Effects of Acetic Anhydride on the Activation and Polymerization Rates in Nitroxide-Mediated Polymerization of Styrene

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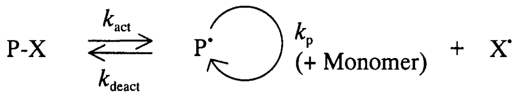
In order to assess the recent suggestion of Hawker et al.[1] that the C–ON bond of an alkoxyamine is weakened by acetic anhydride (Ac_2O), the activation (dissociation) rate constant k_{act} of a polystyrene–nitroxide adduct was directly determined in the presence of Ac_2O. The result showed that Ac_2O has no effect on the activation rate, contrary to the suggestion. On the other hand, Ac_2O was confirmed to accelerate the polymerization rate. The mechanism of acceleration was discussed.

The living radical polymerization (LRP) mediated by nitroxides ($X^\bullet$) such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) has attracted much attention as a new and robust route to the preparation of well-defined, low-polydispersity polymers.[2,3] The basic mechanism of this polymerization involves the alternating activation-deactivation process, in which a dormant species P-X is reversibly activated to a polymer radical $P^\bullet$ by thermal stimulus. In the presence of monomer, $P^\bullet$ undergoes propagation until it is deactivated back to the dormant species.



$$\text{P-X} \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} \text{P}^\bullet \overset{k_p}{\circlearrowleft} (+\ \text{Monomer}) + \text{X}^\bullet \qquad (1)$$

If the number of activation–deactivation cycles is large enough, all the chains will grow at an almost equal rate, giving a low-polydispersity polymer. Hence in a stationary-state polymerization, the activation rate constant k_{act} is a fundamental parameter to characterize the performance of a given LRP. Recently, Hawker et al.[1] suggested that the C–ON bond of an alkoxyamine (P-X) is weakened by acetic anhydride (Ac_2O) with the acyl group possibly coordinating to the nitrogen of the alkoxyamine. In order to directly assess the supposed effect of Ac_2O on the activation process, we determined the k_{act} of a polystyrene (PS)-TEMPO adduct in the presence of Ac_2O. We will also discuss the effect of Ac_2O on the polymerization rate.

The method for determining k_{act} adopted herein is based on the GPC observation of an early stage of the polymerization containing a probe adduct P_0-X.[4,5] A PS-TEMPO adduct with number- and weight-average molecular weights M_n and M_w of 1700 and 1890, respectively, ($M_w/M_n = 1.11$) was used as P_0-X. When P_0-X is activated, the released polymer radical $P_0^\bullet$ will propagate until it is deactivated to give a new adduct P_1-X. Since P_0-X and P_1-X are generally different in chain length and its distribution, they may be distinguishable by GPC. By following the decay of [P_0-X], k_{act} can be determined from the first-order plot

$$\ln(S_0/S) = k_{act}t \qquad (2)$$

where S_0 and S are the concentrations (the GPC peak areas) of P_0-X at time zero and *t*, respectively. With a proper amount of the conventional radical initiator *t*-butyl hydroperoxide (BHP) added to the system, the GPC curve got separated into two distinct peaks, allowing accurate resolution. The role of BHP has been interpreted elsewhere.[6]

Figure 1 shows the first-order plot of *S* for the styrene polymerization at 110 °C with P_0-X and BHP, and with or without Ac_2O. The k_{act} value (the slope of the straight line) in the presence of Ac_2O is almost identical to that in its absence. Namely, Ac_2O has no effect on the activation rate, contrary to the suggestion of Hawker et al. Even if Ac_2O possibly coordinates to the alkoxyamine, the interaction is not strong enough to detectably weaken the C–ON bond of the alkoxyamine.

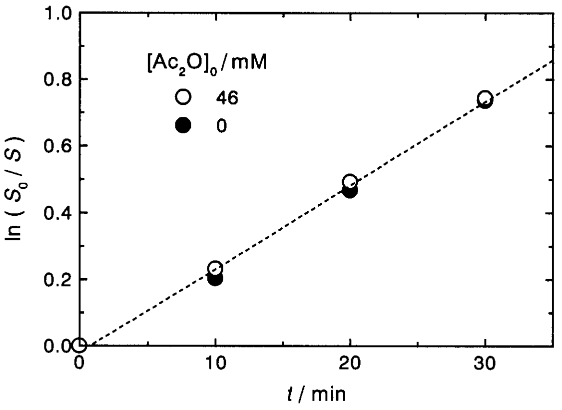


Figure 1. Plot of $\ln(S_0/S)$ vs. *t* for the polymerization of styrene at 110 °C with PS-TEMPO (P_0-X), BHP, and Ac_2O: [P_0-X]$_0$ = 23 mM, [BHP]$_0$ = 20 mM, and [Ac_2O]$_0$ = 0 (●), and 46 (○) mM.

Hawker et al. initially introduced Ac_2O as an effective accelerator of the polymerization rate R_p.[1] Figure 2 shows the first-order plot of the monomer concentration in this experiment. The R_p indeed becomes larger by the addition of Ac_2O. Hawker et al. attempted to explain this rate enhancement in terms of an increase in k_{act}. However, our results showed that k_{act} remains the same.

It was previously verified[7,8] that if the system includes initiation, propagation, termination, reversible activation, and no other side reactions, the system will sooner or later reach the stationary state, where it holds that

$$[P^\bullet] = (R_i/k_t)^{1/2} \qquad (3)$$

where R_i and k_t are the initiation rate and the termination rate constant, respectively. According to equation 3, R_p depends neither on k_{act} nor on k_{deact}: hence the observed increase of R_p was at first supposed to come from the change of R_i. Since Ac_2O increases R_p even in the absence of BHP,[1] Ac_2O was sup-

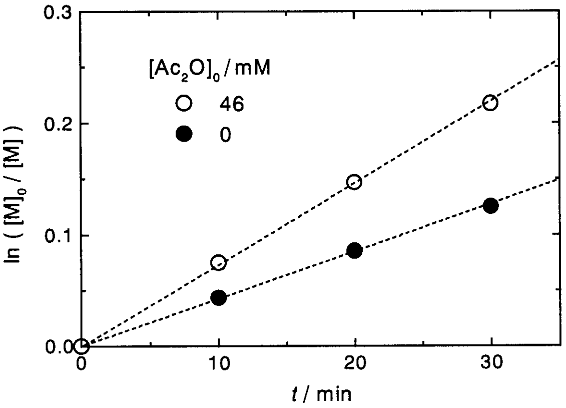


Figure 2. Plot of $\ln([M]_0/[M])$ vs. t: for symbols and experimental conditions, see Figure 1.

posed to enhance thermal initiation. However, an independent experiment showed that Ac_2O (46 mM) has no effect on the rate of the thermal polymerization of styrene. This means that equation 3 is not valid for the present system.

A possible interpretation for the failure of equation 3 would be a decrease of the effective concentration of the stable radical due to the presence of Ac_2O. If the system is assumed to involve degradation,[9] for example, $[P^\bullet]$ and $[X^\bullet]$ should follow the differential equations

$$d[P^\bullet]/dt = k_{act}[P\text{-}X] - k_{deact}[P^\bullet][X^\bullet] + R_i - k_t[P^\bullet]^2 \tag{4}$$
$$d[X^\bullet]/dt = k_{act}[P\text{-}X] - k_{deact}[P^\bullet][X^\bullet] - k_{deg}[Ac_2O][X^\bullet] \tag{5}$$

where k_{deg} is the rate constant of degradation. Assuming the stationary state in which $d[P^\bullet]/dt = d[X^\bullet]/dt = 0$, we have

$$k_{deg}[Ac_2O] = k_{deact}[P^\bullet]\left(\frac{k_t[P^\bullet]^2 - R_i}{k_{act}[P\text{-}X] + R_i - k_t[P^\bullet]^2}\right) \tag{6}$$

where both R_i and $k_t[P^\bullet]^2$ ($\approx 10^{-7}$ M s^{-1}) in the denominator are negligibly small compared with $k_{act}[P\text{-}X]$ ($\approx 10^{-4}$ M s^{-1}) in this system. When $k_{deg}[Ac_2O] = 0$, equation 6 reduces to equation 3. According to this equation, a higher $[Ac_2O]$ results in a higher $[P^\bullet]$, while $[P^\bullet]$ becomes less sensitive to $[Ac_2O]$ as $[Ac_2O]$ increases. This seems approximately consistent with the reported observation.[1] To assess the supposed degradation, a toluene solution of TEMPO (1 mM) and Ac_2O (46 mM) was heated at 110 °C, and monitored by ESR. However, TEMPO showed no decay in concentration over a period of 15 h. This means that Ac_2O does not directly decrease the TEMPO concentration. However, it should not be ruled out that Ac_2O possibly coordinates to TEMPO, thereby decreasing its activity as a capping agent. This would bring about the same effect as degradation. Experimental verification of the assumed coordination would be difficult, however, due to the unavailability of NMR spectroscopy for TEMPO systems.

In conclusion, it was demonstrated that Ac_2O enhances the polymerization rate but not the activation rate. The mechanism of the rate enhancement is still to be established, but neither the change of thermal initiation rate nor the degradation of TEMPO is involved in the mechanism.

References and Notes

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