to increase in chain length, whereas the excluded volume effect would increase without limit.[26]

The experimental and theoretical values of the temperature coefficient $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ are given in the last three rows of Table II. Such coefficients are generally relatively small quantities, corresponding to changes of only a few tenths of a percent per degree.[20] Consequently, they are difficult to determine with accuracy. The fact that the average value of $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ for the two polymers in carbon tetrachloride is somewhat larger than that in benzene may therefore be due to experimental error rather than to a specific solvent effect or excluded volume effect. In any case, the experimental results unambiguously indicate a moderately large increase in $\langle\mu^2\rangle$ with increase in temperature, which is in agreement with theory.

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A Numerical Solution for Sequence Distributions and Relative Rate Constants in Postpolymerization Reactions

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ABSTRACT: Postpolymerization reactions in which A units react to form B units are examined. Rate equations are set up for the triad fractions with the rate of reaction depending on whether 0, 1, or 2 B units surround the reacting A unit. Predictor–corrector methods are used to solve the equations. The predictor–corrector results are compared to analytical solutions and to Monte-Carlo results. The program is modified to calculate the relative rate constants necessary to produce a given set of A centered triad fractions. Experimental uncertainties in the measurements of the triads are propagated through the calculations to give uncertainties in the calculated rate constants.

Conventional copolymers are prepared by the polymerization of a mixture of two monomers. The composition and sequence distribution of these copolymers are dependent on the reactivity ratios and the monomer feed composition. Copolymers can also be produced from homopolymers by reacting the polymer chains with a reagent that effectively changes the monomer type. Polymeric reactions can produce copolymers with compositions and sequence distributions that are not possible to produce through conventional copolymerizations.

Conventional copolymerizations and their reactivity ratios have been studied extensively over the past 40 years. In polymeric reactions a model has been in existence for several years.[1] Relative rate constants take over the function that the reactivity ratios serve in conventional copolymerizations. That is, the sequence distribution of the copolymers produced through postpolymerization reactions is completely defined by the two relative rate constants and the degree of conversion. In conventional copolymers the sequence distribution is completely defined by the two reactivity ratios and the instantaneous monomer feeds, assuming that no penultimate effects are present.

The calculation of relative rate constants in these postpolymerization reactions is more difficult than the calculation of reactivity ratios. If a reliable method of calculating these relative rate constants could be found, the sequence distribution resulting from polymeric re-

Table I
Predictor-Corrector and Exact Results for $k_0 = k_1 = k_2$ ($\Delta t = 0.002$)

time	type	P(AAA)	P(AAB+)	P(BAB)	P(ABA)	P(ABB+)	P(BBB)
$t = k^{-1}$	exact	0.049 787 0	0.171 096 4	0.146 995 9	0.085 548 2	0.293 991 9	0.252 580 5
	P-C	0.049 784 7	0.171 087 4	0.146 984 8	0.085 539 6	0.293 971 9	0.252 563 2
	Δ	0.000 002 3	0.000 009 0	0.000 011 1	0.000 008 6	0.000 020 0	0.000 017 3
$t - 2k^{-1}$	exact	0.002 478 8	0.031 675 8	0.101 812 8	0.015 836 9	0.202 365 5	0.646 462 3
	P-C	0.002 478 5	0.031 669 7	0.101 165 8	0.015 834 9	0.202 340 3	0.646 388 5
	Δ	0.000 000 3	0.000 004 1	0.000 017 0	0.000 002 0	0.000 025 2	0.000 073 8

actions could be better understood and more easily controlled.

The object of this paper is to present a method of calculating the triad fraction distributions as a function of time given the values of the absolute rate constants. Also the relative rate constants are calculated from data on the triad distributions.

Discussion

Rate Equations. Reaction sites along a polymeric chain may react with varying rapidity depending on their environment. Consider a chain composed of a series of A units capable of reacting irreversibly to form B units. If only the state of the nearest neighbors influences the reaction rate, three rates are possible depending on whether 0, 1, or 2 B's are next to the central A unit. The absolute rate constants for these three cases are k_0, k_1, and k_2.

When the central A unit of a triad reacts, three triads are created and three are destroyed. For example, the reaction of the central A unit of a BAB triad destroys a BAB triad and creates a BBB triad. If an A unit borders the triad to the left, an ABA triad is destroyed and an ABB unit is created. If a B unit is present, a BBA triad is destroyed and a BBB triad is created. Similarly, the unit that borders the triad to the right determines which triads change.

The rate equations for the six triad fractions are

$$\frac{dP(\mathrm{AAA})}{dt} = [\mathrm{R}][-k_0P(\mathrm{AAA}) - 2k_0P(\mathrm{AAAA}) - k_1P(\mathrm{AAAB+})] \quad (1)$$

$$\frac{dP(\mathrm{AAB+})}{dt} = [\mathrm{R}][2k_0P(\mathrm{AAAA}) - k_0P(\mathrm{AAAB+}) - 4k_1P(\mathrm{BAAB})] \quad (2)$$

$$\frac{dP(\mathrm{BAB})}{dt} = [\mathrm{R}][-k_2P(\mathrm{BAB}) + k_0P(\mathrm{AAAB+}) + 2k_1P(\mathrm{BAAB})] \quad (3)$$

$$\frac{dP(\mathrm{ABA})}{dt} = [\mathrm{R}][k_0P(\mathrm{AAA}) - k_1P(\mathrm{AABA+}) - k_2P(\mathrm{ABAB+})] \quad (4)$$

$$\frac{dP(\mathrm{ABB+})}{dt} = [\mathrm{R}][2k_1P(\mathrm{AABA+}) + k_2P(\mathrm{ABAB+}) - k_2P(\mathrm{BABB+})] \quad (5)$$

$$\frac{dP(\mathrm{BBB})}{dt} = [\mathrm{R}][k_2P(\mathrm{BAB}) + k_1P(\mathrm{AABB+}) + k_2P(\mathrm{BABB+})] \quad (6)$$

where [R] is the concentration of the reagent that reacts with the A units and a plus indicates the sum of mirror image triads such as AAB+ = AAB + BAA. $P(x)$ is the probability of finding a sequence x and is equal to the fractional abundance of this sequence in the polymer. The rate equations for the six triads are expressed in terms of triads and tetrads. To solve the equations easily, the tetrads must be expressed in terms of triads.

Table II
Predictor-Corrector and Exact Results ($\Delta t = 0.01$)

k_0:k_1:k_2	type	P-(AAA)	P(AAB+)	P(BAB)
1:0:0	exact	0.0	0.270 670 6	0.296 997 1
	P-C	0.0	0.270 609 1	0.296 975 1
	Δ	0.0	0.000 061 5	0.000 022 0
1:1:0	exact	0.0	0.0	0.333 333 3
	P-C	0.0	0.0	0.333 309 1
	Δ	0.0	0.0	0.000 024 2

A useful property of this system is the AA Markovian property.[2]

$$P(\mathrm{ZAAY}) = P(\mathrm{ZAA})P(\mathrm{AAY})/P(\mathrm{AA}) \quad (7)$$

Z and Y are sequences of A's and/or B's. As a result of this property, sequences to either side of an AA dyad are independent of each other. Equations 1 through 3 can now be rewritten by the use of this property in terms of triads only as

$$\frac{dP(\mathrm{AAA})}{dt} = [\mathrm{R}] \times \left[-k_0P(\mathrm{AAA}) - \frac{(2k_0P(\mathrm{AAA}) + k_1P(\mathrm{AAB+}))P(\mathrm{AAA})}{P(\mathrm{AAA}) + P(\mathrm{AAB+})/2}\right] \quad (8)$$

$$\frac{dP(\mathrm{AAB+})}{dt} = [\mathrm{R}]\left[-k_1P(\mathrm{AAB+}) + \frac{(2k_0P(\mathrm{AAA}) + k_1P(\mathrm{AAB+}))(P(\mathrm{AAA}) - P(\mathrm{AAB+})/2)}{P(\mathrm{AAA}) + P(\mathrm{AAB+})/2}\right] \quad (9)$$

$$\frac{dP(\mathrm{BAB})}{dt} = [\mathrm{R}]\left[-k_2P(\mathrm{BAB}) + \frac{(2k_0P(\mathrm{AAA}) + k_1P(\mathrm{AAB+}))P(\mathrm{AAB+})/2}{P(\mathrm{AAA}) + P(\mathrm{AAB+})/2}\right] \quad (10)$$

These are identical with the rate equations derived by Keller.[1] Later work by Alfrey and Lloyd,[3] Arends,[4] Keller,[5] and Lazare[6] proved these original equations to be correct.

The AA Markovian property cannot be used to simplify eq 4 through 6 because the tetrads do not contain AA dyads. To simplify the equations, the A Markovian property must be applied.[2]

$$P(\mathrm{ZAY}) = P(\mathrm{ZA})P(\mathrm{AY})/P(\mathrm{A}) \quad (11)$$

This is true when the rate constants form an arithmetic progression, $k_2 = 2k_1 - k_0$. For any other set of rate constants, the A Markovian property is not exact. This

Table III
Triad Probabilities for Predictor–Corrector and Monte-Carlo Calculations ($\Delta t = 0.002$)[a]

$k_0:k_1:k_2$	P(B)	P(AAA)	P(AAB+)	P(BAB)	P(ABA)	P(ABB+)	P(BBB)
1:1:10 (accelerating)	0.10	0.7344	0.1592	0.0064	0.0757	0.0207	0.0036
		(0.7356)	(0.1578)	(0.0066)	(0.0751)	(0.0208)	(0.0041)
	0.25	0.4570	0.2726	0.0204	0.1072	0.0989	0.0439
		(0.4575)	(0.2712)	(0.0213)	(0.1077)	(0.0984)	(0.0439)
	0.50	0.1904	0.2811	0.0285	0.0696	0.1989	0.2315
		(0.1919)	(0.2804)	(0.0277)	(0.0664)	(0.2030)	(0.2306)
	0.75	0.0533	0.1766	0.0202	0.0221	0.1728	0.5551
		(0.0512)	(0.1764)	(0.0244)	(0.0190)	(0.1832)	(0.5478)
	0.90	0.0115	0.0790	0.0095	0.0047	0.0884	0.8067
		(0.0128)	(0.0758)	(0.0114)	(0.0033)	(0.0920)	(0.8047)
$1:{}^1/_2:{}^1/_4$ (decelerating)	0.10	0.7206	0.1695	0.0099	0.0896	0.0101	0.0003
		(0.7212)	(0.1680)	(0.0108)	(0.0900)	(0.0096)	(0.0004)
	0.25	0.3843	0.3065	0.0592	0.1805	0.0639	0.0056
		(0.3822)	(0.3082)	(0.0596)	(0.1817)	(0.0640)	(0.0043)
	0.50	0.0667	0.2410	0.1923	0.1956	0.2345	0.0699
		(0.0623)	(0.2408)	(0.1969)	(0.2013)	(0.2320)	(0.0667)
	0.75	0.0009	0.0363	0.2128	0.0727	0.3166	0.3607
		(0.0010)	(0.0316)	(0.2174)	(0.0753)	(0.3158)	(0.3589)
	0.90	0.0000	0.0011	0.0989	0.0123	0.1743	0.7130
		(0.0000)	(0.0014)	(0.0986)	(0.0130)	(0.1726)	(0.7144)
$1:{}^1/_2:1$ (mixed)	0.10	0.7213	0.1691	0.0095	0.0888	0.0106	0.0001
		(0.7203)	(0.1702)	(0.0095)	(0.0895)	(0.0102)	(0.0003)
	0.25	0.3938	0.3042	0.0520	0.1700	0.0682	0.0118
		(0.3906)	(0.3062)	(0.0532)	(0.1740)	(0.0646)	(0.0114)
	0.50	0.0985	0.2726	0.1289	0.1531	0.2242	0.1226
		(0.0953)	(0.2758)	(0.1289)	(0.1554)	(0.2228)	(0.1218)
	0.75	0.0117	0.1192	0.1190	0.0495	0.2583	0.4421
		(0.0110)	(0.1172)	(0.1218)	(0.0515)	(0.2578)	(0.4407)
	0.90	0.0010	0.0378	0.0612	0.0081	0.1439	0.7478
		(0.0007)	(0.0392)	(0.0601)	(0.0088)	(0.1418)	(0.7494)

[a] Monte-Carlo results[13] are in parentheses.

A Markovian property can be used to simplify the rate equations for the B-centered triads.

$$\frac{dP(\mathrm{ABA})}{dt} = [\mathrm{R}] \times \left[k_0P(\mathrm{AAA}) - \frac{(k_1P(\mathrm{AAB+}) + 2k_2P(\mathrm{BAB}))P(\mathrm{ABA})}{P(\mathrm{ABA}) + P(\mathrm{ABB+})/2} \right] \tag{12}$$

$$\frac{dP(\mathrm{ABB+})}{dt} = [\mathrm{R}]\left[k_1P(\mathrm{AAB+}) + \frac{(k_1P(\mathrm{AAB+}) + 2k_2P(\mathrm{BAB}))(P(\mathrm{ABA}) - P(\mathrm{ABB+})/2)}{P(\mathrm{ABA}) + P(\mathrm{ABB+})/2} \right] \tag{13}$$

$$\frac{dP(\mathrm{BBB})}{dt} = [\mathrm{R}]\left[k_2P(\mathrm{BAB}) + \frac{(k_1P(\mathrm{AAB+}) + 2k_2P(\mathrm{BAB}))P(\mathrm{ABB+})/2}{P(\mathrm{ABA}) + P(\mathrm{ABB+})/2} \right] \tag{14}$$

While eq 12–14 are not exact, the error involved in such an assumption is small. Platé and co-workers[2] have produced exact expressions for B-centered sequences and found that the A-Markovian assumption (their B approximation) was a good approximation. For most cases, the two results were indistinguishable. Only for extreme cases of mixed rate constants ($k_0{:}k_1{:}k_2$ = 1:0.02:100 or 1:50:0) is there any noticeable discrepancy. These exact expressions require a large amount of computer time.

Thus, a set of nonlinear differential equations (eq 8 through 10 and 12 through 14) is set up. Keller[1] has shown that they can be solved analytically for special cases such as $k_0 = k_1 = k_2$. For the vast majority of sets of rate constants, the equations cannot be solved analytically.

Table IV
Standard Deviation in k_1 and k_2 in RATEFIND

$k_0:k_1:k_2$		25% conversion	50% conversion	75% conversion
1:1:1	σk_1	0.180	0.093	0.326
	σk_2	1.055	0.153	0.135
1:1:10	σk_1	0.209	0.093	0.137
	σk_2	3.956	1.841	2.272
$1:{}^1/_2:{}^1/_4$	σk_1	0.128	0.064	1.274
	σk_2	0.678	0.064	0.345
$1:{}^1/_2:1$	σk_1	0.133	0.057	0.182
	σk_2	0.820	0.111	0.203

Numerical Solution of the Equations. The rate equations need to be solved for any set of rate constants. A numerical solution based on predictor–corrector methods[7] has been obtained. The method used will be referred to as SEQDIST.[8]

The intitial conditions provide the values of the six triads at $t = 0$. A step through time of Δt is taken. A predicted point is calculated by the use of

$$\mathrm{triad}_{t+\Delta t} = \mathrm{triad}_t + \Delta t(\mathrm{derivative}) \tag{15}$$

The derivatives are calculated by the use of eq 8–10 and 12–14. The derivatives at $t + \Delta t$ are then calculated. An average of this derivative and the one at t is taken to give a better estimation of the rate of change of the triad. This average derivative is used in eq 15 to calculate the new values of the triad fractions at $t + \Delta t$. These new fractions are the starting points for the next step of Δt. Further steps are taken using the same method to provide a list of sequence fractions as a function of time.

The accuracy of the method can be checked by using rate constant sets that provide an analytical solution to eq 8–10 and 12–14. When $k_0 = k_1 = k_2 = k$, the solutions are given by

$$P(\mathrm{AAA}) = \exp(-3kt) \tag{16}$$

$$P(\mathrm{AAB+}) = 2\exp(-2kt) - 2\exp(-3kt) \quad (17)$$

$$P(\mathrm{BAB}) = \exp(-kt) - 2\exp(-2kt) + \exp(-3kt) \quad (18)$$

$$P(\mathrm{ABA}) = \exp(-2kt) - \exp(-3kt) \quad (19)$$

$$P(\mathrm{ABB+}) = 2\exp(-kt) - 4\exp(-2kt) + 2\exp(-3kt) \quad (20)$$

$$P(\mathrm{BBB}) = 1 - 3\exp(-kt) + 3\exp(-2kt) - \exp(-3kt) \quad (21)$$

Table I shows the difference between the predicted and actual values at $t = k^{-1}$ and $2k^{-1}$. The numerically predicted values are within one-hundredth of a percent of the actual sequence fractions.

Other tests can be made by assuming that one or two of the rate constants are zero. If $k_1 = k_2 = 0$, A units will become isolated and not react. The remaining triad fractions at infinite time can be calculated analytically. Similarly, if $k_0 = k_1$ and $k_2 = 0$, results at $t = \infty$ can be calculated. Table II shows the actual and predicted values of these limits and their differences. Again, the differences are less than one-hundredth of a percent.

Klesper,[9] Platé et al.,[10] and Harwood et al.[11,12] have set up Monte-Carlo simulations of these rate problems. A units are reacted randomly to form B units. The probability of their reacting is based on the three rate constants. Records are made of the triad fractions as a function of time or as a function of total conversion of the chain.

Table III shows the sequence fractions of three cases at a variety of conversions compared to Monte-Carlo results.[13] The three cases represent accelerating, decelerating, and mixed conditions. The predictor–corrector results are within the scatter of the Monte-Carlo results. Monte-Carlo calculations are valuable due to their inherent simplicity. Results can be obtained without the need to set up and solve rate equations. However, they require large amounts of computer time. Statistical fluctuations cause uncertainties in the calculated values, and these uncertainties can be diminished only by increasing the number of Monte-Carlo experiments performed.

Determination of Relative Rate Constants. SEQDIST[8] predicts the probability of the A centered triads (exact expressions) and the B centered triads (A-Markovian approximation) as a function of time for any set of rate constants. The experimentally available data are the triad fractions and not the rate constants. Therefore the inverse of the problem is important, that is, the determination of the relative rate constants necessary to produce a given set of triad fractions.

SEQDIST typically takes 1 s of computer time per run. It is efficient enough to be used repeatedly in a searching routine. SEQDIST was modified and written as a subroutine. The input is k_1, k_2, and limiting value of $P(\mathrm{AAA})$ from experimental data. The output is the values of $P(\mathrm{AAB+})$ and $P(\mathrm{BAB})$ that would result from these rate constants.

Time is no longer a variable since the subroutine terminates at a given value of $P(\mathrm{AAA})$ and not at a given time. The reagent concentration is also unimportant as long as the reaction mixture is homogeneous. This makes the rate constants relative. If a given set of rate constants produce the three A-centered triads sought, then a constant multiplier times all three rate constants will produce a new set of rate constants that also satisfy the requirements. Therefore k_0 was set equal to 1. Now the calculated values of k_1 and k_2 are relative, being identical with k and k' of previously published papers.[1] Now a set of three A-centered triads is produced by a given set of relative rate constants.

k_1 is calculated first by finding a value that will produce the experimental values of $P(\mathrm{AAA})$ and $P(\mathrm{AAB+})$. Next k_2 is varied to produce the experimentally observed value of $P(\mathrm{BAB})$. Regula-Falsi methods[12] were used to find the proper values of k_1 and k_2. The program will be referred to as RATEFIND.[15] These calculations use only the data on the A-centered triads. Therefore, the A-Markovian property was not used, and the equations are exact.

A method of error estimation is included in RATEFIND. The standard deviation of the A-centered triad is propagated through the calculations to produce a standard deviation in k_1 and k_2. The method used is

$$\sigma^2{}_k = \sigma^2{}_{\mathrm{AAA}}\left(\frac{\partial k}{\partial P(\mathrm{AAA})}\right)^2 + \sigma^2{}_{\mathrm{AAB+}}\left(\frac{\partial k}{\partial P(\mathrm{AAB+})}\right)^2 + \sigma^2{}_{\mathrm{BAB}}\left(\frac{\partial k}{\partial P(\mathrm{BAB})}\right)^2 \quad (22)$$

The partial derivatives are calculated numerically by slightly varying the triad fractions.

Table IV shows the standard deviation of k_1 and k_2 for a variety of pairs of rate constants at 25, 50, and 75% conversion of A to B. The standard deviation for each of the A-centered triads was taken to be 0.5%.

In some cases the uncertainties are large. The best results occur at 50% conversion. In all of the cases examined, reasonable accuracy is present at this conversion. At high or low conversion the uncertainties can be larger than the rate constants themselves for measured uncertainties, of 0.5%

Klesper[15] has developed a successful method of determining the relative rate constants from data on the sequence fractions. The same equations were used in his work as were used here (eq 1 through 6). The equations are modified to express the derivatives of the sequence fractions in terms of A fraction instead of time. Klesper finds $\mathrm{d}(P(\mathrm{XXX}))/d(P(\mathrm{A}))$ directly from experimental data by plotting the six fractions vs. A. The derivatives are the slopes of the plots. The data on the sequence fractions and the derivatives of the fractions are used to calculate the relative constants.

In order to calculate the derivatives of the triad fractions, many data points are necessary. Klesper's methods[15] will work well when enough data are available, but RATEFIND can calculate relative rate constants from a single data point.

The uncertainties in the calculations based on a single data point can be sizable, but a single data point should indicate whether accelerating, decelerating, or random cases are present. Collecting much data and fitting the results to smooth curves should reduce the uncertainties to a low level such that reliable values of k_1 and k_2 could be found.

Conclusions

Equations for the rate of change of the A-centered triads as first proposed by Keller[1] are easily solved numerically by predictor–corrector methods. The same is true for the B-centered triads, but the A-Markovian approximation is necessary. The error produced by this approximation is small. Thus, the sequence fractions as a function of time can be easily calculated.

RATEFIND calculates the relative rate constants necessary to produce a given set of A-centered triads. A single data point will give values of the relative rate constants. Experimental uncertainties cause uncertainties in the relative rate constants, but accurate measurements and repeated experiments should give reliable values of the relative rate constants. Even from a single data point with uncertainties present, the accelerating, decelerating, and random cases should be distinguishable.

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Quenching of Triplet Excitons in Poly(2-vinylnaphthalene) and Poly(acenaphthylene) by Biacetyl

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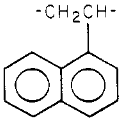
ABSTRACT: Biacetyl is used as a quencher for triplet excitons in poly(2-vinylnaphthalene) (P2VN) and poly(acenaphthylene) (PAcN) in 2-methyltetrahydrofuran glasses at 77 K. The phosphorescence of a polymer–biacetyl mixture shows a strong component of biacetyl at times very long (1–2 s) compared with the biacetyl triplet lifetime (~2 ms), demonstrating that the triplet exciton continues to sensitize the biacetyl. It is shown that for PAcN the sensitization ceases at earlier times than for P2VN. The biacetyl sensitization is also shown to persist to longer times for a higher molecular weight sample of P2VN than for a lower molecular weight sample. This is consistent with previous results that imply that sensitization is more effective for higher molecular weight polymers of P2VN because of the increased number of quencher–polymer contacts. The results are interpreted as implying the following: (1) triplet excitons in PAcN are confined to relatively short segments of the polymer chain, and (2) triplet excitons in P2VN show essentially no trapping at long times.

One of the earliest characterizations of triplet excitons in polymers was the report by Eisinger and Shulman[1] of the quenching of the phosphorescence of poly(riboadenylate acid) by paramagnetic ions and that by Lashkov and Ermolaev[2] on the phosphorescence quenching of poly(vinylphthalimide). Since that time, the two primary observables that implicate the presence of triplet excitons on a polymer are (1) enhanced efficiency of phosphorescence quenching by extrinsic quenchers and (2) delayed fluorescence arising from triplet exciton annihilation.[3] To date, triplet excitons in four homopolymeric naphthalene derivatives have been studied: poly(1-vinylnaphthalene)[4] (**1**), poly(2-vinylnaphthalene)[5] (**2**), poly(2-naphthyl methacrylate)[6,7] (**3**), and poly(acenaphthylene)[8] (**4**). All members of this set of polymers demonstrate triplet exciton annihilation leading to delayed fluorescence except the last polymer, poly(acenaphthylene). According to David et al.,[8] the sensitivity of the phosphorescence of poly(acenaphthylene) to extrinsic quenchers (piperylene) is the same as that of poly(1-vinylnaphthalene), implying that triplet excitons must be present in both polymers. Thus one has an apparent paradox in that triplet excitons exist in poly(acenaphthylene), but triplet exciton annihilation does not occur. Several possible explanations for this observation may be offered, including: (1) the diffusion length of the triplet exciton may be small in poly(acenaphthylene) (because of slow exciton hopping rates or trapping), (2) triplet exciton annihilation may not lead to excited singlet states because of the unusual orientation of neighboring naphthalene groups (or the strained naphthalene to alkane backbone bonds may be susceptible to a photochemical reaction, even at 77 K), or (3) the quantum yield of fluorescence for poly(acenaphthylene) is low, such that no delayed fluorescence can be observed, even when annihilation occurs. This latter possibility can be definitely discounted because the fluorescence of poly(acenaphthylene) is easily observed at



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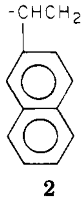

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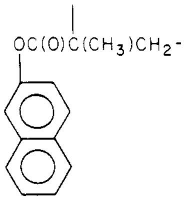

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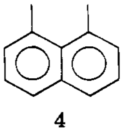

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