First Example of Free Radical Ring-Opening Polymerization with Some Characteristics of a Living Polymerization

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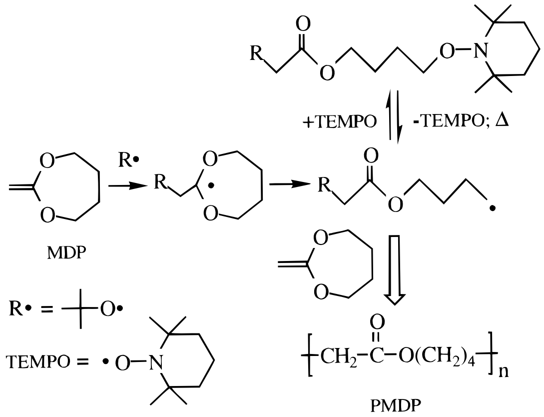
Free radical ring-opening polymerization has been the focus of great interest because functional groups such as esters, amides, and carbonates can be incorporated into the backbone of chain polymers and a low volume shrinkage from monomer to polymer can be achieved.[1−3] In fact, volume expansion has been demonstrated for several monomers in which double ring-opening occurs to yield an open-chain polymer structure.[2] The applications of such monomers have virtually revolutionized the dental materials industry. On the other hand, the living polymerization is probably the best nonbiological imitation of nature in terms of synthesizing polymers with narrow molecular weight distributions.[4] The anionic, cationic, and covalent processes for living polymerization have been well established.[5−7] The possibilities and limitations of "living" (or "controlled") free radical polymerization of vinyl monomers have been explored and debated in recent years.[8,9] Many systems have been identified which allow for the synthesis of elaborate polymer structures such as block copolymers and end-functionalized polymers,[10−12] but until recently few have produced the narrow molecular weight distributions indicative of a "living" radical process. The theoretical lower limit for the molecular weight distribution (or polydispersity as represented by the ratio of weight-average to number-average molecular weight, i.e., M_w/M_n) of a conventional free radical polymerization is 1.5.[9,13] The preparation of polymers with polydispersity less than 1.5 is often considered as one of the direct evidence of "living" conditions. Recently, there have been several pioneering works in achieving polydispersities lower than 1.5 via various approaches.[14−17] For example, styrene has been polymerized with a conventional free radical initiator such as benzoyl peroxide in the presence of a stable free radical (SFR) such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to yield polystyrene with a polydispersity of ≤1.3.[16] In this communication, we present the first "living" free radical ring-opening polymerization of a cyclic ketene acetal using the SFR method.[18] Thus, we demonstrate that 2-methylene-1,3-dioxepane (MDP) undergoes a free radical polymerization with quantitative ring-opening in the presence of TEMPO with di-*tert*-butyl peroxide (DTBP) as initiator to yield the polyester (PMDP) with polydispersities less than 1.5 (Scheme 1).

Scheme 1



$$\left[\mathrm{CH_2}-\overset{\overset{\displaystyle O}{\|}}{C}-\mathrm{O(CH_2)_4}\right]_n$$

A series of bulk polymerizations were conducted, following the similar literature procedures for the conventional free radical ring-opening polymerization,[3] at 125 °C in vacuum-sealed 5-mL ampules containing the monomer, initiator, and TEMPO at various concentrations for 48 h or other reaction times as summarized in Table 1. The [TEMPO]/[DTBP] molar ratio was varied from 0 to 1.80. The polymers were purified by repeated dissolution in chloroform and precipitation in an excess amount of *n*-hexane. Quantitative ring-opening to form the polymers with ester repeat units was evidenced by the complete disappearance of the acetal carbon signal at 70.4 ppm and the appearance of a carbonyl peak at 174 ppm in the ^{13}C NMR spectra of the polymers, the disappearance of the signal of vinyl protons at 3.57 ppm in the ^{1}H NMR, and the disappearance of the IR absorption at 1670 cm^{-1} for C=C stretching.[3]

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Table 1. Conditions and Results of Free Radical Ring-Opening Polymerization of 2-Methylene-1,3-dioxepane[a]

entry	[TEMPO][b]/ [DTBP]	reaction time (h)	yield (%)	$M_n \times 10^{-3}$	M_w/M_n
1	0	2[c]	87	11.4	6.5
2	0.80	48	71	8.3	4.9
3	1.00	48	69	15.3	4.5
4	1.20	48	61	9.5	2.9
5	1.40	48	54	8.5	1.5
6	1.60	48	44	7.9	1.3
7	1.80	96[d]	41	7.4	1.2

[a] All the polymerizations were performed at 125 °C with 10 mol % of the initiator (DTBP) based on the monomer. [b] Molar ratio of TEMPO to DTBP. [c] Long reaction time (e.g., 48 h) resulted in polymers with low solubility in THF. [d] Long reaction time was used to obtain a reasonable yield.

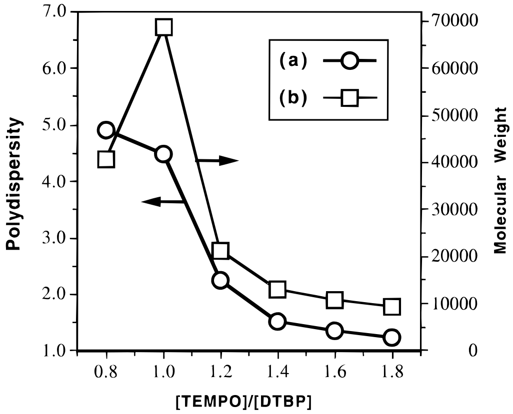

Figure 1. Effect of [TEMPO]/[DTBP] ratio on the (a) polydispersity (M_w/M_n) and (b) weight-average molecular weight (M_w) of the polymer obtained from the free radical ring-opening polymerization of 2-methylene-1,3-dioxepane.

The molecular weights (M_n and M_w) and polydispersity (M_w/M_n) for each of the polymer samples were determined from gel-permeation chromatograph (GPC) measurements using tetrahydrofuran as eluant with polystyrene calibration. As shown in Figure 1a, there is a clear trend of decreasing polydispersity with increasing [TEMPO]/[DTBP] ratio. At the [TEMPO]/[DTBP] ratios of 1.4, 1.6, and 1.8, the polydispersity of the polymers was found to be 1.5, 1.3, and 1.2, respectively, suggesting the attainment of certain "living" conditions. Although the detailed mechanism is still being investigated, these observations can be explained by a simplified scheme similar to that proposed for the living radical polymerization of vinyl monomers.[8,9,16] Thus, initiation is accomplished by homolysis of DTBP to *tert*-butoxy free radicals, which attack the ring monomers to afford propagating chain radicals. These chain radicals are then reversibly capped with the SFR, i.e., TEMPO, and an equilibrium between dormant (capped) and activated (uncapped) chain ends is reached (Scheme 1). The bond between the propagating radical and TEMPO is sufficiently labile at the high polymerization temperature (125 °C) to allow for the polymer growth mainly by the reaction of the activated chain ends with incoming monomers. At high concentrations of TEMPO, the stationary concentration of activated radicals remains low and the occurrence of chain transfer and termination reactions should be negligible, resulting in the "living" radical ring-opening polymerization. In contrast, the polymer prepared in the absence of TEMPO with 2 h polymerization time (Table 1, entry 1) showed a very large polydispersity (6.5), which is typical for a conventional nonliving free radical polymerization. When a longer reaction time (e.g., 48 h) was used without TEMPO, the polymer was found to have very low solubilities in common organic solvents such as chloroform, benzene, THF, and 1-methyl-2-pyrrolidinone, probably because of cross-linking. In comparison to the living radical polymerization of styrene in the presence of TEMPO,[8c,16,19] the polymerization of MDP should be slower as evidenced by relatively low yields obtained (Table 1, entries 5−7), because the uncapped primary alkyl radical is thermodynamically less stable than the uncapped polystyrene benzyl radical.

The achievement of "living" polymerization at high TEMPO concentrations is further evidenced by the observation that both M_n and M_w of the polymers initially increased as the [TEMPO]/[DTBP] ratio was increased, reached maxima at the ratio of 1.0, and then decreased as the ratio was increased. Such a trend is exemplified in Figure 1b. The initial increase can be attributed to the occurrence of conventional, nonliving chain propagation at the low TEMPO concentrations. That is, an insufficient amount of TEMPO is present in the systems to cap all of the propagating chain ends. Since uncapped chains propagate at a much faster rate than their capped counterparts, the majority of the monomer in these systems is likely consumed by the uncapped chains. Thus, the polymerization effectively becomes a conventional free radical polymerization with TEMPO serving only to decrease the initiator efficiency leading to an increase in molecular weight. Further, the probability of chain-transfer and termination reactions occurring in these systems is high, which would explain the initially broad polydispersity (Figure 1a). As the concentration of TEMPO is increased, the stationary concentration of uncapped chains decreases until finally, at a molar ratio of approximately 1.0, all of the propagating chains become capped and the polymer propagates mainly by the "living" mechanism. After this point, the molecular weight begins to decrease due to an increase in initiator efficiency. Because the chain ends have to be activated by the thermal uncapping process for further growth, the overall rate of propagation becomes slower relative to initiation. This expected decrease in the propagation rate is consistent with the observed decrease in the polymer yield as the [TEMPO]/[DTBP] ratio is increased (Table 1). Our preliminary kinetic results showed that the molecular weight of the polymer progressively increases with the conversion of MDP monomer, another indication of the "living" character of the polymerization process. As exemplified in Figure 2, M_n of the polymer was found to increase linearly from 4000 to 7300 when the conversion was increased from 31 to 55% at the [TEMPO]/[DTBP] ratio of 1.6.

In summary, we have presented some evidence for achieving the first "living" free radical ring-opening polymerization of 2-methylene-1,3-dioxepane in the presence of a nitroxyl stable free radical (TEMPO) with di-*tert*-butyl peroxide (DTBP) as initiator. The polydis-

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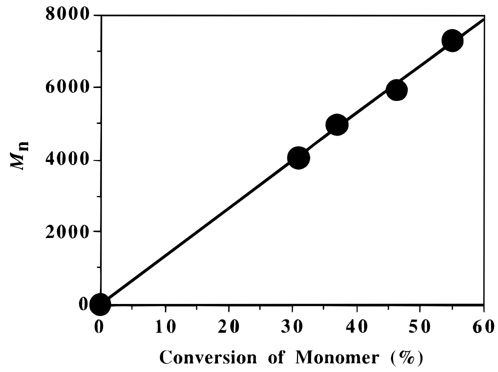

Figure 2. Relationship between the number-average molecular weight (M_n) of the polymer and the monomer conversion at the [TEMPO]/[DTBP] ratio of 1.6.

persity of the polymers decreases as the concentration of TEMPO is increased. At high TEMPO concentrations, the polydispersity as low as 1.2 was obtained. The molecular weights were found to increase, reach maxima, and then decrease as the [TEMPO]/[DTBP] ratio was increased from 0.8 to 1.8. There is a linear increase in the molecular weight with the monomer conversion. These results are suggestive of the "living" polymerization process. Currently, we are studying the kinetics of the polymerization and using other methods, such as the synthesis of block copolymers and functionalization of the polymer chain ends, in order to *fully establish* the "living" nature of this system. We are also exploring other ring monomers and applying other living radical polymerization techniques in the ring-opening polymerization system.

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Supporting Information Available: Listing of the detailed synthetic procedures, instrumentation, and characterization data (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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