Kinetic Study on Nitroxide-Mediated Free Radical Polymerization of *tert*-Butyl Acrylate

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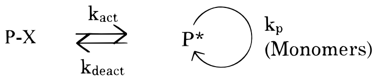
ABSTRACT: The kinetics of nitroxide-mediated free radical polymerization of *tert*-butyl acrylate (tBA) was studied. It was demonstrated that the polymerization rate can be increased by addition of a proper amount of a radical initiator, dicumyl peroxide (DCP), without causing any appreciable broadening of the polydispersity. The use of di-*tert*-butyl nitroxide (DBN) allowed the controlled polymerization of tBA to proceed at a lower temperature than the polymerization controlled by a TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) derivative, which was conducted by Georges et al. [*Macromolecules* **1996**, *29*, 8993]. The pseudo-first-order activation rate constant k_{act} of the poly(tBA)−DBN adduct was also determined by the GPC curve-resolution method to be 1.0×10^{-3} s^{-1} at 120 °C, which indicates that the adduct experiences activation−deactivation cycles frequently enough to afford a low polydispersity. Nevertheless, the polydispersity markedly increased and the rate of polymerization decreased at later stages of polymerization due to the decomposition of the alkoxyamine and the subsequent hydrogen transfer.

Introduction

The recent progress of controlled/“living” radical polymerization methods has offered new and robust synthetic routes to well-defined, low-polydispersity polymers.[1] One of the most extensively studied systems is the polymerization of styrene mediated by stable nitroxides such as TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy).[2] The key reactions in this system have been shown to be the alternating activation−deactivation process in which the polymer−nitroxide adduct P−X is reversibly activated by thermal homolysis:[3]



+ X* (1)

Here k_p is the propagation rate constant, and k_{act} and k_{deact} are the rate constants of activation and deactivation, respectively. A number of these activation−deactivation cycles allow all the chains to propagate at a nearly equal rate, thus controlling the chain length and its distribution.

The nitroxide method has been successfully applied to styrene and its derivatives[4] and also proved to be effective in controlling random copolymerizations of styrenics with other monomers such as acrylates, methacrylates, and acrylonitrile.[5] However, it has achieved limited success in controlling the homopolymerizations of these monomers other than styrenics: the first attempt with acrylates was made by Solomon et al.,[2a] who obtained oligomers with rather high polydispersities ($M_w/M_n > 1.5$). More recently, Listigovers et al.[6] have carried out the homopolymerization of *tert*- and *n*-butyl acrylates (tBA and nBA) at high temperatures (145−155 °C) using 4-oxo-TEMPO as a mediator and successfully obtained polymers with high molecular weights (e.g., $M_w \sim 27\,000$) and appreciably low polydispersities ($M_w/M_n < 1.5$). However, the maximum conversion achieved in their system was rather low (about 35%, according to their published data[6]). Benoit et al.[7] have used *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethyl)propylnitroxyl (DEPN) together with azobis(isobutyronitrile) (AIBN) to yield low-polydispersity poly(nBA)s ($M_w/M_n = 1.1−1.2$) with high conversions. However, this remarkable result was obtained at the expense of a long polymerization time (e.g., 42 h to reach conversions of 72−95%).

In this report, we study the polymerization of tBA mediated by di-*tert*-butyl nitroxide (DBN). The reason we have chosen this nitroxide, rather than TEMPO, is the possibly larger rate of activation (homolysis) of the polymer−DBN adduct than that of the TEMPO counterpart.[8,9] There are two main purposes in this work. One is to confirm the role of a radical initiator as an accelerator. Previous studies have shown that radical initiators such as *tert*-butyl hydroperoxide (BHP)[10] and dicumyl peroxide (DCP),[11] which have a moderate rate of decomposition at high temperatures, enhance the polymerization rate R_p of styrene in the presence of a styrenic−TEMPO adduct without causing any appreciable broadening of the chain length distribution, at least in a limited range of the initiator concentration. The tBA system is distinguished from the styrene system by the fact that the spontaneous (thermal) polymerization is appreciable in the bulk polymerization of styrene at high temperatures, whereas it is much less significant in that of tBA. Hence, the use of a radical initiator is a possible way to manipulate the rate of polymerization of tBA. The other purpose of this work is to make clear factors affecting the chain length distribution of this system. A preliminary result on the tBA polymerization in the presence of a poly(*tert*-butyl acrylate)−DBN adduct (PtBA−DBN) has suggested that the chain length distribution of this system does not narrow as in a styrene−nitroxide system. The reason for this will be unequivocally established by determining the rate constant of activation k_{act} and comparing it to that in the styrene system. Results of such experiments will be presented below.

Experimental Section

Materials. Commercially obtained benzoyl peroxide (BPO), styrene, and DCP were purified by the standard methods described elsewhere.[12,13] tBA was purified in the same manner

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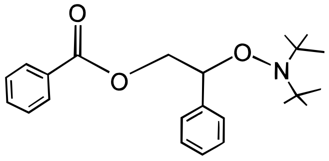

BS-DBN

Figure 1. Structure of BS−DBN.

as styrene. Di-*tert*-butyl nitroxide (DBN) was purchased from Aldrich and used without further purification. 2-Benzoyloxy-1-phenylethyl−DBN adduct (BS−DBN, Figure 1) was prepared starting with BPO, styrene, and DBN in the same manner as described previously,[13] except that the reaction temperature was 60 °C.

GPC. The GPC measurement was made on a Tosoh HLC-802 UR high-speed liquid chromatograph equipped with Tosoh gel columns G2500H, G3000H, and G4000H. THF was used as eluent (40 °C). The column system was calibrated with Tosoh standard polystyrenes (PSs). Sample detection and quantification were made with a Tosoh differential refractometer RI-8020 calibrated with known concentrations of PtBA−DBN adducts in tetrahydrofuran (THF).

General Procedure for Polymerization of tBA. BS−DBN (40 and 80 mM) and DCP (0, 1.0, and 3.0 mM) were dissolved in tBA, degassed, sealed off under vacuum, and heated at 120 °C for a prescribed time *t*. The mixture was then quenched to room temperature, diluted by tetrahydrofuran to a known concentration, and directly analyzed by GPC.

Preparation of PtBA−DBN Adduct. A tBA solution of BS−DBN (82 mM) and DCP (3.0 mM) in a glass tube was degassed and heated at 120 °C for 1 h (conversion: 20.2%). The produced polymer was purified by reprecipitation with chloroform and methanol/water (8/2) used as a solvent and a nonsolvent, respectively, and then thoroughly dried. According to PS-calibrated GPC, number- and weight-average molecular weights, M_n and M_w, of the purified polymer were found to be 2100 and 2700, respectively. The chain extension test,[2h] that is, the polymerization of tBA with this sample used as an "initiator", showed that the fraction of potentially inactive species (without nitroxide moiety at the chain end) is approximately 7%. Another model adduct with $M_n = 1200$ and $M_w/M_n = 1.16$ was prepared similarly, except that the reaction was stopped at 20 min. This polymer was used for the decomposition experiments.

Results and Discussion

Enhancement of Polymerization Rate. Since TEMPO is most widely employed as a nitroxyl mediator, we initially attempted the polymerization of tBA with TEMPO at 120 °C. However, the polydispersity index M_w/M_n of the resultant polymer remained approximately 2.0 throughout the course of polymerization. This was presumed to be due to a very small value of k_{act} in the tBA/TEMPO system at this temperature. It has been reported that k_{act} depends on the structure of nitroxides. The model experiment[8] and molecular orbital calculations[8,9] show that k_{act} of the open-type nitroxide like DBN is larger than that of the ring-type one like TEMPO, mainly due to the difference in steric factors. This encouraged us to use DBN instead of TEMPO.

Figure 2a shows the GPC traces for the bulk polymerization of tBA with BS−DBN adduct at 120 °C. It can be seen that the molecular weight increases with polymerization time *t*. However, the chains almost stopped growing after about 6 h, where the conversion reached only about 30%. To increase R_p and chain length, we attempted to add a small amount of DCP as a radical initiator. It will supply new growing radicals to compensate the loss of P* through termination, resulting in a stationary rate of polymerization. This rate increases with increasing DCP, as in a conventional system. (For more details about the role of radical initiator, see ref 10.) DCP was chosen for its desirable decomposition rate at this temperature.[14] The resultant chromatograms are presented in Figure 2b. Clearly, the polymerization proceeded faster, and M_n and conversion exceeded 10 000 and 50%, respectively, at 6 h. The polydispersity remained as small as that in the system without DCP. Thus, the addition of a radical initiator has proved to be effective to increase R_p of the tBA/DBN system.

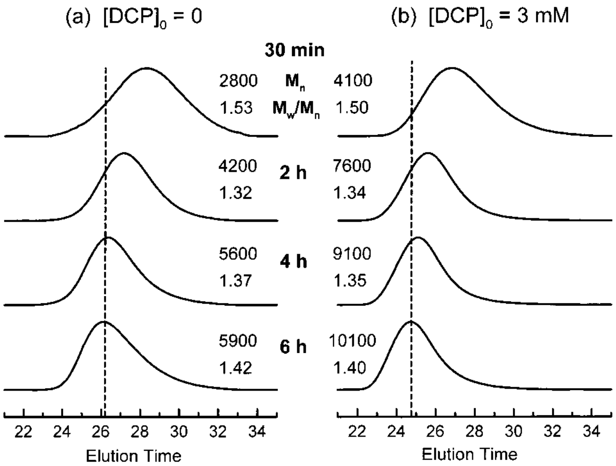

Figure 2. GPC charts for the tBA polymerization at 120 °C with $[\text{BS−DBN}]_0 = 40$ mM: (a) $[\text{DCP}]_0 = 0$ and (b) 3 mM. The broken vertical lines are an aid for the eye.

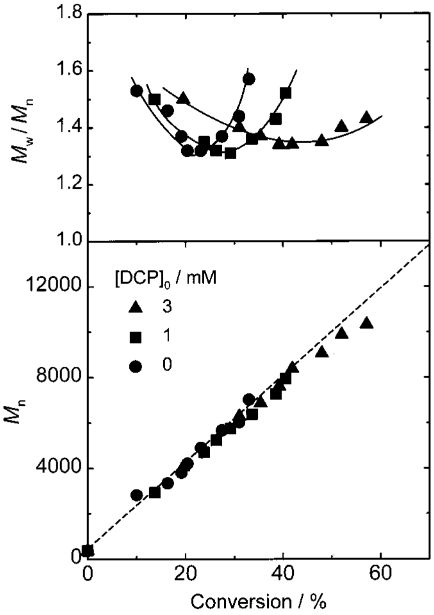

Figure 3. Plot of M_w/M_n and M_n (estimated by PS-calibrated GPC) vs monomer conversion for the tBA polymerization at 120 °C with $[\text{BS−DBN}]_0 = 40$ mM: $[\text{DCP}]_0 = 0$ (●), 1 mM (■), and 3 mM (▲). The broken line is theoretical, and the solid lines are an aid for the eye.

Figure 3 shows M_n and M_w/M_n of the product polymers as a function of conversion. Apparently, M_n increases linearly with conversion and agrees with the theoretical value (broken line in the figure) calculated from the conversion/$[\text{BS−DBN}]_0$ ratio, irrespective of DCP concentrations. This indicates that the number of DCP-initiated polymers is negligibly small compared to

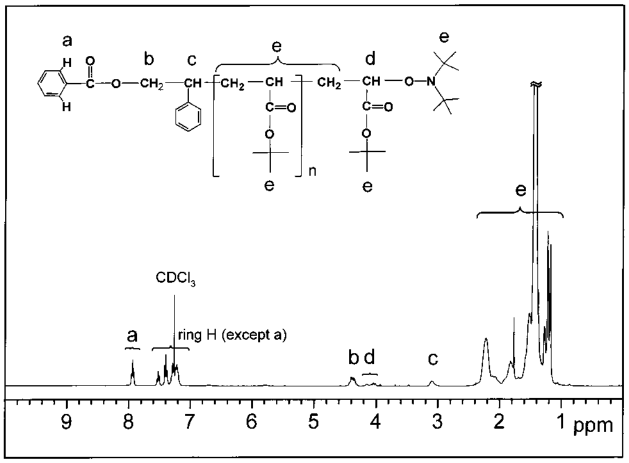

Figure 4. ^{1}H NMR spectrum of the model PtBA−DBN adduct (M_n = 2100 and M_w/M_n = 1.29).

that of the BS−DBN-initiated molecules, and the role of DCP is only to increase R_p. The M_w/M_n ratio also commonly becomes smaller with conversion in an initial stage and then tends to increase after passing through the minimum at which M_w/M_n is approximately 1.3. The increase in polydispersity in the later stage of polymerization would be ascribed to side reaction(s), which will be discussed below.

Since the presented values of M_n of PtBA were estimated by PS-calibrated GPC, they may be inaccurate on an absolute scale. ^{1}H NMR analysis will give more reliable M_n in this case. Figure 4 shows the spectrum of the model PtBA−DBN (see Experimental Section) with M_n of 2100 estimated by GPC, where the ortho protons of the benzoyloxy ring at the BPO-initiated chain end clearly appear at 7.9 ppm (peak a). The protons at the DBN moiety and tBA units are observed in a group at 1.0−2.5 ppm (peaks e), while the methine proton in the main chain neighboring to the DBN moiety appears at 4.05−4.15 ppm (peak d). Since DCP-initiated polymers are negligibly small in population as pointed out above, it can be assumed that all the polymers possess a benzoyloxy group at the initiating chain end. For the same reason, there must be very few polymers with two benzoyloxy groups at both chain ends (formed by combination of polymer radicals). Therefore, from the intensity of peak a relative to that of peaks e**,** we estimated the M_n to be 2100, which (accidentally) coincides with the GPC value. Thus, it can be concluded that M_n obtained by GPC is close to the actual values.

Effects of Hydrogen Transfer on Polymerization Rate. Figure 5 shows the ln([M]$_0$/[M]) vs *t* plot for the polymerization with varying amounts of DCP, where M represents the monomer and the subscript zero denotes the initial state (t = 0). Clearly, R_p increases with increasing [DCP]. However, even in the DCP-containing system, R_p became smaller and smaller as time elapsed. It was previously shown that, in the presence of initiation, a system with or without a polymer−nitroxide adduct should sooner or later reach the stationary state with respect to the concentrations of P* and X*: the stationary state [P*] is given by[2h]

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

where R_i is the rate of initiation and k_t is the rate constant of termination. This equation has been confirmed to hold in the styrene/TEMPO/BHP system, for example.[10] The decreasing trend in R_p observed here may be partly ascribed to the change of [DCP] with time. The decomposition rate constant k_d' of DCP in dodecane is known in the range of 128−158 °C,[14] which allows us to estimate the k_d' at 120 °C to be 3.9×10^{-5} s^{-1}. Since k_d' is nearly independent of solvents,[14] we may use this value for the tBA system: we thus expect that R_p after 8 h will become about half that at the initial stage of polymerization. However, the observed decrease in R_p is much more significant. This indicates that a side reaction may be a main cause for the decrease of R_p.

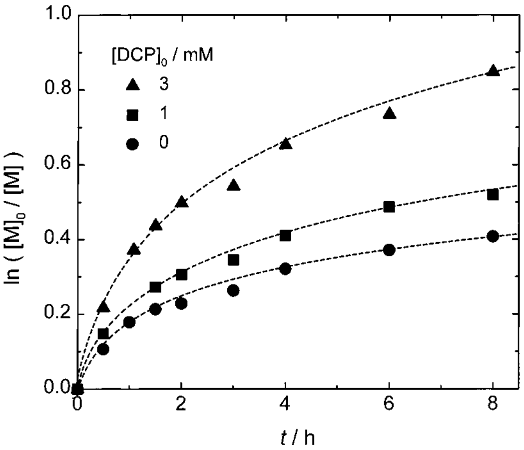

Figure 5. Plot of ln([M]$_0$/[M]) vs polymerization time *t*. For symbols and experimental conditions, see Figure 3.

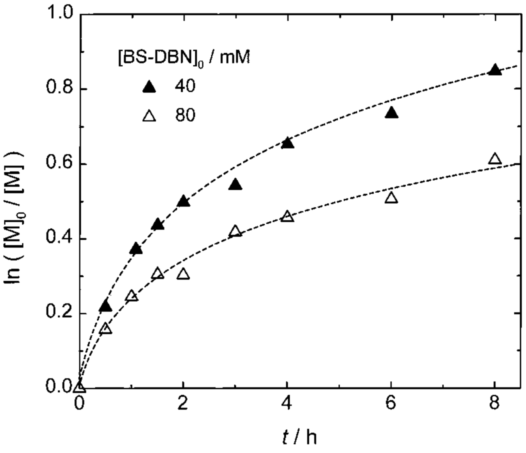

Figure 6. Plot of ln([M]$_0$/[M]) vs polymerization time *t* for the tBA polymerization at 120 °C with [DCP]$_0$ = 3 mM: [BS−DBN]$_0$ = 40 mM (▲) and 80 mM (△).

A possible one may be the decomposition of P−X, in which the nitroxyl radical X* abstracts the β-proton attached to the nitroxide moiety of P−X, forming a terminally unsaturated polymer and a hydroxyamine XH.[15,16] It has been suggested that XH works as a retarder on R_p, since it reacts with P* through a hydrogen transfer to give a terminally saturated polymer PH and X*, resulting in a decrease in [P*].[17] It was also reported that the rate of decomposition (formation of XH) depends on both monomers and nitroxides.[17] Since [XH] depends on the initial amount of BS−DBN as well as polymerization time, R_p will also depend on them. Figure 6 shows the ln([M]$_0$/[M]) vs *t* plot for the polymerization with varying amounts of BS−DBN and

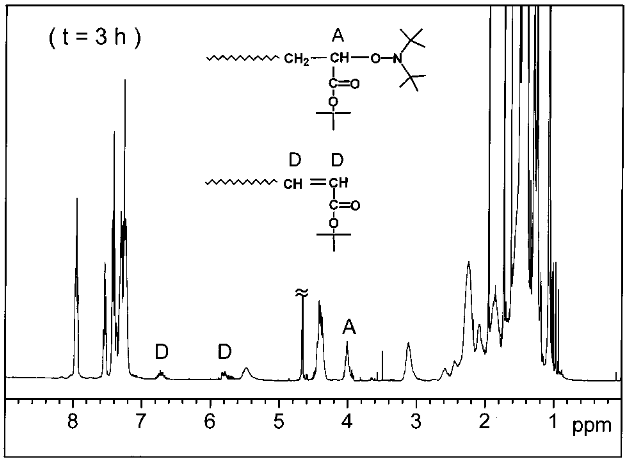

Figure 7. ^{1}H NMR spectrum of the model PtBA−DBN adduct (M_n = 1200 and M_w/M_n = 1.16) after the heat treatment at 120 °C. (This model adduct originally contained no detectable terminal unsaturation, unlike the one whose ^{1}H NMR is given in Figure 4.)

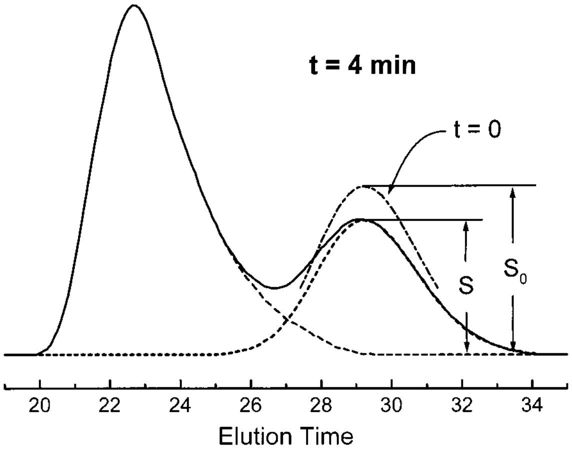

Figure 8. Two-component resolution of the GPC curve for the tBA polymerization at 120 °C for 4 min with $[P_0{-}X]_0$ = 15 mM and $[DCP]_0$ = 1 mM, where $P_0{-}X$ is the PtBA−DBN adduct used as a probe.

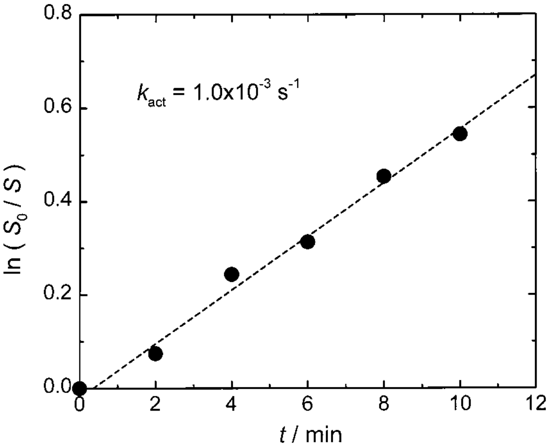

Figure 9. Plot of $\ln(S_0/S)$ vs polymerization time t at 120 °C for the activation of PtBA−DBN.

a fixed initial concentration of DCP. Clearly, the higher is $[BS{-}DBN]_0$, the smaller is R_p, as expected.

The decomposition of P−X into a terminally unsaturated polymer was directly confirmed by ^{1}H NMR spectroscopy. Figure 7 shows the ^{1}H NMR spectrum for the model PtBA−DBN adduct (M_n = 1200 and M_w/M_n = 1.16) dissolved in $CDCl_3$ and heated at 120 °C for 3 h. The peaks at about 5.8 and 6.7 ppm, which were absent before the heat treatment, can be assigned to the double-bond protons at the ω end of PtBA. (To avoid confusion, it should be noted that the PtBA−DBN adduct used for the decomposition study is different from the one used for other studies. Owing to the short preparation time (20 min), this adduct contains no detectable terminal unsaturation before the heat treatment.) Their intensities (2D) relative to that of the α-proton (A) next to the DBN moiety allow us to estimate the rate constant of decomposition k_{dec} from

$$\ln[A/(A + D)] = -k_{dec}t \tag{3}$$

An approximate value of k_{dec} thus obtained is 1.1×10^{-5} s^{-1}, which is about 4 times as large as that for the decomposition of the PS−TEMPO adduct.[16] Thus, the decomposition of the active end in the tBA polymerization with PtBA−DBN should be more serious than that in the styrene polymerization with PS−TEMPO at the same temperature. (The decomposition rate is essentially independent of the concentration of free nitroxyl.[16] However, the monomer can exert a “solvent effect” on k_{dec},[15] so that k_{dec} in the actual polymerization system can be somewhat different from that in the model system.)

Determination of k_{act}. Now we turn to another main subject of this paper. We have attempted to determine the activation rate constant k_{act} of this system by the GPC “curve-resolution” method.[3] This method is based on the GPC observation of an early stage of the polymerization containing a probe adduct $P_0{-}X$: when the $P_0{-}X$ bond is dissociated, the produced radical P_0* will undergo propagation until it is deactivated again by the X* radical 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. What is important in this method is to accurately follow the devolution of the concentration of $P_0{-}X$: k_{act} can be determined from the first-order plot

$$\ln(S_0/S) = k_{act}t \tag{4}$$

where S_0/S is the ratio of the $P_0{-}X$ concentration at time zero to that at time t. It has been shown that lowering the original concentration of $P_0{-}X$ and increasing the stationary rate of polymerization (by adding a radical initiator like DCP) are effective in enhancing the resolution of the GPC peaks of $P_0{-}X$ and other components. In this regard, there are optimum concentrations of $P_0{-}X$ and DCP to be used in these experiments.

The PtBA−DBN adduct (M_n = 2100 and M_w/M_n = 1.29) was used as a probe polymer $P_0{-}X$. $P_0{-}X$ (15 mM) and DCP (1 mM) were dissolved in tBA and heated at 120 °C for a prescribed time t. Figure 8 shows the GPC trace of the solution quenched at t = 4 min. It comprises two well-separated peaks. Clearly, the lower molecular weight peak is due to (undissociated) $P_0{-}X$, and the higher molecular weight one includes $P_1{-}X$ and all other minor components stemming from the decomposition of DCP and further activation of $P_1{-}X$. Figure 9 shows the plot of $\ln(S_0/S)$ vs t. Since $P_0{-}X$ contains 7% of potentially inactive species (see above), we have corrected the experimental data by subtracting $0.07S_0$ from both S_0 and S in eq 4. (Incidentally, the 7% of inactive species is composed partly of a few percent of

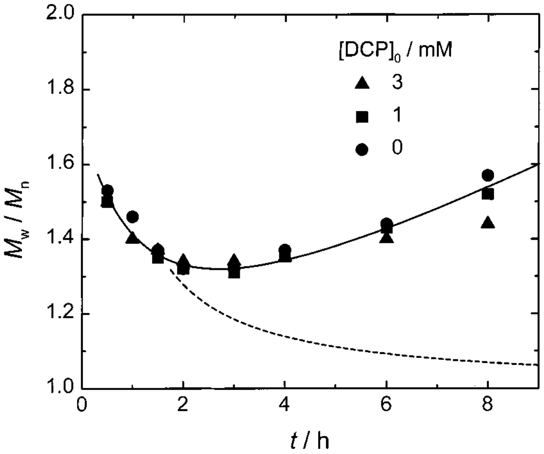

Figure 10. Plot of M_w/M_n vs polymerization time t. The broken line shows eq 5, and the solid line is an aid for the eye; for symbols and experimental conditions, see Figure 3.

terminally unsaturated species, as is observed in the ^{1}H NMR spectrum, Figure 4, at about 5.8 and 6.7 ppm.) As Figure 9 shows, the plot is linear passing through the origin, and its slope gives $k_{act} = 1.0 \times 10^{-3}$ s^{-1}.

This value of k_{act} happens to be the same as the k_{act} value of 9.9×10^{-4} s^{-1} for the PS−TEMPO system at the same temperature.[3b] (For the PS−TEMPO system,[3a] k_{act} has been shown to be identifiable with k_d, the rate constant of thermal homolysis, and the degenerative transfer[1c] plays no detectable role. This would also be the case with the PtBA−DBN system.) The PS−TEMPO system is known to provide low-polydispersity polymers (M_w/M_n < 1.2). The fact that the PtBA−DBN system does not give so low-polydispersity polymers as the PS−TEMPO system is, therefore, ascribed to the larger rate constant of decomposition in the former system than in the latter. If this is the case, the polydispersity in the PtBA−DBN system should be determined essentially by polymerization time, since both the activation and decomposition in this system are first-order reactions. Figure 10 shows the plot of M_w/M_n vs time for the PtBA polymers given in Figure 3. As expected, all the data points for different DCP concentrations (different conversions for common t) fall on the same curve, showing that other reactions such as chain transfer and radical−radical termination, if any, have minor effects on the polydispersity of this system. The dotted line in the figure shows the value of M_w/M_n calculated with

$$M_w/M_n = 1 + (2/k_{act}t) + (1/x_n) \qquad (5)$$

which is valid for the "ideal" living system with a constant polymerization rate and no side reactions other than the activation, deactivation, and propagation reactions.[10] Deviations of the experimental points from the calculated curve are indeed more significant at larger polymerization time.

Conclusions

It was demonstrated that the polymerization rate of tBA in the presence of the alkoxyamine BS−DBN can be enhanced by the addition of a limited amount of radical initiator DCP without causing any appreciable broadening of polydispersities. The use of the nitroxide DBN allowed us to conduct a controlled polymerization at a relatively low temperature of 120 °C. The decomposition of the alkoxyamine into a terminally unsaturated compound and a hydroxyamine occurred to a rather serious degree, causing a decrease of the polymerization rate through the subsequent hydrogen transfer. Direct determination of k_{act} showed that a PtBA−DBN adduct will experience, during the course of polymerization, a sufficient number of activation−deactivation cycles to achieve as low a polydispersity as in the PS−TEMPO system. However, the observed M_w/M_n ratio showed a large deviation from what was expected from the k_{act} value alone, due to the mentioned decomposition of the alkoxyamine.

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