Macromolecules

Volume 38, Number 14 July 12, 2005

Communications to the Editor

Polymerization of Cyclic Acetals by a Free Radical Initiator, Perfluorodibenzoyl Peroxide, in the Presence of Oxygen

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Received March 17, 2005
Revised Manuscript Received May 20, 2005

Introduction. Ring-opening polymerization of cyclic acetals has been intensively investigated using cationic initiators such as strong protonic acids, Lewis acids, and organic salts (carbenium, oxonium, or carboxonium).[1] However, the polymerization does not proceed using a free radical initiator or an anionic initiator.[1] We have discovered that 1,3-dioxolane, 1,3-dioxepane, and 1,3,5-trioxane were polymerized slowly but smoothly by a free radical initiator, perfluorodibenzoyl peroxide (FBPO), in the presence of oxygen.

Results and Discussion. Figure 1 shows the kinetics of the bulk polymerization of 1,3-dioxolane (17.0 mmol) initiated by FBPO (0.048 mmol) at 60 °C. The amounts of oxygen present in the polymerization were 0.18, 0.03, trace, and 0 mmol, respectively.[2] The polymerization follows first-order kinetics. The polymerization rate depends on the amount of oxygen present. Polymerization did not proceed without oxygen, and more oxygen enhanced the polymerization rate. Induction periods were observed with the polymerizations. However, the cause is not clear at present.

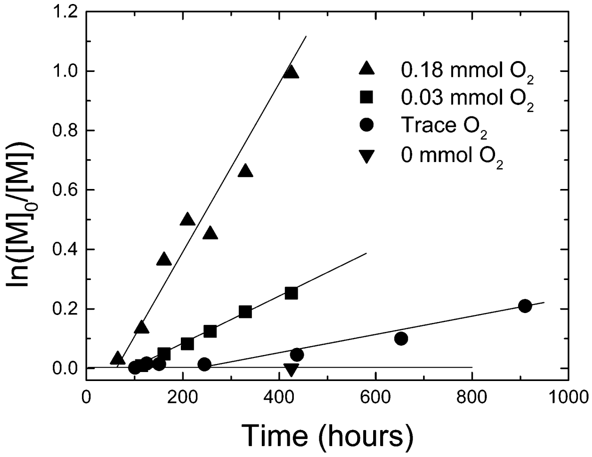

Figure 1. Bulk polymerization kinetics of 1,3-dioxolane in the presence of different amounts of oxygen. Polymerization conditions: 1,3-dioxolane (17.0 mmol), perfluorodibenzoyl peroxide (0.048 mmol), 60 °C.

The 1,3-dioxolane conversion dependence of the number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers obtained is illustrated in Figure 2.[3] The molecular weight increases linearly with monomer conversion. However, increasing amount of oxygen decreases the molecular weight. The polydispersity remains nearly constant over a wide range of conversions. These are characteristic of living polymerizations.

^1H and ^{13}C NMR spectra of the polymerization reaction mixtures are presented in Figure S1 of the Supporting Information.[4] Both spectra indicated that the polymer obtained is composed of $-CH_2OCH_2CH_2O-$ repeating units formed by ring-opening of 1,3-dioxolane.[5] The signals in the spectra correspond to the monomer and polymer, indicating that no detectable side reactions occur. The unreacted monomer can be recovered by simple distillation and used for a new polymerization.

To investigate the end groups of the polymer obtained, an oligomer was prepared [1,3-dioxolane (6.4 mmol), FBPO (0.8 mmol), and O_2 (0.18 mmol) at 80 °C for 4 days]. ^1H, ^{19}F, and ^{13}C NMR spectra of the isolated oligomer are presented in Figure S2 of the Supporting Information.[4] The spectra clearly show that the oligomer with 7.0 repeating units on average (calculated from the integrals of proton signals of $HCOO-$, $-OCH_2O-$, and

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10.1021/ma050568y CCC: $30.25 © 2005 American Chemical Society
Published on Web 06/10/2005

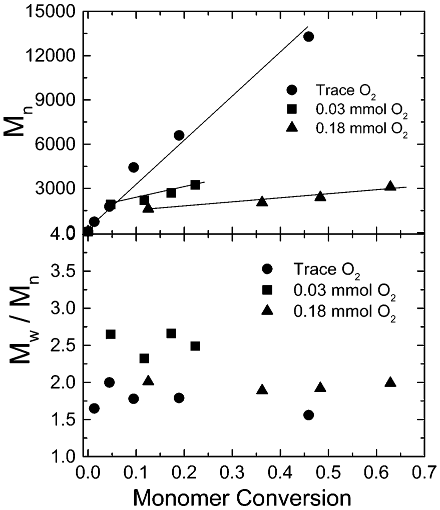


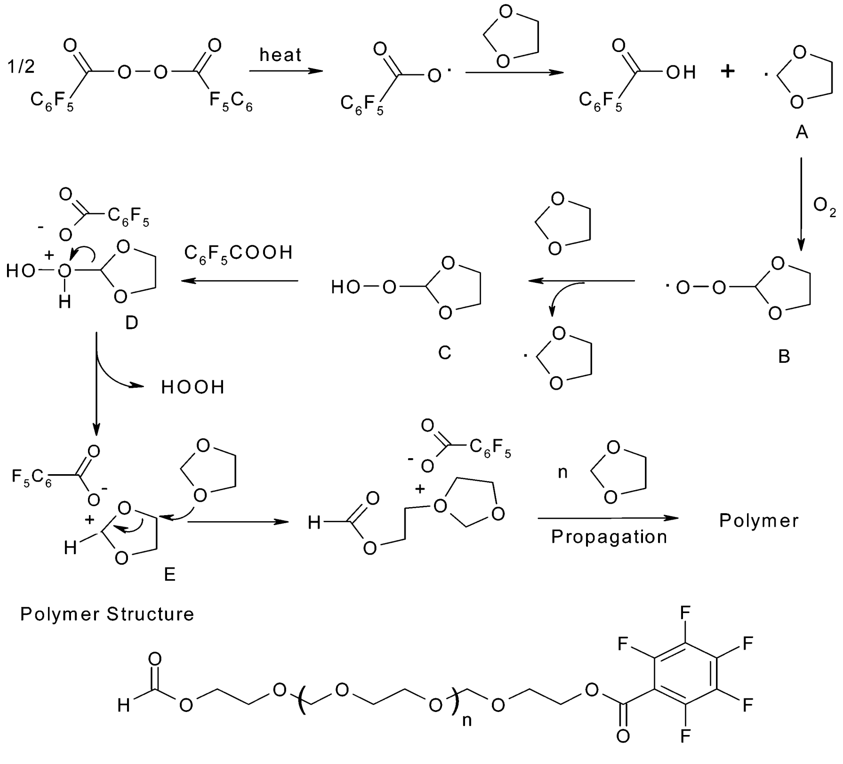
Figure 2. Evolution of the number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers with conversion of 1,3-dioxolane. Polymerization conditions: see Figure 1.

$-OCH_2CH_2O-$ groups) has a linear structure and $HCOO-$ and C_6F_5COO- groups are end-caps. The crystalline polymer (M_n = 3671 and polydispersity of 2.1) with a melting point of 46 °C (55 °C in the literature[6]) has a high decomposition temperature (onset 376 °C), which confirms the end-capping of the polymer obtained.

According to these experimental data, a plausible polymerization mechanism of 1,3-dioxolane is proposed as described in Scheme 1. The perfluorobenzoyl radical abstracts one hydrogen atom at the 2-position of 1,3-dioxolane and yields the 1,3-dioxolane radical (**A**). Radical **A** combines with oxygen and then abstracts the hydrogen atom from another 1,3-dioxolane, producing 1,3-dioxolane 2-hydroperoxide (**C**). Alkyl hydroperoxides with strongly electron-releasing alkyl groups readily undergo alkyl−oxygen heterolysis under acidic conditions.[7] Thus, 1,3-dioxolane 2-hydroperoxide (**C**) easily releases hydrogen peroxide to give the oxonium ion (**E**) with the help of a strong acid, perfluorobenzoic acid. An intermediate similar to **E** was previously reported by Slomkowski and Penczek et al.[8] They prepared 1,3-dioxolane 2-ylium SbF_6^- salt via hydride transfer from the 2-position of 1,3-dioxolane using triphenylmethylium SbF_6^- salt. Compared to SbF_6^- as the counterion, $C_6F_5COO^-$ is more nucleophilic and interacts more strongly with the oxonium ion. Thus, the polymerization rate of 1,3-dioxolane initiated by FBPO is much slower than that by triphenylmethylium SbF_6^- salt. To further support the proposed mechanism, we have investigated the polymerization of 1,3-dioxolane using perfluorobenzoic acid and *tert*-butyl peroxide. The polymerization proceeds neither using perfluorobenzoic acid in the presence of oxygen nor using *tert*-butyl peroxide in the presence of oxygen. However, the polymerization did occur smoothly by using the combination of the acid and peroxide in the presence of oxygen. For example, a mixture of 1,3-dioxolane (8.56 mmol), *tert*-butyl peroxide (0.17 mmol), and perfluorobenzoic acid (0.34 mmol) was heated in the presence of oxygen (0.17 mmol) at 80 °C for 4 days, and polymer (M_n = 2600, M_w/M_n = 1.9) was obtained in 72% yield. These results clearly demonstrated the function of acid and radical initiator during the formation of **E**. Instead of FBPO, we attempted to utilize dibenzoyl peroxide to polymerize 1,3-dioxolane in the presence of oxygen. No polymerization was observed probably because the benzoic acid is not acidic enough to enable the transformation of **C** to **E**, or $C_6H_5COO^-$ is so nucleophilic that a covalent species, instead of the dioxolenium ion (**E**), is formed and propagation could not continue.

We also investigated the effects of the molar ratio of FBPO to oxygen and the temperature on the conversion

Scheme 1. Plausible Ring-Opening Polymerization Mechanism of 1,3-Dioxolane Promoted by Perfluorodibenzoyl Peroxide and Oxygen



of 1,3-dioxolane and M_n (Figures S3 and S4 in the Supporting Information). A dramatic increase followed by a sluggish rise in conversion occurs as the ratio of FBPO to O_2 increases. At the same time, a maximum M_n was observed with the ratio around 1.7, and leveling-off appeared at the ratio higher than 2.5. Thus, high molecular weight and high conversion can be obtained when molar ratio of perfluorodibenzoyl peroxide to O_2 is around 1.7. Moreover, a temperature window for a high M_n and a high conversion is between 60 and 80 °C.

We have found that 1,3,5-trioxane and 1,3-dioxepane were also polymerized in the presence of FBPO and oxygen. Heating a mixture of 1,3,5-trioxane (11.1 mmol) and perfluorodibenzoyl peroxide (0.075 mmol) in the presence of oxygen (0.075 mmol) at 80 °C for 76 h produced a crystalline polymer (mp 176 °C, decomposition temperature under nitrogen is 210 °C) in 54% yield. When a mixture of 1,3-dioxepane (12.9 mmol) and FBPO (0.056 mmol) in the presence of oxygen (0.039 mmol) was heated at 80 °C for 196 h, a polymer [9] ($M_n = 4017$, $M_w/M_n = 2.2$) was obtained in 64% yield.

In summary, we have demonstrated that cyclic acetals (such as 1,3-dioxolane, 1,3-dioxepane, and 1,3,5-trioxane) polymerize with a free-radical initiator, FBPO, in the presence of oxygen. The propagation step is a living cationic ring-opening, and polymer obtained was end-capped with formate and perfluorobenzoate groups. Thus, the polymer obtained was thermally stable without an additional reaction for the end-capping.

Supporting Information Available: ^1H, ^{13}C, and ^{19}F NMR spectra of polymer and oligomer and figures for the effects of the molar ratio of FBPO to oxygen and the temperature on the number-average molecular weight and conversion. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Penczek, S.; Kubisa, P. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press Ltd.: London, 1989; Vol. 3, pp 787−812.

(2) A typical procedure for polymerization: A glass tube with diameter of 0.6 cm was charged with 1,3-dioxolane and perfluorodibenzoyl peroxide. The glass tube was shortened, and a desired free space was reserved. In the case of a trace amount of O_2, the free space was filled with argon gas by purging argon gas at room temperature for 5 min (because of incomplete removal of oxygen), air (3.2 mL, approximate content of O_2 in air is 21% in v/v) in the case of 0.03 mmol of O_2, and pure oxygen gas (4.0 mL) in the case of 0.18 mmol of O_2. Then, the tube was sealed. The amount of oxygen was calculated on basis on the volume of free space. In the case of oxygen-free condition, the tube was sealed after three freeze−pump−thaw cycles. Polymerization was carried out at specific temperatures.

(3) GPC analysis was carried out using a Waters Eupower Software with a Waters 510 pump and a Waters 2414 refractive index detector under the following conditions: Polymer Laboratory PLgel 10000A and PLgel 5000A as columns and THF eluent at a flow rate of 1.0 mL/min at 25 °C. The calibration was performed using polystyrene standards.

(4) NMR data for polymer (in $CDCl_3$): ^1H: δ 4.75 (s, $-OCH_2O-$), 3.72 (s, $-CH_2CH_2-$). ^{13}C: δ 95.57 (s, $-OCH_2O-$), 66.88 (s, $-CH_2CH_2-$). NMR data for monomer (in $CDCl_3$): ^1H: δ 4.90 (s, $-OCH_2O-$), 3.87 (s, $-CH_2CH_2-$). ^{13}C: δ 95.09 (s, $-OCH_2O-$), 64.56 (s, $-CH_2CH_2-$). NMR data for oligomer (in $CDCl_3$): ^1H: δ 8.10 (s, $HCOO-$), 4.76 (s, $-OCH_2O-$), 4.56 (t), 4.34 (t), 3.88 (t), 3.80 (t), and 3.73 (s) attributable to $-CH_2CH_2-$. ^{19}F NMR: 138.6, 149.0, 160.9 (C_6F_5-). ^{13}C: δ 96.40−95.40 ($-OCH_2O-$), 71.00−61.00 ($-CH_2CH_2-$), 148.00−134.00 (C_6F_5-), 160.89 ($HCOO-$), 158.95 ($C{=}O$ attached to C_6F_5-).

(5) Fleischer, D.; Schulz, R. C. *Makromol. Chem.* **1975**, *176*, 677−689.

(6) Sasaki, S.; Takahashi, Y.; Tadakoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 2363−2378.

(7) Davies, A. C. *Organic Peroxides*; Butterworth: London, 1961; pp 35−36.

(8) (a) Slomkowski, S.; Penczek, S. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1718−1720. (b) Slomkowski, S.; Penczek, S. *Chem. Commun.* **1974**, 1347−1749. (c) Slomkowski, S.; Kubisa, P.; Penczek, S. *J. Macromol. Sci., Chem.* **1977**, *A11*, 2047−2064. (d) Jedlinski, Z.; Gibas, M. *Macromolecules* **1980**, *13*, 1700−1703.

(9) ^1H NMR data for polymer (in $CDCl_3$): δ 4.66 (s, 2H, $-OCH_2O-$), 3.52 (s, 4H, $-OCH_2-$), 1.68 (s, 4H, $-CH_2CH_2-$ between two $-OCH_2-$). ^{13}C: δ 95.56 (s, $-OCH_2O-$), 67.84 (s, $-OCH_2-$), 26.89 (s, $-CH_2CH_2-$ between two $-OCH_2-$).

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