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Received October 9, 1985

Fluorescence Quenching in Pyrene/Benzil End-Labeled Poly(tetramethylene oxide). Cyclization Dynamics in Polymers. 19

Cyclization rates provide an important measure of the large-amplitude dynamics of polymer chains.[1,2] While these rates are not trivial to measure, reliable values of the rate constant k_1 for diffusion-controlled cyclization can be obtained from careful fluorescence quenching experiments on polymers of the form $F\sim\sim\sim Q$ containing a fluorescent group F on one chain end and a quencher group Q on the other.

While the fluorescence measurements themselves require great care, the most demanding aspects of the experiments are the synthesis and characterization of polymers of low molecular weight distribution (MWD) containing appropriate end groups. From the point of view of synthesis, it is much easier to obtain polymers with identical end groups.[3] This limits the choice of fluorescent dyes that can be used, since F* must have a suitably long lifetime and interact with F at the diffusion-controlled rate. These criteria are met by pyrene, whose derivatives have lifetimes of ca. 200 ns and which undergo diffusion-controlled excimer formation. In consequence, most of the experiments published describing cyclization dynamics have employed pyrene end groups and report rates of intramolecular pyrene excimer formation. The greatest effort has focused on polystyrene.[3a,b,4] The effect of chemical structure on cyclization rates is an important question. There is a particular interest in polymers more flexible than polystyrene, where in principle current techniques should permit one to study the end-to-end cyclization of longer chains. Two such polymers for which some cyclization rates have been reported are poly(ethylene oxide)[5] and poly(dimethylsiloxane).[6]

It was our hope to extend these studies to poly(tetramethylene oxide) (polyTHF). It is flexible, soluble in a wide variety of solvents, and amenable to synthesis from tetrahydrofuran by cationic living polymerization. One of the attractive features of the polymerization mechanism is that it seemed possible to use a derivative of one chromophore (F or Q) to initiate polymerization in order to obtain a polymer containing a specific group on one end and a functional group capable of further transformation on the other. In a polymer such as $Q\sim\sim\sim CH_2OH$, one can study cyclization by a variety of means depending upon which F group one attaches to the CH_2OH group. Here we report a brief outline of two syntheses of polyTHF molecules which satisfy these requirements and our initial results on measurements of cyclization rates by intramolecular fluorescence quenching studies. Full details of the synthesis will be reported elsewhere.

Scheme I

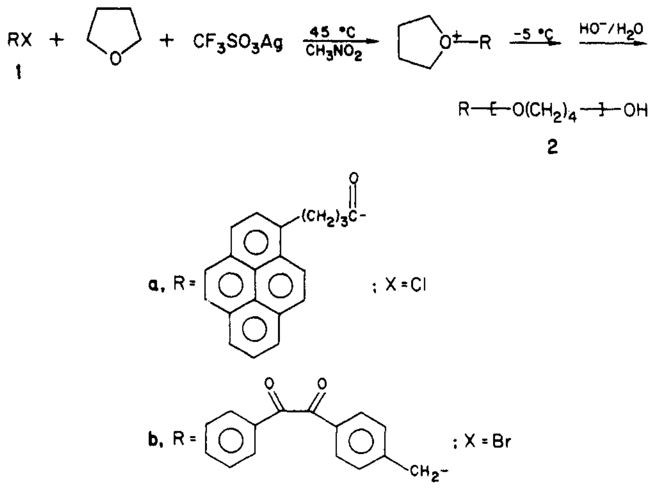


Table I
Characterization of PolyTHF Samples and Cyclization Rate Constants in Toluene at Room Temperature

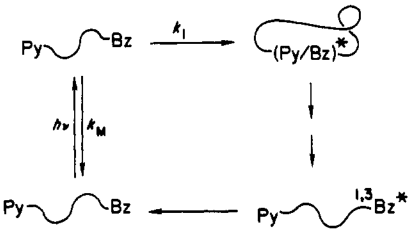
sample	N^a	M_n GPC	M_n UV^b	M_w/M_n	τ, ns	$10^{-6}\langle k_1\rangle$, s^{-1}
Py-polyTHF-OH (2)		20100	24500	1.12	186.0	
Py-polyTHF-Bz (3)	740	10700	11300	1.15	162.6	7.8
Py-polyTHF-Bz (3)	440	6700	6800	1.08	140.3	17

other polymers	N	M_n (interpolated)^c	$10^{-6}\langle k_1\rangle$, s^{-1}
Py-PDMS-Py	440	16400	23^d
Py-polystyrene-Py	440	23000	0.29^e
Py-polystyrene-Py	740	38000	0.05^e

[a] Number of backbone bonds calculated from M_n. [b] Based upon pyrene absorption. [c] Interpolated from previously reported values of $\langle k_1\rangle$ for various chain lengths. [d] Reference 6. [e] Reference 3a.

As shown in Scheme I, treatment of **1a** or **1b** with silver triflate in THF (7.8 M)/nitromethane at room temperature or below, using standard vacuum-line techniques, gave polymers of the form **2**, but with substantial polydispersities ($M_w/M_n \sim$ 1.3-1.5). When the initiation step was carried out at 45 °C, above the ceiling temperature for the polymer, and rapidly cooled to −5 °C, polymerization to low (ca. 10%) conversion produced polymer samples of acceptably low MWD ($M_w/M_n \sim$ 1.1). Two samples of **2b** were esterified with **1a** to produce polymers Bz-polyTHF-Py (**3**) with benzil (Bz) groups on one end and Py groups on the other. Characterization of the polymers, Table I, indicated quantitative benzil groups in **2b** and **3**, whereas **3** contained approximately 0.85 Py group per chain.

Benzil has a lower singlet energy than pyrene whereas pyrene has a much higher molar extinction coefficient at 345 nm. Irradiation of the dilute solutions **3** at 345 nm should excite the Py groups selectively. Subsequently cyclization will lead to intramolecular fluorescence quenching by singlet energy transfer. Because of the weak oscillator strength of the benzil absorbance between 380 and 410 nm, energy transfer should require close proximity (adjacency) between Py* and Bz.



The important term of interest to us is the cyclization rate constant $\langle k_1 \rangle$, where the angle brackets emphasize that the experimental value is an average over the finite polydispersity of the polymer. It is obtained from fluorescence decay studies on polymers **2a** and **3**, degassed in dilute (2×10^{-6} M) solution in toluene and sealed under vacuum. All decays were cleanly exponential over more than 2 decades. We assign to k_M the value of **2a** for the polymer containing a pyrene but no benzil group, and calculate $\langle k_1 \rangle$ from the expression

$$\langle k_1 \rangle = 1/\tau_3 - 1/\tau_{2a}$$

Values of τ and of $\langle k_1 \rangle$ for two different chain lengths are shown in Table I. It is interesting to compare these cyclization rate constants with values obtained earlier for cyclization of polystyrene and PDMS of similar chain length. Those results, Table I, indicate the magnitudes of cyclization rates of PDMS and polyTHF are similar, whereas the cyclization of polystyrene is much slower. That is the order expected for chains of decreasing dynamic flexibility. Nonetheless we must be careful not to overinterpret these results. The quality of toluene as a solvent for each of these polymers is different. Cyclization is much more sensitive to excluded volume than other chain properties such as intrinsic viscosity. Toluene is a good solvent for polystyrene and causes nearly an order of magnitude decrease in k_{cy} relative to a chain of similar length in a Θ-solvent of similar viscosity.[8,9]

These experiments do open the possibility for a new series of experiments on cyclization dynamics. Since the benzil group phosphoresces in solution with a lifetime of tens of microseconds (and pyrene quenches that emission), it should also be possible to extend these studies to include much longer chain lengths. Such experiments have the obvious difficulty of trying to excite the benzil groups selectively in the presence of pyrene. Benzil does absorb at 405 nm where pyrene does not, but this absorption is very weak. One needs to work at concentrations high enough that polymer–polymer interactions become important. Such studies are under way in our laboratory, and these results will be reported in due course.

Acknowledgment. We thank NSERC Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous financial support.

Registry No. PolyTHF (SRU), 25190-06-1; Py-polyTHF-OH, 99559-99-6; Py-polyTHF-Bz, 99560-00-6.

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Received July 30, 1985