Notes

Mechanism and Kinetics of Nitroxide-Controlled Free Radical Polymerization. Thermal Decomposition of 2,2,6,6-Tetramethyl-1-polystyroxypiperidines

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Introduction

The free radical polymerization mediated by stable nitroxyl radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and its derivatives has aroused much interest as a novel and simple synthetic route to well-defined polymers.[1−11] The key process of this method is the reversible dissociation−combination reaction of the alkyl−nitroxyl adduct (Scheme 1a).[3,12] In hopes of comprehensively understanding and evaluating this new branch of "living" polymerization, we have been studying for some time the mechanism and kinetics of TEMPO-mediated styrene polymerization and succeeded in determining the rate constants of dissociation (k_d) and combination (k_c) of that system.[13−15]

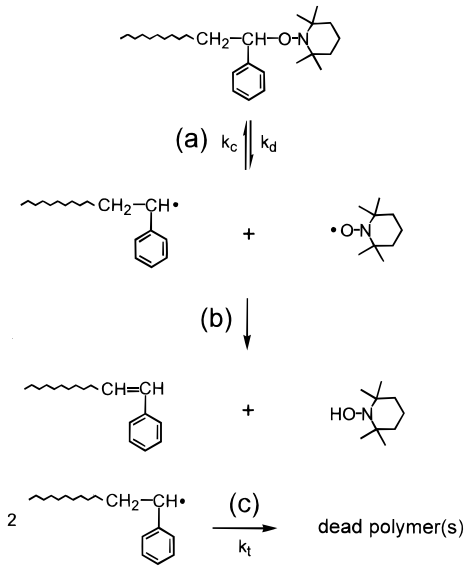
Even though the reversible combination is a main reaction, a side reaction can possibly occur. It is the decomposition of the adduct molecule through the abstraction of the β-proton of the polymer radical by the nitroxyl, producing terminally unsaturated polymer and hydroxyamine (Scheme 1b). This reaction was suggested by Li et al.,[16] who observed the decomposition of the model compound S−TEMPO (Figure 1a) according to a similar mechanism.[17] Depending on the magnitude of the decomposition rate constant, k_{dec}, this reaction can bring about a severe limitation to the "livingness" of the system, causing a serious broadening of the product polydispersities. Therefore, k_{dec} also is another essential parameter characterizing a given polymer/nitroxyl system.

We have determined k_{dec} of two model compounds, i.e., an oligomeric PS adduct with TEMPO (PS−TEMPO; Figure 1b) and its unimer model (BS−TEMPO; Figure 1c). The results indicate that the thermal decomposition of these compounds are less serious than that of the model compound S−TEMPO, as will be reported below.

Experimental Section

The PS−TEMPO was synthesized as follows: freshly distilled styrene, benzoyl peroxide (BPO, 0.094 mol L^{-1}), and TEMPO (0.112 mol L^{-1}) were charged in a round-bottomed flask, degassed by several freeze−thaw cycles, and sealed off under vacuum. The mixture was heated at 95 °C for 2.5 h to achieve complete decomposition of BPO and then at 125 °C for 2 h. After unreacted monomer was removed by vacuum evaporation, the viscous oily product was diluted with chloroform and subjected to fractionation on a Tosoh semipreparative gel permeation chromatograph (GPC) Model HLC-827 with chloroform as eluent. This gave a PS−TEMPO adduct as a main fraction. The unimer model compound BS−TEMPO was prepared according to Hawker.[8]

Scheme 1. Main Reactions That a PS−TEMPO Adduct Can Make at High Temperatures: (a) Reversible Dissociation; (b) Decomposition (β-Proton Abstraction); (c) Bialkyl Combination (Termination).



Parts a and c of Figure 2 show the proton nuclear magnetic resonance (^{1}H-NMR) spectra of the two model compounds. Figure 2a suggests that the BS−TEMPO adduct is contaminated by some impurities (about 5%), but it should not affect the results. The number-average molecular weight M_n of the PS−TEMPO estimated from the spectrum in Figure 2c was 1100 after appropriately correcting for the protonous toluene impurities included in toluene-d_8 used as solvent (see below for the main assignments). The polydispersity index M_w/M_n estimated by GPC was 1.03. Incidentally, the GPC value of M_n is less reliable for such a low-mass sample because of the differences in end groups between this sample and the standard PSs used for calibration.

The process of thermal decomposition was followed by ^{1}H-NMR spectroscopy: each model compound was dissolved in toluene-d_8 ([BS−TEMPO] = 0.080 mol L^{-1}, and [PS−TEMPO] = 0.040 mol L^{-1}), charged in a NMR tube, carefully degassed, and sealed off under vacuum. It was heated at a prescribed temperature T for a prescribed time t, quenched to room temperature, and studied by ^{1}H-NMR.

Results and Discussion

Parts b and d of Figure 2 show the ^{1}H-NMR spectra of BS−TEMPO and PS−TEMPO, respectively, taken after the thermal treatment. In the case of BS−TEMPO (Figure 2b), we followed the signals of the α-proton (5.2−5.3 ppm) next to the TEMPO moiety for the concentration E of active molecules, and those of the double-bond protons (6.5−6.7 and 7.7−7.8 ppm) for the concentration D of decomposed molecules. In the case of PS−TEMPO (Figure 2d), the α-proton (E) next to the TEMPO moiety and the methylene protons ($2A$) connected to the oxygen of the BPO moiety appear in group at 4.2−4.6 ppm ($S = E + 2A$), the double-bond protons ($2D$), at 6.2−6.4

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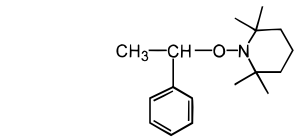
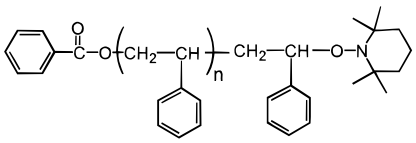
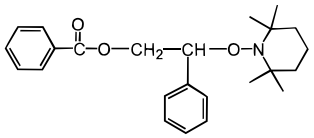


(a) S-TEMPO



(b) PS-TEMPO



(c) BS-TEMPO

Figure 1. Chemical structures of (a) S−TEMPO, (b) PS−TEMPO, and (c) BS−TEMPO.

ppm, and the two *ortho* protons (2*B*) of the BPO phenyl ring at 8.1−8.3 ppm. Because *A* has to be equal to *B*, we obtained *E* as $E = S - 2B$.

Here we make two assumptions, which will be justified later on: (1) the decomposition is a first-order reaction and (2) other side reactions such as bialkyl termination (see Scheme 1) are unimportant. Then, since $E + D = E_0$, where E_0 is the concentration of active (adduct) molecules at $t = 0$, we may write

$$\ln[E/(E + D)] = -k_{dec}t \qquad (1)$$

Figure 3 shows the plot of ln $[E/(E + D)]$ vs t for BS−TEMPO and PS−TEMPO at 160 °C. In each case, the data points fall on a straight line, from which a well-defined value of k_{dec} can be obtained.

Figure 4 shows the Arrhenius plots of k_{dec} thus determined at three different temperatures. The straight lines read

$$k_{dec} = A_{dec} \exp(-E_{dec}/RT) \qquad (2)$$

with

$$A_{dec} = 4.7 \times 10^{14}\ s^{-1}\ (BS-TEMPO) \qquad (3a)$$

$$E_{dec} = 157\ kJ\ mol^{-1}\ (BS-TEMPO) \qquad (3b)$$

and

$$A_{dec} = 5.7 \times 10^{14}\ s^{-1}\ (PS-TEMPO) \qquad (4a)$$

$$E_{dec} = 153\ kJ\ mol^{-1}\ (PS-TEMPO) \qquad (4b)$$

Regarding this analysis, several points may need discussion. It would be reasonable to consider that the β-proton abstraction occurs competitively with the alkyl−nitroxyl dissociation as well as combination. The chances of abstraction at the two stages would be essentially equal and usually small compared with the frequencies of dissociation and combination. Since, in the absence of other side reactions, a dissociation is necessarily followed by a combination, the proton abstraction or decomposition has to be first order in the adduct concentration, like the dissociation is. The nitroxyl concentration just controls the "transient" lifetime τ_t of the alkyl radicals,[15] but not the frequency

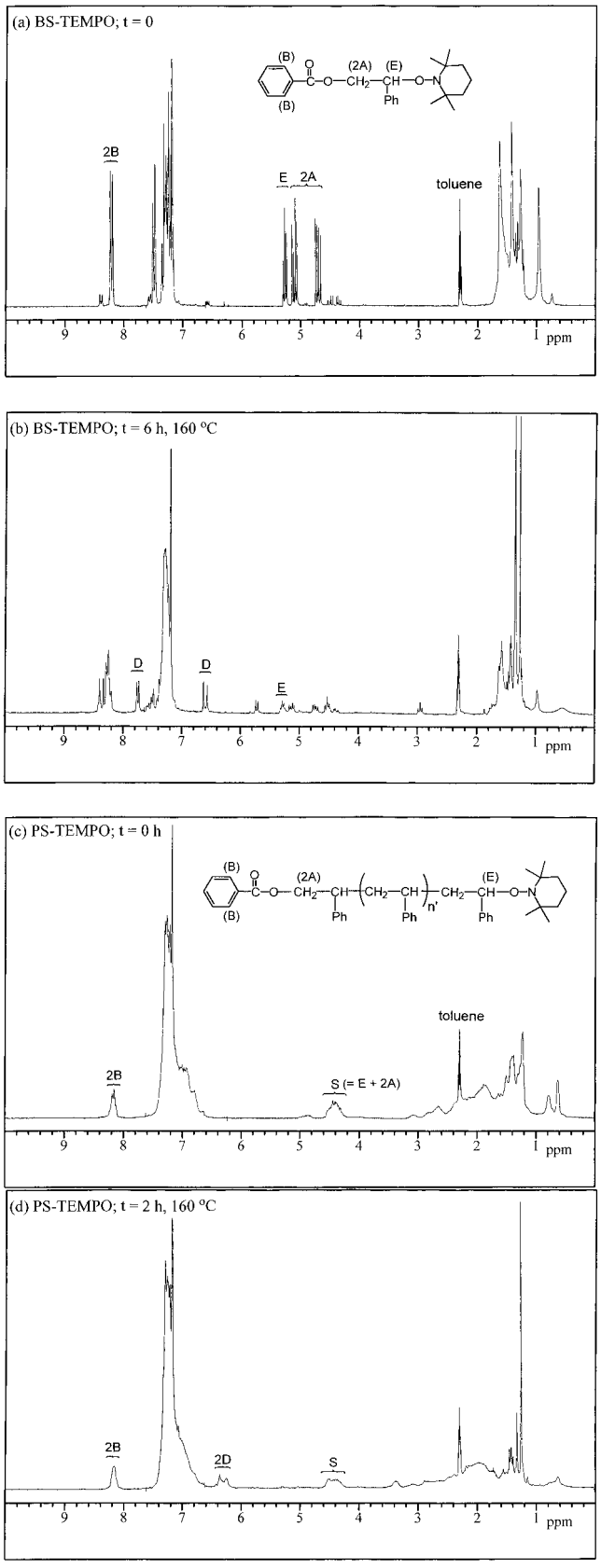


Figure 2. ^{1}H-NMR spectra of BS−TEMPO (a and b) and PS−TEMPO (c and d) before (a and c) and after (b and d) the thermal treatment at 160 °C. See the text for assignments.

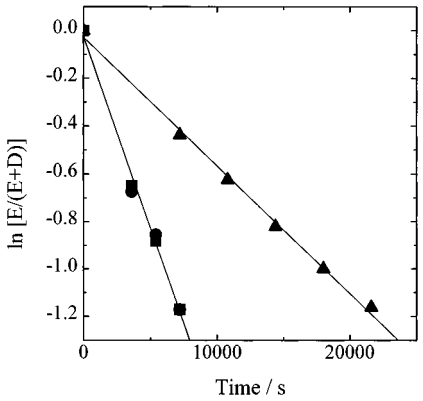


Figure 3. Plot of ln[$E/(E + D)$] vs t for the decomposition experiment at 160 °C: (■) PS−TEMPO; (●) PS−TEMPO containing 1.8 mM of TEMPO; (▲) BS−TEMPO. The lines shown are the best least-squares linear fits.

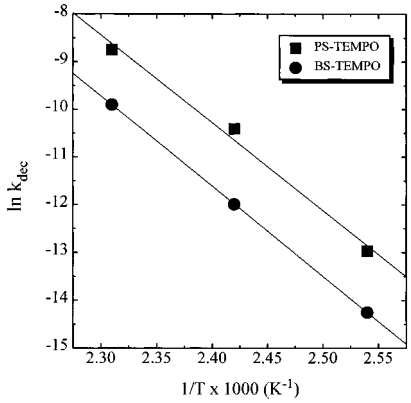


Figure 4. Arrhenius plots of k_{dec}: (■) PS−TEMPO; (●) BS−TEMPO.

of decomposition. In fact, if we add (free) TEMPO molecules to the PS−TEMPO system, we observe no change in k_{dec}, as Figure 3 shows. Thus the first assumption given above is justified.

The alkyl−alkyl termination, if any occurs, is believed to have no important influence on these results. According to a computer simulation[18] based on the known kinetic data of the PS−TEMPO system,[14,15] the termination occurs at an appreciable rate only at an early stage of thermal treatment, because free TEMPO molecules, rapidly accumulating in the system due to the termination, make the radical lifetime τ_t shorter and shorter or its concentration lower and lower as time elapses. As a result, the total amount of bimolecularly terminated species is estimated to be much less than 10% of the originally active molecules in all studied cases. The above-mentioned result that the addition of free TEMPO has no influence on k_{dec} indicates also that the termination is unimportant here.

On the other hand, the rate of bialkyl termination in the BS−TEMPO system may not be so small. The extra peaks at around 2.9 and 4.5 ppm observable in Figure 2b can be assigned to dimerized 2-(benzoyloxy)-1-phenylethyl. The production rate of this compound is similar to that of 2,3-diphenylbutane in the S−TEMPO system started with the same adduct concentration of 0.080 mol/L (cf. Figure 1 in ref 16). In the case presented in Figure 2b, about 19% of the original adduct has gone to the dimer after 6 h of the heat treatment, while 56% has changed to the unsaturated compound. Nevertheless, it can be confirmed that the presented results of analysis are correct as a remarkably good approximation owing to the mathematical structure of eq 1. The

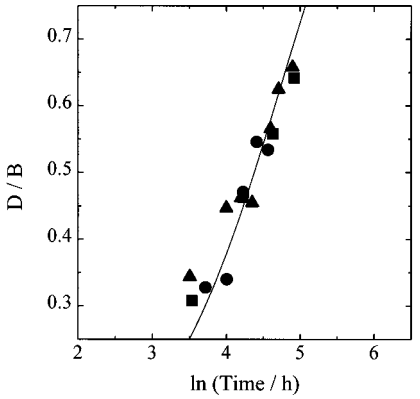


Figure 5. A master plot of D/B vs t for the data collected at different temperatures: (■) 160 °C (shift factor $a_T = 4.2$); (●) 140 °C ($a_T = 2.6$); (▲) 120 °C ($a_T = 0$). The solid curve shows the theory, eq 5 with $E_0/B_0 = 1$.

analysis based on this equation is admirably insensitive to impurities present from the onset and/or produced afterward. This is the main reason why we have adopted this analysis. The alkyl−alkyl termination in the PS−TEMPO system should occur at a much lower level, since the initial adduct concentration is half that in the BS−TEMPO and S−TEMPO systems (hence the chance of bialkyl reaction is 1/4) and since polymer−polymer reactions should be slower than those between low-mass radicals. This has been confirmed by the computer simulation mentioned above.

In the NMR analysis of the PS−TEMPO system, the signals of the active chain end (E) could not be separately observed, and E was evaluated indirectly (see above). This may pose some question about the reliability of the analysis. We have attempted an alternative analysis, which is based on the following relation (again with neglect of side reactions):

$$D/B = (E_0/B_0)[1 - \exp(-k_{dec}t)] \qquad (5)$$

where the subscript "0" denotes the initial state ($t = 0$), and it should hold, for any t, that $B = B_0$. Since E_0/B_0 is a constant for a given sample, the plots of D/B vs ln t for different temperatures should form a master curve, if an appropriate horizontal shift a_T, a function of T, is given to each curve. Figure 5 shows this master curve with $T = 120$ °C as a reference temperature. The slope of the plot of the shift factor a_T against T^{-1} gave an activation energy E_{dec} substantially the same as is given by eq 4b. This analysis has the merit that it is independent of the purity of the sample or its degrees of chain-end capping by the BPO and TEMPO moieties. By setting $E_0/B_0 = 1$, we recover substantially the same value of A_{dec} as in eq 4a.

As already implied, the decomposition reaction is first order in the adduct concentration, and the rate constant k_{dec} may be properly written

$$k_{dec} = p_{dec}k_d \qquad (6)$$

where k_d is the rate constant of dissociation and p_{dec} is a probability factor ($p_{dec} \ll 1$, usually). Combination of the present result for k_{dec} (eqs 2 and 4) with the previous one for the dissociation rate constant,[15] $k_d = 2.0 \times 10^{13} \exp(-124200/RT)$, allows us to write

$$p_{dec} = 29 \exp(-29000/RT) \qquad (7)$$

Namely, the activation energy of the β-proton abstraction is estimated to be 29 kJ mol^{-1}.

As for the model compound S−TEMPO, Li et al.[16] have observed activation energies of decomposition E_{dec} in the range 100−120 kJ mol^{-1}, depending on the solvents. This value should be compared with the above-cited activation energy of 124 kJ mol^{-1} for the *dissociation* (k_d) of PS−TEMPO. Since zero activation energy in the proton abstraction is unlikely, their result may indicate that S−TEMPO has a k_d value considerably smaller than that of PS−TEMPO. The absolute values of k_{dec} are significantly different for the different model compounds: k_{dec} (S−TEMPO) > k_{dec} (PS−TEMPO) > k_{dec} (BS−TEMPO). The difference between PS−TEMPO and BS−TEMPO may be ascribed to the deactivating effect of the carbonyl group in BS−TEMPO. The difference between S−TEMPO and PS−TEMPO may be too large to be ascribed simply to differences in the number of β-protons and the solvents used (at 125 °C, for example, they differ by a factor of 6−14, depending on the solvents[16]). It is suggested that the PS segment linked at the β-position is playing a role against the dissociation/abstraction reaction, energetically or sterically or in both ways.

To summarize, we have determined the decomposition rate constants of the two model compounds BS−TEMPO and PS−TEMPO. The results indicate that in the TEMPO-mediated polymerization of styrene, the decomposition of the active chain ends would occur less seriously than implied by the experiments with S−TEMPO[16] but still at an important level especially at high temperatures. For reference, Figure 6 gives the times required for PS−TEMPO to decompose by 10% at various temperatures. These results should be important for designing polymerization processes and predicting product characteristics.[18] However, it should be stressed that these results refer to the reactions in the particular solvent. In the presence of the monomer or other solvent, results can be different.

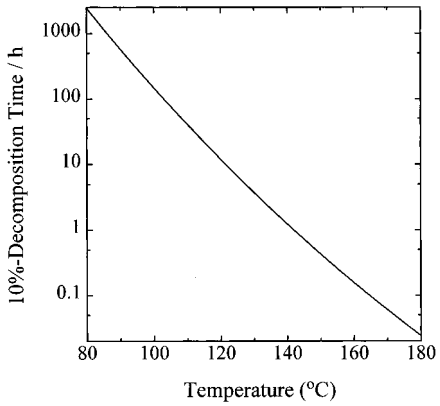


Figure 6. The 10% decomposition time of PS−TEMPO as a function of temperature (in toluene).

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