires an estimate of the value of S^∞, the total number of scissions after all the dioxetane has been decomposed (*i.e.*, $t \rightarrow \infty$). This was done by estimating a value of S^∞ from plots such as those in Figure 3. A computer program was then written to search for values of S^∞ which would minimize the least-squares standard error of the straight line calculated according to eq 20. Figure 4 shows the line obtained from such a procedure using the data points from curve 1 of Figure 3. An excellent straight line is obtained with a correlation coefficient of 0.9996 and the standard error of the slope is 0.34%.

Experiments in toluene solution using dioxetane (1.03 × 10^{-2} mole l.$^{-1}$) and *cis,cis*-1,3-cycloctadiene (COD) as a triplet quencher showed that all degradation was suppressed by concentrations of 1.03 × 10^{-2} and 3.25 × 10^{-2} mol l.$^{-1}$ and with 1.5 × 10^{-3} mol l.$^{-1}$ only about 10% of the expected change occurred. This quenching thus verifies the mechanism we propose for the sensitized degradation of the polymer.

The results of further quenching experiments in 1,2-dichloroethane solution are shown in Figure 5. These curves were all obtained using only 5 mg of dioxetane with varying quantities of COD. The values of S^∞ obtained with three levels of COD give a reasonable Stern–Volmer relation when plotted according to eq 19. The slope of the line is 1.5

Table I
Sensitized Degradation of PS-MIPK Copolymer (E 171R1)

	Flowtimes					$(\bar{M}_v(0)/\bar{M}_v(T)) - 1$	
Time	Uncorrected	Corrected	Spvis	Invis	Mol wt		$S/c_0 \times 10^6$
0.0	20.490	20.490	0.21551	0.67513	206,013	0.0	0.0
19.55	20.473	20.472	0.21439	0.67181	204,477	0.00751	7.79
39.10	20.461	20.459	0.21357	0.66942	203,375	0.01297	13.44
58.65	20.451	20.448	0.21288	0.66738	202,439	0.01765	18.30
78.20	20.443	20.439	0.21232	0.66571	201,673	0.02152	22.31
97.75	20.434	20.429	0.21169	0.66386	200,822	0.02585	26.79
117.30	20.426	20.420	0.21112	0.66220	200,063	0.02974	30.83
136.85	20.420	20.413	0.21068	0.66090	199,465	0.03282	34.02
156.40	20.411	20.403	0.21005	0.65904	198,617	0.03723	38.60
175.95	20.402	20.392	0.20943	0.65719	197,771	0.04167	43.20
195.50	20.397	20.386	0.20905	0.65607	197,264	0.04435	45.97
215.05	20.393	20.381	0.20873	0.65514	196,840	0.04660	48.30
234.60	20.389	20.376	0.20842	0.65422	196,418	0.04884	50.63
254.15	20.384	20.370	0.20804	0.65309	195,908	0.05158	53.46
273.70	20.380	20.365	0.20772	0.65216	195,485	0.05385	55.83
293.25	20.376	20.360	0.20741	0.65123	195,062	0.05614	58.19
312.80	20.373	20.356	0.20715	0.65048	194,721	0.05799	60.11
332.35	20.369	20.351	0.20684	0.64954	194,297	0.06029	62.50
351.90	20.364	20.345	0.20646	0.64842	193,790	0.06307	65.38
371.45	20.363	20.343	0.20633	0.64805	193,623	0.06399	66.33
391.00	20.361	20.340	0.20614	0.64749	193,365	0.06541	67.80
410.55	20.360	20.338	0.20601	0.64710	193,193	0.06636	68.78
430.10	20.357	20.334	0.20576	0.64635	192,851	0.06825	70.74
449.65	20.355	20.331	0.20557	0.64578	192,595	0.06967	72.22
469.20	20.354	20.329	0.20544	0.64541	192,425	0.07061	73.20
488.75	20.353	20.326	0.20531	0.64503	192,255	0.07156	74.18
508.30	20.352	20.324	0.20518	0.64465	192,083	0.07252	75.17
527.85	20.351	20.322	0.20505	0.64427	191,912	0.07347	76.16
547.40	20.350	20.320	0.20492	0.64388	191,736	0.07446	77.19
566.95	20.349	20.318	0.20479	0.64350	191,565	0.07542	78.18
586.50	20.349	20.317	0.20473	0.64330	191,476	0.07592	78.70
606.05	20.349	20.316	0.20466	0.64311	191,389	0.07641	79.20
625.60	20.348	20.314	0.20453	0.64274	191,222	0.07735	80.18
645.15	20.348	20.313	0.20447	0.64254	191,130	0.07787	80.72
664.70	20.347	20.311	0.20434	0.64215	190,958	0.07884	81.72
684.25	20.347	20.310	0.20427	0.64196	190,872	0.07932	82.23
703.80	20.347	20.309	0.20421	0.64176	190,782	0.07983	82.75
723.35	20.347	20.308	0.20414	0.64157	190,697	0.08032	83.25
742.90	20.347	20.307	0.20407	0.64138	190,608	0.08082	83.77
762.45	20.347	20.306	0.20401	0.64117	190,515	0.08135	84.32
781.99	20.348	20.306	0.20400	0.64117	190,513	0.08135	84.33
801.54	20.349	20.306	0.20400	0.64115	190,505	0.08140	84.38
821.09	20.349	20.304	0.20393	0.64095	190,416	0.08191	84.90
840.64	20.349	20.303	0.20387	0.64076	190,330	0.08240	85.41
860.19	20.350	20.303	0.20386	0.64076	190,329	0.08240	85.42
879.74	20.350	20.302	0.20380	0.64055	190,236	0.08293	85.96
899.29	20.351	20.302	0.20379	0.64054	190,231	0.08296	86.00
918.84	20.352	20.302	0.20379	0.64054	190,230	0.08296	86.00
938.39	20.352	20.301	0.20372	0.64033	190,138	0.08349	86.55
957.94	20.352	20.300	0.20366	0.64015	190,054	0.08397	87.04
977.49	20.353	20.300	0.20365	0.64013	190,046	0.08401	87.09

× 10^3 l. mol^{-1} which is equal to k_q'/k_r. The value of k_q' for COD quenching of acetone triplets in dichloroethane was measured in a separate phosphorescence quenching experiment and found to be of the order of 1.2×10^9 l. mol^{-1} sec^{-1}. This gives a value of k_r of 1×10^6 sec^{-1} or a lifetime of 10^{-6} sec for the acetone triplet under these conditions.

Assuming that $f = 1$ and $\psi_{II}^T \simeq 0.1$, the value obtained for k_{tr} is 0.5×10^6 l. mol^{-1} sec^{-1} which is one order of magnitude smaller than that reported for triplet exchange between acetone molecules.[9] Since the diffusion-controlled rate constant would be of the order of 10^{10} it is apparent that transfer occurs only for about one collision in 20,000.

This relatively low value may be due to the fact that some of the acetone triplets could be quenched by the alkyl phenyl groups of the polystyrene by a process which does not lead to chain scission. This would be consistent with the observed shorter lifetime of the triplets in toluene.

In conclusion, these experiments show that "photodegradation" processes can be induced in a polymer containing ketone groups by energy exchange from acetone triplets generated by the thermal decomposition of tetramethyl-1,2-dioxetane. The reaction can be completely eliminated by a triplet quencher, COD, and the inhibition seems to follow Stern–Volmer kinetics. The method should be of considerable value for establishing the rate constants for inter- and intramolecular energy exchange in polymer systems.

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Notes

Influence of the Alternate Chair Conformation on the Unperturbed Dimensions of Alginic Acid

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Alginic acid is a 1,4-linked copolymer of β-D-mannuronic acid and α-L-guluronic acid. Haug and coworkers have shown that the molecule contains long homopolymeric blocks of each monomer together with blocks of the alternating sequence;[1] the relative amounts of the two comonomers (and the details of the block structure) depend on the source of the sample.[2] Smidsrφd and coworkers[3,4] have recently determined the unperturbed dimensions of various alginate samples containing different amounts of the three kinds of structure, and the results are in qualitative agreement with calculations of unperturbed dimensions, provided that the mannuronic acid residues are assumed to adopt the $^4C_1$ conformation and the guluronic acid residues are assumed to adopt the $^1C_4$ conformation.[4,5] Evidence from X-ray crystallography[6,7] and nuclear magnetic resonance[8] strongly favors these as the predominant ring conformations. However, Angyal[9] estimates that the free energy difference between the two chair forms of the guluronic acid monomer is only about 750 cal/mol, so that small, but appreciable, amounts of the guluronic acid units in the polymer will be expected to adopt the energetically unfavorable $^4C_1$ chair form. This is interesting in that, although the calculated and experimental values of the unperturbed dimensions are qualitatively in agreement, the calculated values are higher than the experimental values, especially for samples rich in guluronic acid. In this communication we wish to investigate the effect on the unperturbed dimensions of including small amounts of the alternate chair form of the guluronic acid residues.

The possibility of incorporating some guluronic acid residues in the unfavorable chair conformation raises two interesting questions. The first of these stems from the curious block structure of alginic acid; the effect of such "conformational impurities" might be quite different depending on whether they occur in guluronic acid blocks or in the alternating blocks. The second question concerns the sequence statistics of the conformational impurities themselves. That is, are they likely to occur as isolated impurities along the chain or in blocks of the alternate ring form? Detailed answers to these questions must await estimation of the free energy difference between the $^1C_4$ and $^4C_1$ forms with *different neighbors* in the polymer. In this communication we wish to investigate the first question, with the assumption that the sequence statistics of the conformational impurity are Bernoullian.

We are interested in examining the effect of conformational impurities on the unperturbed dimensions of the polymer, as a function of the block structure with respect to the two chemically distinct comonomers. The averaging process can be thought of in three stages. In the first stage the chemical sequence of the polymer is sampled. That is, a sample of monomer sequences of mannuronic and guluronic acid residues is constructed, consistent with the assumed sequence statistics. In the second stage some of the guluronic acid residues are inverted from the $^1C_4$ to the $^4C_1$ chair form, the residues to be inverted being chosen at random from the guluronic acid residues in the polymer. In the third stage the unperturbed dimensions of this particular sequence of monomers and conformers is calculated. The first two averaging processes are carried out using a Monte Carlo method which has been described elsewhere[10] and the final averaging is effected analytically using the technique described by Flory and Jernigan.[11] The whole process is a straightforward extension of a method which has been described previously.[12] Sample sizes of about 500 chains of 2000 monomers were used, and the error bars shown in the figures correspond to one standard deviation. The monomer coordinates used were obtained by epimerization and inversion of the Arnott and Scott[13] values for β-D-xylose, with a bridge angle of 116°. Other details of the calculations are as described in ref 12.