Mechanism of "Living" Radical Polymerization Mediated by Stable Nitroxyl Radicals

Takeshi Fukuda* and Tomoya Terauchi
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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It is shown that in order for the "living" radical polymerization mediated by stable nitroxyl radical (SNR) to proceed successfully, a constant supply of initiating radicals (by, e.g., thermal initiation) to make up for the loss of polymer radicals due to irreversible bimolecular termination is essential in addition to the frequent reversible combination of polymer radical with SNR. The stationary rate of SNR-mediated polymerization is totally independent of the SNR concentration, being equal to the polymerization rate of the SNR-free system. Experimental evidence is presented showing that in the "living" polymerization of styrene, both of these requirements are met in fact.

The free radical polymerization mediated by stable nitroxyl radicals (SNRs) has attracted much renewed interest as a simple and robust synthetic route to polymers with well-defined structure. This method has enabled one to synthesize polystyrene (PS)[1-8] and styrene copolymers[1,9,10] with a narrow polydispersity and/or controlled chain architecture. The key to the success of this method is believed to be the reversible combination of the polymer radical (P*) with the SNR (N*) to form the adduct (P-N), a dormant species :

$$\mathrm{P^* + N^*} \underset{k_d}{\overset{k_c}{\rightleftarrows}} \text{P-N} \quad \left(K = \frac{k_d}{k_c}\right) \qquad (1)$$

where k_c and k_d are the rate constants of combination and dissociation, respectively. While the radical N* is active only to P*, P* is active not only to N* and the monomer (propagation) but to other P* (bimolecular termination) and neutral molecules (chain transfer). When the last two reactions are unimportant relative to the first two, the system may be regarded as a pseudoliving or "living" one. The structural and process control achievable by this method is necessarily limited to relatively short polymers (say, molecular weight < 10^5).[11]

The above is a brief summary of the SNR mediated radical polymerization. However, very little is known about the kinetics and real mechanism of this polymerization. For example, the equilibrium constant K in eq.1 has never been successfully determined as yet. In other words, the "reversible combination" is still a hypothesis that lacks in experimental evidence. Another fundamental question that remains to be answered is as to the velocity of polymerization of an SNR-mediated system. A recent report[12] showed that the polymerization velocity of styrene is independent of the concentration of PS-DBN adduct, where DBN is di-*tert*-butyl nitroxide, an SNR. As a possible explanation of this seemingly curious phenomenon, the authors suggested an association of the dormant species, which we believe is unlikely. In what follows, we would like to make clear these fundamental aspects of the "living" radical polymerization.

Table 1. Comparison of the values of rate coefficient A / 10^{-6} s^{-1} for the SNR-mediated and thermal polymerizations of styrene

System	80 °C	90 °C	100 °C	125 °C
DBN[a]	1.7	3.9	8.0	
TEMPO[b]				42
Thermal[c]	2.1	4.4	9.2	48

[a] Initiated by the R-DBN adduct (R=1-phenylethyl) with [R-DBN] = 3.7×10^{-3} mol L^{-1} (80 °C and 100 °C) and 3.7×10^{-3}, 7.4×10^{-3}, 2.2×10^{-2}, and 4.4×10^{-2} mol L^{-1} (90 °C) : Ref.12.

[b] Initiated by the PS-TEMPO adduct with [PS-TEMPO] = 3.5×10^{-2} mol L^{-1} : this work.

[c] Computed with eq.51 in Ref.13.

In the presence of the reversible reaction in eq.1, the concentrations of P* and N* should generally follow the differential equations

$$\mathrm{d[P^*]}/\,\mathrm{d}t = R_i - k_t[\mathrm{P^*}]^2 + k_d[\text{P-N}] - k_c[\mathrm{P^*}][\mathrm{N^*}] \qquad (2)$$

$$\mathrm{d[N^*]}/\,\mathrm{d}t = k_d[\text{P-N}] - k_c[\mathrm{P^*}][\mathrm{N^*}] \qquad (3)$$

where R_i is the rate of initiation due to an initiator and/or thermal (spontaneous) initiation, and k_t is the termination rate constant. Except in an early stage of polymerization, a stationary state should be reached with respect to the concentrations of P* *and* N* : setting d[P*]/dt = d[N*]/dt = 0, we have

$$[\mathrm{P^*}] = (R_i / k_t)^{1/2} \qquad (4)$$

$$[\mathrm{N^*}] = K[\text{P-N}] / [\mathrm{P^*}] \qquad (5)$$

The (stationary) rate of polymerization, R_p = -d[M]/dt = k_p[P*][M], is given by

$$R_p = (k_p{}^2 R_i / k_t)^{1/2}[\mathrm{M}] \qquad (6)$$

where [M] is the monomer concentration, and k_p is the propagation rate constant.

Equation 6 is just the same as the familiar equation for the conventional system (without SNR). This means that the polymerization rate is independent of the equilibrium reaction in eq.1, and hence of the concentrations [P-N] and [N*]. This gives a very simple explanation of the above-cited result of Catala et al.[12] Since their system is initiated by an alkyl adduct of DBN, which will completely decompose at an early stage of high-temperature polymerization, a stationary supplier of P* is only the thermal initiation of styrene. In Table 1, we compare the values of the rate coefficient A = R_p / [M] read from Figure 2 in Ref.12 with those for the thermal polymerization of styrene.[13] The table also includes our data on the styrene polymerization at 125°C initiated by the adduct PS-TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy). All these data are concerned with the incipient (low-conversion) polymerization. The table shows that the rate of SNR-mediated polymerization agrees with that of the thermal polymerization in all cases, irrespectively of temperature, adduct concentration, and the kind of adduct. This confirms the kinetic scheme presented above.

In all of the SNR-mediated systems presented in Table 1, the polymerization proceeded in a "living" fashion to give narrow polydispersity PSs with M_w/M_n = 1.1~1.2, where M_w and M_n are the weight- and number-average molecular weights, respectively.

This indicates the existence of the equilibrium reaction in eq.5 with a sufficiently large value of K. In order to confirm this, we have made an electron spin resonance (ESR) analysis on the above-noted PS-TEMPO system ([PS-TEMPO] = 3.5x10^{-2} mol L^{-1}). The ESR data showed the existence of TEMPO radicals with [TEMPO] = 4.5x10^{-5} mol L^{-1} at t = 2 h, for example, when $A = k_p[\mathrm{P}^*] = 2.1\mathrm{x}10^{-5}$ s^{-1} by dilatometry.[14] Taking the bench mark value[15] of k_p of 2300 L mol^{-1} s^{-1}, we then have $K = 1.2\mathrm{x}10^{-11}$ mol L^{-1} at 125 °C. This is the first plausible value of K that has been determined so far for a "living" radical system.[16] Since a radical-radical reaction in solution is diffusion-controlled, and hence the k_c in eq.1 should be on the order of 10^9 L mol^{-1} s^{-1}, k_d is thus estimated to be 1x10^{-2} s^{-1}, approximately. It follows that the dissociation of each adduct occurs once every 100 s, and about 0.3 styrene unit is added to the PS radical before it recombines with TEMPO about 2x10^{-5} s after the dissociation. The obtained value of K may thus be understood to be large enough to set the system under control.

As shown above, the occurrence of sufficiently frequent dissociation of the P-N adduct *and* thermal initiation are essential for the "living" radical polymerization to proceed. Styrene meets both of these requirements. This may give a possible explanation to the fact that only styrene and styrene-related systems have so far been confirmed to be controllable by SNR. There possibly can be other systems in which adduct dissociation does occur but thermal polymerization does not. This work gives the important suggestion that such systems can be made "living" by adding an initiator to provide just as many radicals as the thermal polymerization of styrene does. The total number of radicals to be added in this way may be small, say, less than 10% of the P-N adduct molecules, so that they will have no serious effect on the molecular weight and polydispersity, as in the SNR-controlled styrene polymerizations described above.

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