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Synthesis of Low-Polydispersity Poly(tetramethylene oxide) Using Benzil and Pyrene Derivatives as Initiators

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ABSTRACT: The synthesis of low-polydispersity poly(tetramethylene oxide) (polyTHF) labeled at one end with benzil or pyrene and polyTHF labeled at one end with benzil and the other end with pyrene is described. The process involves initiation with 4-(bromomethyl)benzil/AgO_3SCF_3 or 4-(1-pyrene)butyryl chloride/AgO_3SCF_3 above the ceiling temperature (at 45 °C, $[THF]_0$ = 7.8 mol/L, CH_3NO_2 solvent) and subsequent polymerization at −5 °C. Reaction of benzil–polyTHF–OH with 4-(1-pyrene)butyryl chloride yields benzil–polyTHF–pyrene. Polymers and model compounds of end groups are characterized by GPC, ^1H and ^{13}C NMR, and UV spectroscopy. The design of the synthesis is discussed.

Physicochemical studies of macromolecules require polymers of well-defined chemical structure and narrow polydispersity. Experiments on polymer cyclization depend upon appropriate end groups as well. Until recently, virtually all experiments were carried out on polymers containing identical groups (B···B) on both chain ends.[1–5] These experiments include studies of intramolecular excimer formation (B = pyrene)[1–4] and intramolecular triplet–triplet annihilation (B = anthracene).[5]

For two quite different reasons, it is now necessary to extend these experiments to polymers which contain different groups at the two chain ends (B···Q). First and most obvious is the need to carry out reliable experiments for long chains in the long-time domain. For this purpose, B should be capable of phosphorescence in solution: one should choose an aromatic ketone or α-diketone derivative as B and a quencher of its emission as Q.

The second issue is rather subtle. The theory of diffusion-controlled cyclization[6,7] predicts that the distance over which B* and Q interact (the "capture radius") plays a role in the experimental value one obtains for the cyclization rate constant, k_{cy}. Rigorously speaking, chemical reactions of excited states have distance-dependent rate constants, $k(r)$. One can meaningfully define a characteristic distance, R_0, where the magnitude of $k(r)$ equals the unquenched decay rate of B*.[8] The net effect of this prediction is that different quenching processes, characterized by different R_0 values, will give different values of k_{cy} when applied to cyclization dynamics measurements. The one experiment carried out to test this prediction[10] indicated that it is correct.

The prediction is in fact somewhat more curious, because this dependence upon R_0 is severe only for "short" chains and may disappear in the limit of very long chains.[7] What this does is to add an unforeseen dimension to the study of cyclization processes: one must determine the interplay between R_0 and k_{cy} as well as the dependence of k_{cy} upon chain length. This is no easy task. As difficult as the excited state quenching experiments may be, the first limitation here is the synthesis of appropriate polymers. Not only must these polymers contain different groups at the two chain ends, but the strategy of synthesis should allow different pairs of groups to be attached to the same polymer sample. These needs can be satisfied if a derivative of B or Q is used to initiate living polymerization, and the polymerization is terminated to generate a functional group such as CH_2OH capable of further transformation.[9,10]

One of the flexible polymers that is interesting for the studies of macromolecular dynamics is poly(tetramethylene oxide) (polyTHF). Synthesis of a narrow distribution polyTHF was described previously by Croucher and Wetton.[11] However, this synthesis leads to macromolecules terminated with two OH groups. Therefore, from such samples, only polymers labeled at both ends with the same kind of chromophore can be obtained. Introduction of the required substituent only at one end of polyTHF macromolecules can be achieved by using the appropriate initiator, fragments of which are added to the monomer (THF) during initiation. Penczek et al.[12] summarized several methods of THF initiation.

The simplest, most versatile, and therefore the most appropriate for synthetic purposes is a silver salt method which consists of initiation with carbenium or oxocarbenium cations formed in situ from organic halides and

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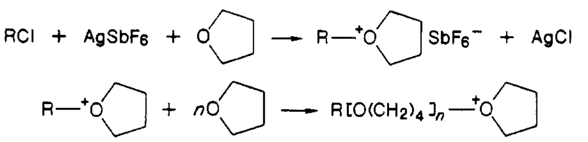
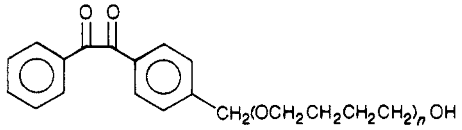
corresponding silver salts ($AgSbF_6$, $AgPF_6$, $AgClO_4$, and AgO_3SCF_3). For example,

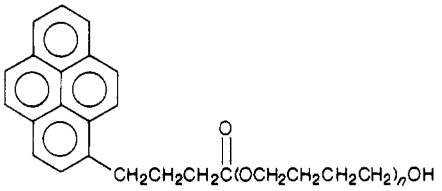


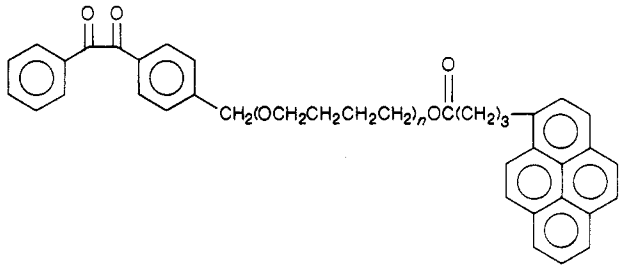
(1)

This method was used for grafting polyTHF from halogenated polymers[13-15] and for synthesis of star-type polyTHF.[15] The silver salt method enabled Richards et al.[16-18] to synthesize polystyrene–polyTHF and polystyrene–polyTHF–polystyrene block copolymers. In spite of side reactions preventing the quantitative formation of blocks, optimization of the polymerization conditions led to block copolymers with low polydispersity (M_w/M_n = 1.04).

This paper describes the synthesis of low-polydispersity samples of polyTHF with benzil and pyrene moieties as the end groups. Our aim was to obtain and characterize







polymers with a chromophore attached to only one end and also those with two different chromophores attached to both ends, of each macromolecule. Polymers ($\bar{M}_n$ from 3000 to 40 000) were synthesized for further studies of the cyclization dynamics by the intramolecular fluorescence quenching method. High purity of these materials is essential.

Experimental Section

Syntheses of polymers were performed by using a high-vacuum line evacuated by a system of mechanical and three-step diffusion oil pumps. Isolated polymers were dried under vacuum by using a mechanical pump only.

Materials. Monomer. Tetrahydrofuran (Caledon, reagent grade) was distilled twice under nitrogen over fresh portions of sodium. The middle fraction was collected and stored over sodium in a flask attached to a vacuum line. Portions of THF, ca. 150 mL, were distilled on the vacuum line into an ampule containing freshly prepared sodium–potassium alloy. The ampule was equipped with a Teflon (Rotaflo) stopcock. The blue color of the solution, due to the potassium ionization and presence of solvated electrons, indicated that monomer was moisture free.

Solvent. CH_3NO_2 (Fisher, ACS) was dried over P_2O_5 in a glass ampule closed with a Rotaflo stopcock. Air from the ampule containing nitromethane was removed by five freeze–pump–thaw cycles on the vacuum line.

AgO_3SCF_3 (Aldrich) was used without further purification. The amounts of AgO_3SCF_3 required for polymerization were placed into thin-walled glass phials which, after removing air on the vacuum line, were sealed off.

4-(Bromomethyl)benzil (Toronto Research Chemicals) was used without further purification.

4-(1-Pyrene)butyryl chloride (Toronto Research Chemicals) was stored in a desiccator and used without further purification.

Synthesis of Benzil-PolyTHF–OH and Pyrene–PolyTHF–OH. Polymerizations were carried out in glass ampules in which thin-walled glass phials containing known amounts of organic halide (4-(bromomethyl)benzil or 4-(1-pyrene)butyryl chloride) and AgO_3SCF_3 were placed. AgO_3SCF_3 was used in slight excess. In a typical synthesis, 15 mL of CH_3NO_2 and 26 mL of THF were distilled into an ampule on the vacuum line, and the ampule was sealed off. The initial monomer concentration, 7.8 mol/L, was maintained in all polymer syntheses. Polymerizations were initiated by crushing consecutively phials with AgO_3SCF_3 and organic halide. Initiation was carried out for 5 min at 45 °C and was accompanied by the rapid precipitation of silver halide. Subsequent polymerization was carried out at −5 °C.

After the required reaction time, ampules were opened and the polymerizing mixture was added to a KOH solution in ca. 10 mL of H_2O. The amount of KOH was 2–3-fold in excess with respect to the silver salt. After 10 min of stirring, ca. 100 mL of CH_2Cl_2 was added to dilute the viscous mixture, which was treated for an additional 10 min with activated charcoal. Thereafter, the solution containing quenched polyTHF was filtered and washed 5 times with water. The organic layer was separated, solvents were removed using a rotary evaporator, and the isolated polymer was dissolved in a small amount of toluene.

Subsequently, polyTHF samples with molecular weight higher than ca. 15 000 were twice precipitated in cold (dry ice bath) methanol. We found it essential to handle the isolated polymer at low temperature (glassware cooled with dry ice) before drying. Otherwise, at this stage of purification, the polymer, when warmed to room temperature, becomes waxy, difficult to dry, and hard to manage. Finally, polyTHF was dried on a vacuum line for 48 h.

Polymers with molecular weights lower than ca. 15 000 cannot be precipitated in common precipitants for polyTHF (methanol, hexanes) and if not purified further are contaminated by low molecular weight compounds absorbing UV light. Purification of low molecular weight polyTHF was carried out by using silica gel column chromatography.[19]

Typically, 0.5 g of Bz–polyTHF–OH in 5 mL CH_2Cl_2 was placed on a short, broad (2.5-cm × 5-cm diameter) column of silica gel and eluted rapidly with, first, 300 mL of CH_2Cl_2 to remove impurities and, then, with 300 mL of 4:1 CH_2Cl_2/CH_3OH to elute the polymer. This latter solution was concentrated, freeze-dried from benzene, and finally dried on the vacuum line for 48 h.

Synthesis of 4-(Ethoxymethyl)benzil. Sodium ethoxide was prepared from 0.41 g (1.78×10^{-2} mol) of Na in 50 mL of absolute ethanol. To this was added dropwise 1.00 g (3.31×10^{-3} mol) of 4-(bromomethyl)benzil in ethanol. The reaction was carried out at room temperature for 4 h. During this time, the color of the solution changed from yellow to red and subsequently to violet, but when poured into a mixture of 300 mL of water and 200 mL of ethanol, its color changed back to yellow. After removal of ethanol and some part of water on a rotary evaporator, the product was extracted with CH_2Cl_2. Evaporation of CH_2Cl_2 yielded an oily compound which was dried on the vacuum line for 5 days. ^1H NMR ($CDCl_3$, TMS) δ 7.7–8.0 (4 H), 7.2–7.6 (5 H), 4.53 (s, 2 H, $ArCH_2O$), 3.52 (q, 2 H), 1.22 (t, 3 H, CH_3).

Conversion of Bz–PolyTHF–OH into Bz–PolyTHF–Py. Bz–polyTHF–Py was prepared by esterification of Bz–polyTHF–OH (M_n = 5700 and 10 700) with 4-(1-pyrene)butyryl chloride in the presence of triethylamine in toluene solution.[1] The reaction was carried out for 3 days at room temperature. These polymers could not be purified by precipitation. Attempts to purify them using column chromatography (silica or Bio-Rad SX-8 gels) were not satisfactory. GPC analysis still indicated the presence in the samples of low molecular weight compounds absorbing UV light (pyrene derivatives). We therefore used a set of analytical μ-Styragel columns (10^4, 10^3, 500 Å; toluene 1.5 mL/min) for isolation of high-purity polymer. Polymer solutions (5 g/L, 0.75-mL portions) were injected and polymer-containing fractions were collected. Thereafter, solvent was removed;

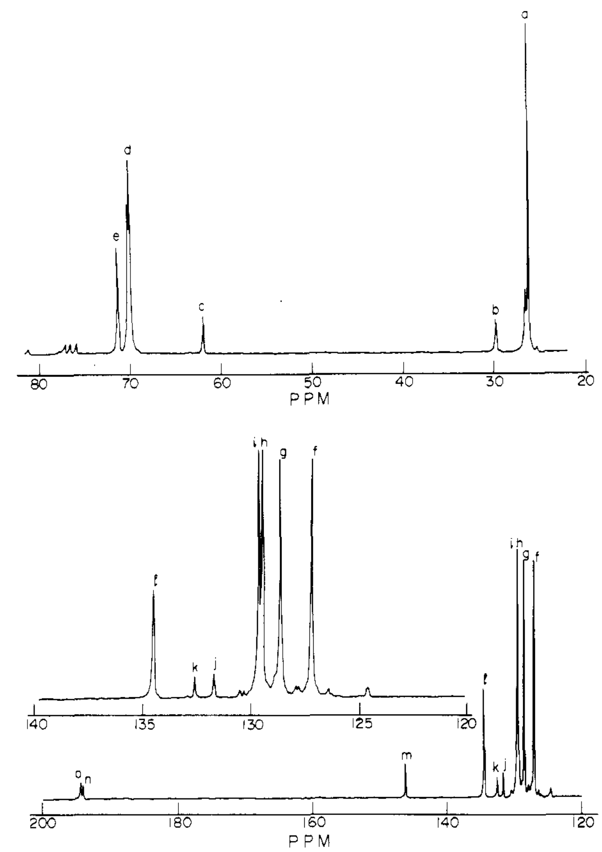


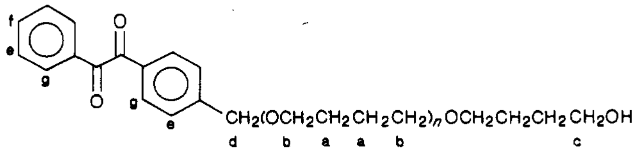
Figure 1. ^{13}C NMR spectrum of benzil-oligoTHF-OH, M_n = 404. Solvent $CDCl_3$.

polymers were freeze-dried from benzene and finally dried for 48 h on the vacuum lines. From Bz-polyTHF-OH, M_n = 5700 (0.16 g) and M_n = 10 700 (0.18 g), 0.09 and 0.10 g, respectively of the corresponding pure Bz-polyTHF-Py samples were obtained.

Polymers were characterized by UV, NMR, and GPC; model compounds (4-(ethoxymethyl)benzil and benzil-polyTHF-OH oligomer) were characterized by ^1H NMR and UV. ^1H NMR spectra in $CDCl_3$ were recorded by using Varian T60 and XL 20 spectrometers. UV spectra were recorded in CH_2Cl_2 by using a Hewlett-Packard 8451A diode array spectrometer. The equipment used for GPC analysis consisted of a Waters chromatograph 600A pump, μ-Styragel columns (10^4, 10^3, 500 Å), Waters R401 differential refractometer, and Hitachi 100-40 UV-vis spectrometer detectors. Toluene was used as an eluent at 1.5 mL/min flow rate; 90 μL of solutions with polymer concentrations of 5 g/L was injected for each analysis.

Results

NMR. The ^1H NMR of Bz-oligoTHF-OH in $CDCl_3$ gave signals of aromatic protons (δ_e 7.40–7.55, δ_f 7.6–7.7, δ_g 7.8–7.9; integration e:f:g = 4:1:4), the methylene group linking benzil and the polymer chain (δ_d 4.58 (s)) and the polyTHF chain (δ_a 1.60–1.70, δ_b 3.30–3.50). Signals of the methylene protons adjacent to the terminal OH groups can be seen separately at δ_c 3.63 (t). Integration gave M_n = 425, corresponding to DP = 2.8. The value of M_n determined from UV spectroscopy is 408.



In the spectrum of Bz-polyTHF-OH with M_n = 3700, the signals of the Bz end group are clear but relatively much weaker compared to those of the chain protons. Discrete signals for the CH_2OH group are too weak and too close to the main chain signals to be detected.

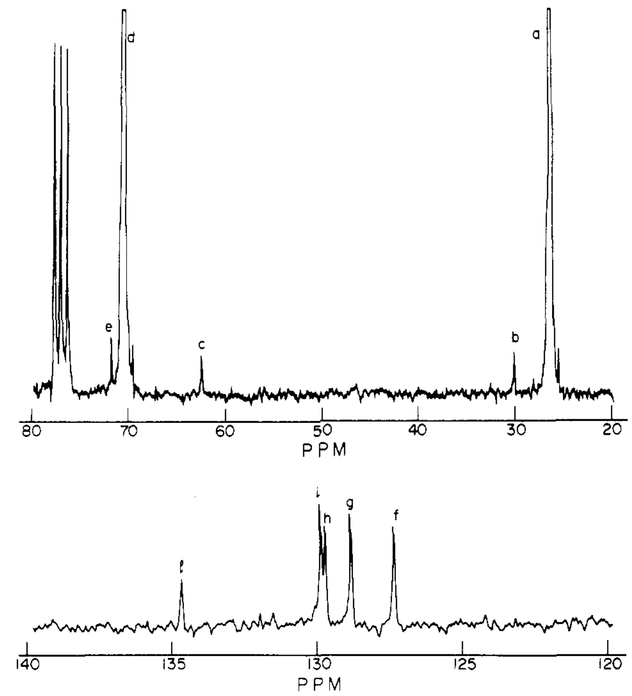
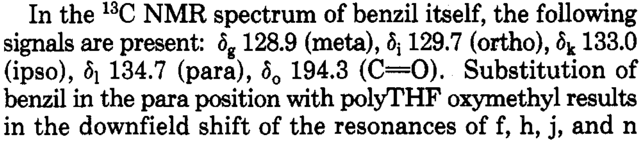


Figure 2. ^{13}C NMR spectrum of benzil-polyTHF-OH, M_n = 3700. Solvent $CDCl_3$.

Table I
^{13}C NMR T_1 Relaxation Times for Benzil-PolyTHF-OH in $CDCl_3$ at 20 °C

type of carbon	M_n = 404, T_1 (s)	M_n = 3700, T_1 (s)
benzil ortho C	0.921 ± 0.010	1.101 ± 0.202
methylene C (a)	0.698 ± 0.013	0.817 ± 0.003
methylene C (d)	0.767 ± 0.005	0.927 ± 0.003

^{13}C NMR spectra of benzil-polyTHF-OH with M_n = 404 and 3700 are given in Figures 1 and 2. Signals were assigned as follows:



δ_a 26.2–27.0, δ_b 29.9, δ_c 62.3, δ_d 70.2–70.5, δ_e 71.7, δ_f 127.3, δ_g 128.8, δ_h 129.6, δ_i 129.8, δ_j 131.8, δ_k 132.7, δ_l 134.6, δ_m 146.3, δ_n 194.0, δ_o 194.4. Assignments were made on the basis of the comparison of this spectrum with the reference spectra of benzil[20a] and 1-butanol.[20b]

In the ^{13}C NMR spectrum of benzil itself, the following signals are present: δ_g 128.9 (meta), δ_i 129.7 (ortho), δ_k 133.0 (ipso), δ_l 134.7 (para), δ_o 194.3 (C=O). Substitution of benzil in the para position with polyTHF oxymethyl results in the downfield shift of the resonances of f, h, j, and n carbons. Splitting of the main-chain methylene signals derives from the differences in the particular chain lengths of the oligomer components.

In the spectrum of Bz-polyTHF-OH with M_n = 3700 (Figure 2), the weakest signals of the quarternary carbon atoms are not registered but the signals due to the b and c carbons adjacent to the terminal OH can be clearly seen.

T_1 relaxation times were measured at 20 °C for the ortho carbons of the benzil end groups and for the carbons of the main polymer chain. The results given in Table I indicate that in the polymer with M_n = 3700 there is substantially less motion than in the oligomer with the short chain.

Table II
Reaction Conditions and Molecular Weights of End-Labeled PolyTHF Polymers

$10^3[\mathrm{In}]$[a]	$10^3[\mathrm{Ag}]$[b]	time (%)[c]	$\bar{M}_n$ UV	$\bar{M}_n$ GPC	$\bar{M}_w/\bar{M}_n$
		Benzil-PolyTHF-OH			
40	52	1.6 (12)	3670	3200	1.22
20	23	3 (7)		5700	1.11
9.7	13	5 (3.5)	11200	10700	1.09
4.9	8.0	10 (4)	20000	20300	1.13
6.3	7.7	11 (2.6)	23100	22300	1.12
3.1	4.3	15 (1.5)		25600	1.12
4.1	5.9	16 (3.7)	30000	26000	1.12
2.5	3.2	18 (2.6)	40400	32000	1.10
		Pyrene-PolyTHF-OH			
12	14	8 (5.3)	19300	17200	1.06
4.8	5.9	15 (4.5)	20100	24500	1.12
		Pyrene-PolyTHF-Benzil (from Benzil-PolyTHF-OH)			
	from $\bar{M}_n$ = 5700		6670	6800	1.08
	from $\bar{M}_n$ = 10700		10700	11300	1.15

[a] Concentration of 4-(bromomethyl)benzil or 4-(1-pyrene)butyroyl chloride, *M*. [b] Concentration of silver triflate. [c] Reaction time in hours (% conversion). All polymerizations in nitromethane with $[\mathrm{THF}]_0$ = 7.8 M. Initiation at 45 °C for 5 min, followed by polymerization at −5 °C.

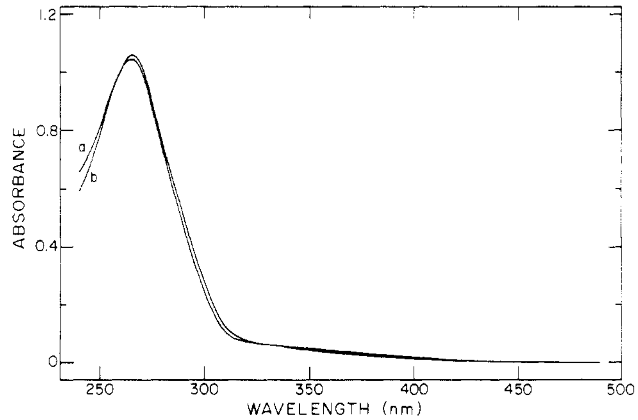


Figure 3. (a) UV spectrum of benzil-polyTHF-OH in CH_2Cl_2, concentration = 0.65 g/L; (b) fit of the simulated spectrum of 4-(ethoxymethyl)benzil, concentration = 5.82×10^{-5} mol/L. M_n of benzil-polyTHF-OH from end group analysis is 11 200.

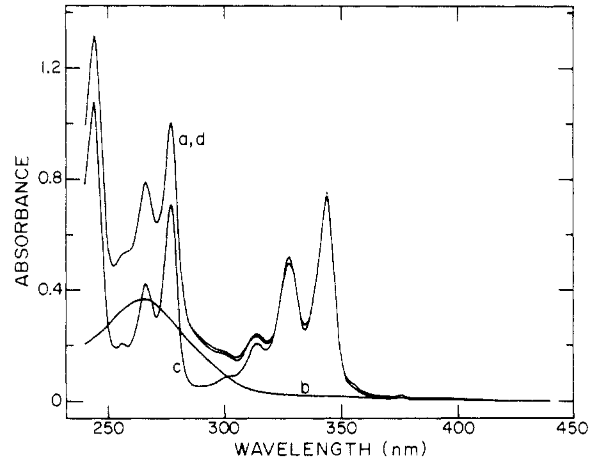


Figure 4. (a) UV spectrum of benzil-polyTHF-pyrene in CH_2Cl_2, concentration = 0.134 g/L; (b) calculated contribution of benzil end groups [4-(ethoxymethyl)benzil] = 2.01×10^{-5} mol/L; (c) calculated contribution of pyrene end groups, [1-pyrenebutyric acid methyl ester] = 1.70×10^{-5} mol/L. Sum of spectra (b) + (c) = (d).

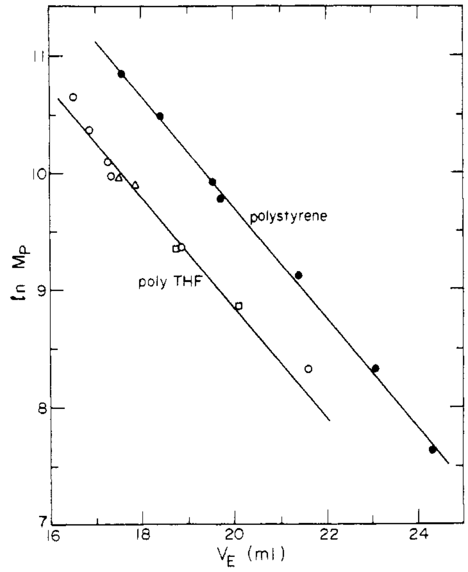


Figure 5. Dependence of ln M_p on V_E for (●) polystyrene, (○) Bz-polyTHF-OH, (□) Py-polyTHF-OH, (△) Bz-polyTHF-Py.

Characterization by UV. 4-(Ethoxymethyl)benzil and the methyl ester of 4-(1-pyrene)butyric acid were used as models of the end groups of functionalized polyTHF. With the aid of the computer of the diode array spectrometer, we could obtain their extinction coefficients at all wavelengths. Spectra of benzil-polyTHF-OH and benzil-polyTHF-pyrene, together with the simulated spectra of the corresponding model compounds, are presented in Figures 3 and 4. Simulated spectra were calculated using appropriate extinction coefficients and concentrations of model compounds leading to the best fit (least-squares method) of the simulated and actual polymer spectra. Concentrations of the polymer end groups were assumed to be equal to the concentrations of model compounds yielding the best fit. The number-average molecular weight (M_n) of polymer samples was determined. The results are given in Table II. UV analysis revealed that in benzil-polyTHF-pyrene polymers the ratio of benzil: pyrene end groups was 1:0.85.

Characterization of PolyTHF by GPC. Chromatograms of polyTHF were related to chromatograms of polystyrene standards (Pressure Chemical Co.) with low polydispersity (M_w/M_n = 1.06). The following calibration dependence was obtained (cf. Figure 5):

$$\ln M_p(\mathrm{PS}) = 19.12 - 0.470V_E \qquad (2)$$

where M_p(PS) is the molecular weight at peak maximum

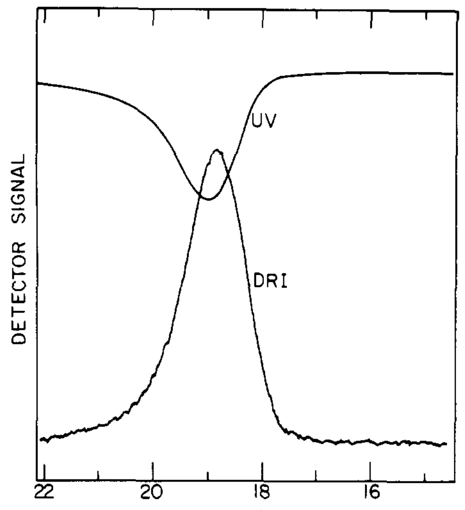


Figure 6. GPC trace for Bz-polyTHF-OH, $M_n = 10\,700$; $M_w/M_n = 1.09$. Detectors: UV absorption at 310 nm; DRI, differential refractive index.

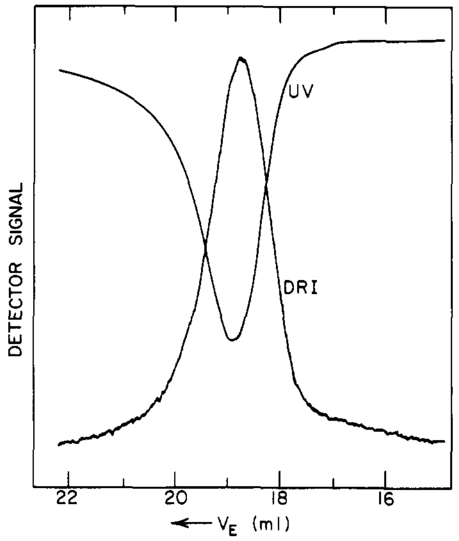


Figure 7. GPC trace for Bz-polyTHF-Py prepared by transformation of the polymer sample shown in Figure 6. Here $M_n = 11\,300$, $M_w/M_n = 1.15$. UV absorption at 345 nm.

and V_E is the elution volume in milliliters. Chromatograms of polystyrene standards indicated slight broadening for elution volumes larger than 17 mL, and this instrumental spreading was taken into account in analysis of polyTHF samples (cf. Table II).[21]

The shapes of polyTHF chromatograms registered by the differential refractometer detector were close to Gaussian (cf. Figure 6). It is worth noting the difference between shapes of chromatograms registered by the differential refractometer and UV detectors. Signals detected by the differential refractometer are proportional to the product of the number of macromolecules and their degree of polymerization (i.e., to the total number of mers in the eluted macromolecules). Signals recorded by the UV detector are due to the absorption of benzil and/or pyrene end groups and, therefore, depend only on the number of macromolecules. This leads to apparent tailing in the UV trace of the chromatograms.

We treated our data in a manner similar to that of Croucher and Wetton.[11] We assumed that the ratio of molecular weights of polyTHF and polystyrene corresponding to the same elution volume is constant:

$$M(\text{polyTHF})/M(\text{PS}) = \alpha \qquad (3)$$

Hence, the polystyrene calibration could be used for determination of $M_w(\text{polyTHF})/M_n(\text{polyTHF})$ using the formula

$$\frac{\bar{M}_w(\text{polyTHF})}{\bar{M}_n(\text{polyTHF})} = \frac{\left[\int F(v)M(\text{polyTHF})\,dv\right]\left[\int F(v)/M(\text{polyTHF})\,dv\right]}{\left[\int F(v)\,dv\right]^2} = \frac{\left[\int F(v)M(\text{PS})\,dv\right]\left[\int F(v)/M(\text{PS})\,dv\right]}{\left[\int F(v)\,dv\right]^2} \qquad (4)$$

where $F(v)$ is the response of the differential refractometer in the polyTHF chromatogram. Values of $M_w(\text{polyTHF})/M_n(\text{polyTHF})$ which were found directly by using eq 4 and corrected for instrumental spreading are given in Table II.

The calibration dependence for polyTHF was found by using values of $M_n(\text{polyTHF})$ determined by UV end group analysis and values of $M_w(\text{polyTHF})/M_n(\text{polyTHF})$ obtained by GPC with polystyrene calibration. Assuming Gaussian peak shapes of the polyTHF chromatograms, molecular weights at peak maxima were calculated:

$$M_p(\text{polyTHF}) = M_n(\text{polyTHF})[M_w(\text{polyTHF})/M_n(\text{polyTHF})]^{1/2} \qquad (5)$$

A plot of ln $M_p(\text{polyTHF})$ versus V_E is shown in Figure 5. The straight line describing this dependence corresponds to a conversion factor of $\alpha = 0.426$. This leads to the calibration dependence for polyTHF

$$\ln M_p(\text{polyTHF}) = 18.26 - 0.470V_E \qquad (6)$$

used for the determination of $\bar{M}_w$ and $\bar{M}_n$ of polyTHF samples:

$$\bar{M}_w = \int F(v)M(\text{polyTHF})\,dv \Big/ \int F(v)\,dv \qquad (7)$$

$$\bar{M}_n = \int F(v)\,dv \Big/ \int F(v)/M(\text{polyTHF})\,dv \qquad (8)$$

The results are given in Table II.

Discussion

The synthesis of low-polydispersity polyTHF functionalized with benzil and pyrene chromophores was designed on the basis of previous extensive studies of the mechanism and kinetics of THF polymerization. Penczek et al.[12] have recently summarized these studies. The silver salt method was used for initiation because in this way the prior synthesis and isolation of the relatively unstable arylmethylium and acylium cations (e.g., benzil—CH_2^+ and pyrene$(CH_2)_3C{\equiv}O^+$) were avoided. The choice of counterion for the polymerization was dictated by the superior stability of AgO_3SCF_3 in comparison with other silver salts, e.g., $AgSbF_6$, $AgPF_6$, and $AgClO_4$. According to literature data,[14] $AgClO_4$ in THF may even pose a significant explosion hazard.

Previous studies of the THF polymerization revealed that both ionic and covalent species participate in the propagation:[18–20]

(9)

The reactivities of free ions and ion pairs toward monomer (k_p^i) were found to be equal and much higher than the reactivity of covalent active centers (k_p^c).[22,23] The differences in the reactivities of these two types of species could cause broadening of the molecular weight distribution. It was found, however, that in nitromethane the equilibrium between ionic and covalent active centers is shifted to the ion pair side[24] and that the participation of covalent active species can be neglected.[22] These results suggested the use of CH_3NO_2 as a cosolvent for polyTHF synthesis with $CF_3SO_3^-$ as counterion.

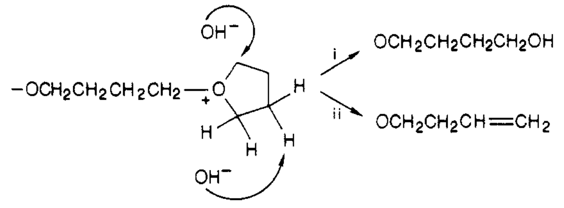
Low-polydispersity polymer samples can be obtained in the living process when initiation does not interfere with propagation, when the concentration of active centers is constant, and when side reactions (in THF polymerization depropagation and transetherification) can be excluded. By carrying out the polymerization at low temperature and to low conversion, the problems of transetherification and depropagation can be eliminated. At low temperatures, however, initiation is comparable to or slower than propagation, and we obtained samples with poor polydispersity ($\bar{M}_w/\bar{M}_n = 1.3$).

Data published by Penczek and co-workers[22-24] on equilibrium concentrations of monomer as a function of temperature and CH_3NO_2 concentration allowed us to estimate the ceiling temperature under our reaction conditions ($[THF]_0 = 7.8$ M in CH_3NO_2). Above this temperature, 43 °C, simultaneous initiation and propagation should not occur. We tested this prediction by quenching one sample under conditions where $[THF]_0$ was less than the equilibrium value and obtained the sample Bz-oligoTHF-OH of $\overline{DP} = 2.8$. These results suggested that initiation above the ceiling temperature followed by polymerization at low temperature would lead to a polymer of narrow molecular weight distribution. By initiating polymerization at 45 °C and carrying out polymerization at low temperature (−5 °C) and to low conversion (10%), we obtained polymers with acceptable molecular weight distributions ($M_w/M_n \geq 1.1$). (See Table II.)

All evidence indicates the presence of one chromophore per chain, both in benzil-initiated polymerization to yield Bz-polyTHF-OH and pyrene-initiated polymerization to yield Py-polyTHF-OH. These same measurements suggest, however, that treatment of Bz-polyTHF-OH with $Py(CH_2)_3COCl$ leads to Bz-polyTHF-Py containing less than one pyrene per chain. By UV analysis, we calculate that 85% of the chains contain a pyrene group.

Additional qualitative information is available from phosphorescence decay measurements in carbon tetrachloride solutions, where the fluorescence from Py is quenched. Here we observe in Bz-polyTHF-Py a weak emission with the same lifetime as that of Bz-polyTHF-OH. This result implies that the Bz-polyTHF-Py sample contains some chains containing the Bz group at one end but no Py group at the other.

Fluorescence measurements in toluene indicate that intramolecular quenching of pyrene fluorescence by benzil is very effective and that the rate of quenching decreases with increasing chain length. Some preliminary experiments have already been published.[9] Detailed studies on these molecules will be the subject of future work. Here our interest is in using these data for characterization of the polymer end groups. Careful examination of the fluorescence decay curves of the Bz-polyTHF-Py samples gives no indication of the presence of chains containing a Py but lacking a Bz group. This technique is quite sensitive and in principle is capable of detecting 0.5% or less polymer containing Py at one end with no quencher in the molecule. Hence, we have confirmation of the UV analysis that our chromophoric initiators provide polymers containing one luminescent dye group on one end of each and every polymer chain.



One last aspect of the synthesis needs to be explained: our inability to attach ester groups quantitatively to the opposite end of Bz-polyTHF-OH. Previous experience in our laboratory suggests that this reaction should be nearly quantitative.[1-4] As a consequence, we believe that the chains which do not contain Py groups after esterification may not possess terminal CH_2OH functionality. A plausible explanation is that elimination (path ii above) competes with substitution (path i) in the termination step, leading to a small amount of terminal olefin formation.

Summary

Halogen derivatives of benzil and pyrene have been used to initiate THF polymerization by treating these molecules with silver triflate in the presence of THF and nitromethane. Polymer samples of very narrow molecular weight distribution could be obtained if initiation was carried out at 45 °C, above the ceiling temperature for the polymer, followed by polymerization to low conversion at lower temperature (−5 °C). Quenching by aqueous hydroxide produced polymers of the form Bz-polyTHF-OH and Py-polyTHF-OH containing exactly one chromophore per chain. We have some indication that the termination step is not quantitative and that only 85% of the polymers also contain the CH_2OH group on the other chain end.

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Registry No. Bz-polyTHF-OH, 117021-80-4; Py-polyTHF-OH, 99559-99-6; Bz-polyTHF-Py, 117021-81-5; 4-(ethoxymethyl)benzil, 117021-82-6; sodium ethoxide, 141-52-6; 4-(bromomethyl)benzil, 18189-19-0; methyl 4-(1-pyrenyl)butyrate, 70570-29-5.

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Synthesis, Characterization, and Deblocking of Poly(4-*tert*-butoxystyrene) and Poly(4-*tert*-butoxy-α-methylstyrene)

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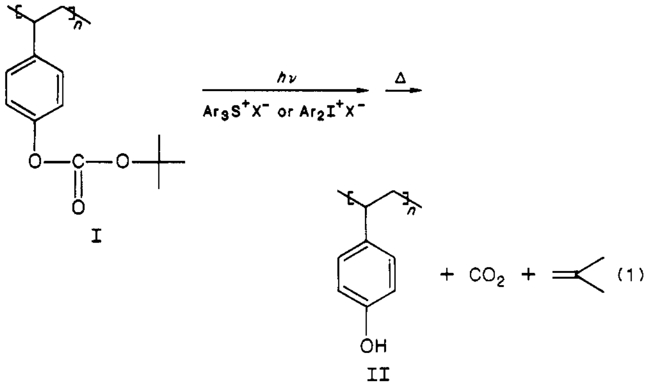
ABSTRACT: The monomers 4-*tert*-butoxystyrene and 4-*tert*-butoxy-α-methylstyrene were prepared by reaction of the corresponding 4-styryl and 4-α-methylstyryl Grignard reagents with *tert*-butyl peroxybenzoate. While 4-*tert*-butoxystyrene was polymerized by both free radical and ionic methods, the corresponding 4-*tert*-butoxy-α-methylstyrene could be polymerized only by cationic techniques. Model reactions employing 4-*tert*-butoxytoluene and various photosensitive diaryliodonium salts showed that deblocking the phenolic group takes place readily and requires a short thermolysis after irradiation. Poly(4-*tert*-butoxystyrene) and poly(4-*tert*-butoxy-α-methylstyrene) were successfully deblocked by using various acids to yield the corresponding poly(4-hydroxystyrene) and poly(4-hydroxy-α-methylstyrene).

Introduction

The growing applications of polymers in the field of microelectronics represents one of the newest, most exciting, and challenging areas of research in polymer synthesis today. Currently, a particularly active field lies in the area of the design and synthesis of imageable polymeric materials which can serve as photoresists. The chief requirement of a photoresist is that on exposure to light or radiation, the irradiated portions of the photoresist undergo some chemical transformation which allows them to be distinguished, usually on the basis of solubility, from the nonirradiated portions of the photoresist. If the solubility in a given solvent of the irradiated areas is enhanced relative to the nonirradiated ones, the photoresist is said to have positive tone. Conversely, a negative tone results from decreased solubility of the photoresist on irradiation.

In this laboratory in recent years, we have been exploring a number of applications of photosensitive onium salts including those involving imaging.[1] The discovery that certain onium salts such as diaryliodonium and triarylsulfonium salts produce strong Brønsted acids on photolysis presented a unique opportunity to design novel imaging systems which rely on various acid-catalyzed processes for their action. One such approach to the design of a new photoresist has been described recently by Willson and his co-workers[2-5] and is shown in eq 1. Poly(4-(*tert*-butoxycarbonyloxy)styrene) (I) is insoluble in aqueous base; however, when it is irradiated in the presence of a photosensitive onium salt, the acid which is produced catalytically removes the (*tert*-butoxycarbonyl)oxy groups yielding poly(4-vinylphenol) (II), carbon dioxide, and isobutylene. Discrimination between the irradiated and nonirradiated portions of the resist to produce fine patterns in a positive tone can now be made since poly(4-hydroxystyrene) is very soluble in dilute aqueous base. Negative tone images can be made by using chlorinated solvents in which poly(4-(*tert*-butoxycarbonyloxy)styrene) is preferentially removed by dissolution. Similarly, the corresponding poly(4-(*tert*-butoxycarbonyloxy)-α-methylstyrene) could also be employed as a photoresist. Since the deblocking reaction shown in eq 1 is catalytic, a kind of photomultiplication effect is observed in which the overall quantum yield for deblocking is very large and of the order of magnitude of 1000. This photomultiplication effect has been termed "chemical amplification". Consequently, such resists have an inherently high photosensitivity.



It occurred to us that it should be possible to design other photoresist systems based on analogous chemistry. Along with good sensitivity to UV irradiation and excellent

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