Macromolecules **1999,** *32,* 9051−9053

Notes

Lifetimes of Polystyrene Chains in Atom Transfer Radical Polymerization

Krzysztof Matyjaszewski[†]

Department of Chemistry, Carnegie Mellon University,
4400 Fifth Ave., Pittsburgh, Pennsylvania 15213

Received July 15, 1999
Revised Manuscript Received October 26, 1999

Atom transfer radical polymerization (ATRP) employs the reversible transfer of halogen atoms between growing chains and a redox active transition metal catalyst.[1−3] In the key reaction, macromolecular alkyl halides are activated (k_a) by reduction to free radicals and transition metals are simultaneously oxidized by accepting the halogen atom to its inner coordination sphere.[4] The free radicals generated are involved in three major reactions (neglecting other reactions such as transfer, etc., to simplify the analysis):

1. They can reversibly abstract a halogen atom from the oxidized form of transition metals and convert themselves to dormant alkyl halides. This is the deactivation process (k_d).
2. They can react with monomer, i.e., propagate (k_p).
3. They can terminate (k_t) by recombination or disproportionation.

The relative proportion of these three processes determines the degree of control exhibited by the ATRP process and therefore also the polymers obtained.[5−7]

Polymerization of styrene initiated by 1-phenylethyl bromide and catalyzed by CuBr/2dNbpy (dNbpy: 4,4′-di(5-nonyl)-2,2′-bipyridine) is perhaps the most detailed ATRP system studied.[8] At 110 °C, using 1 mol % of both initiator and catalyst, approximately 30% monomer conversion is reached after 1 h. Molecular weights are close to theoretical, indicating quantitative initiation and insignificant transfer, and polymers with polydispersities close to the Poisson distribution, $M_w/M_n = 1.04$, are obtained.[9] All of these facts indicate satisfactory control of polymerization.

Scheme 1 presents the plausible mechanistic steps involved in the ATRP of styrene with the CuBr/dNbpy catalytic system. The role of the dormant species is played by the macromolecular alkyl halides with the chemical structure resembling the initiator, i.e., 1-phenylethyl bromide. The active species is presumably a polystyryl free radical. The activator may be best represented by the distorted tetrahedral complex of Cu(I) cation ligated by two bipyridine molecules. Such complexes have been well characterized in the solid state by X-ray crystallography.[10] It is, however, possible that in solution the structure of the activator may be more complex. The deactivator may be represented by the trigonal bipyramidal complex of the Cu(II) cationic species with two bipyridine molecules and one halogen atom. Again, the actual structure of the complex in nonpolar media may be different, as has been discussed before.[11−13]

The rate constants of the elementary reactions indicated in Scheme 1 have been determined in the following manner.

1. Activation. The rate constant of activation has been directly measured by conversion of the low molar mass Br-terminated polystyrene to high molar mass polymer in the presence of CuBr/2dNbpy under conditions when concentration of deactivator was very low. At 110 °C, the bimolecular rate constant of activation was $k_a = 4.5 \times 10^{-1}$ mol^{-1} L s^{-1}.[14]

2. Deactivation. The rate constant has been calculated from either the evolution of polydispersities with conversion, or from the overall rate of polymerization, provided that the concentration of the Cu(II) species is known. The latter has been either measured directly by electron paramagnetic resonance (EPR)[15] or excess Cu(II) has been added in the amount which exceeds that formed spontaneously via persistent radical effect.[8]

(a) Evaluation of k_d from polydispersity is based on the following equation:

$$M_w/M_n = 1 + \{(k_p[RX]_0)/(k_d[X{-}Cu^{II}])\}(2/(p - 1))$$

Polydispersity decreases with the ratio of propagation to deactivation rate constants, with the concentration of Cu(II) species, with conversion, p, and also with the chain length (which is reciprocally correlated with $[RX]_0$).

(b) Evaluation from the rate of polymerization is based on the following equation:

$$R_p = k_p[M][RX]_0 k_a[Cu^I]/(k_d[X\text{-}Cu^{II}])$$

The rate of polymerization increases with the rate constants of activation and propagation and the concentration of initiator and activator, and it depends reciprocally on the deactivation rate constant and concentration of deactivator.

The deactivation rate constant calculated using both methods were in a fairly good agreement providing a value $k_d = 1.1 \times 10^7$ mol^{-1} L s^{-1} at 110 °C. This value is very large but significantly smaller than diffusion-controlled.[14]

3. Monomer Addition. The propagation rate constant has been measured by pulsed laser polymerization (PLP), EPR and rotating sector techniques and can be extrapolated to 110 °C to $k_p = 1.6 \times 10^3$ mol^{-1} L s^{-1}.[16] This value should not be strongly chain length dependent. It is assumed here that propagation in ATRP and other controlled radical polymerizations involves free radicals.

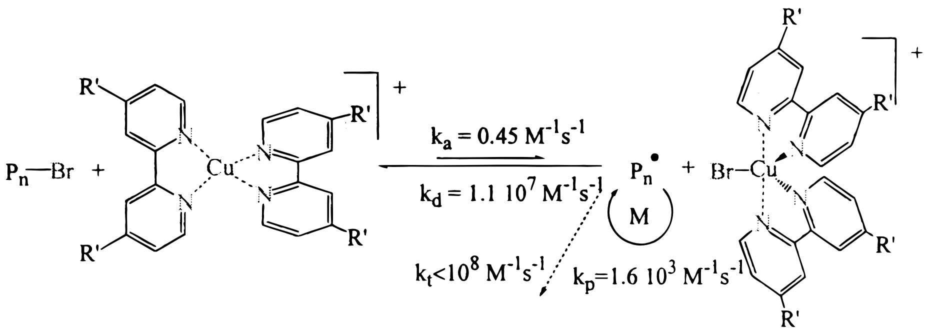
4. Termination. Two benzyl and 1-phenylethyl radicals terminate with diffusion-controlled rates ($k_t > 10^9$ mol^{-1} L s^{-1}).[17] However, with the progress of the

---

[†] E-mail: km3b@andrew.cmu.edu.

10.1021/ma991145x CCC: $18.00

Scheme 1



reaction, the termination rate coefficient (which is a better description than the rate constant since it continuously changes) is strongly reduced due to increasing chain length and increasing viscosity (less monomer = solvent, more polymer and higher molecular weight). The values of the termination rate coefficients drop continuously but they reach a level around $k_t \approx 10^8$ mol^{-1} L s^{-1} at 30% conversion.[18] It is worth noting that in ATRP after a certain conversion only termination between long chains can happen because all low molar mass radicals are consumed to form polymeric chains. This is in contrast to conventional radical polymerization where short–short and long–short terminations dominate, meaning that growing chains are terminated by the continuously generated initiator/oligomeric radicals.[19]

Molecular Events in Styrene ATRP. It is interesting to have a closer look at what happens to an average chain end in the ATRP of styrene. The following analysis describes the average lifetimes of the major reactions involved in ATRP. The time interval between two consecutive events is the reciprocal value of the unimolecular rate constants ($\tau = 1/k_1$) or the reciprocal value of the products of the bimolecular rate constants and the concentration of the reagents involved ($\tau = 1/[C]k_2$). The time interval for an average event determines the time needed for approximately half of chains to be involved (more precisely 63%, i.e. 1 − 1/e).

Because the monomer concentration continuously decreases and the deactivator concentration slightly increases during polymerization, we will take a “snapshot” at approximately 30% monomer conversion when

$$[M] \approx 5\ M$$

$$[P_n{-}Br] \approx 0.1\ M$$

$$[Cu^{I}Br/2dNbpy] \approx 0.1\ M$$

$$[Cu^{II}Br_2/2dNbpy] \approx 0.005\ M$$

$$[P_n{*}] \approx 10^{-7}\ M$$

The concentrations of dormant chains and activator are within 5% of their initial values. The concentration of the deactivating Cu(II) species has been measured directly by EPR.[15] The concentration of growing radicals is easily accessible from the overall propagation rate and k_p ($[P*] = d(\ln[M])/k_p\,dt$).[8]

Using these concentrations and the rate constants presented in the previous section, the average time of the following events can be calculated.

1. Activation. The time separating two average activation steps (periodicity) is the reciprocal of the product of activation rate constant and concentration of the activator:

$$\tau_a = 1/(k_a\ [Cu^{I}Br/2dNbpy]) = 22\ s$$

2. Deactivation. The periodicity of deactivation is the reciprocal of the product of deactivation rate constant and concentration of the deactivator:

$$\tau_d = 1/(k_d[Cu^{II}Br_2/2dNbpy]) = 0.018\ ms$$

3. Propagation. The time between two propagation acts is the reciprocal of the product of propagation rate constant and concentration of the monomer:

$$\tau_a = 1/(k_p[M]) = 0.12\ ms$$

Thus, propagation is 6 times slower than deactivation, meaning that six activation–deactivation cycles occur on the average before the incorporation of one monomer unit, indicating that every chain will grow with a frequency of 2 min per unit. This process will become progressively slower with conversion, since [M] will be reduced.

4. Termination. The time for an average termination step is the reciprocal of the product of the termination rate coefficient and the concentration of the radicals:

$$\tau_a = 1/(k_t[P*]) = 0.1\ s$$

Thus, termination is 800 times slower than propagation, meaning that on the average chains would die after 1600 min, i.e., 27 h. However, this value should increase with conversion, because the termination rate coefficient will decrease with increasing chain length and viscosity. It is important to note that the definition of an average chain indicates time at which approximately half of all chains would die. The real time would be even longer, due to a buildup of Cu(II) species and decrease of the concentration of dormant/growing chains. Of course, chains terminate continuously.

Thus, a typical picture of the ATRP of styrene can be briefly described as follows. At the very beginning of the polymerization a large number of radicals are generated and terminate very quickly, resulting in the loss of approximately 5% of chains and the formation of 5% of Cu(II) species from the initial Cu(I) species. This buildup of Cu(II) species leads to the decrease of radical concentration, very fast deactivation, and a significant reduction of termination. When 30% monomer conversion is reached, then an average chain is activated ("wakes up") every 22 s. However, it is nearly immediately deactivated ("goes back to sleep") after 0.018 ms. Since propagation is six times slower than deactivation, i.e., 0.12 ms vs 0.018 ms, six activation–deactivation cycles are required for the average addition of one monomer unit. Thus, the effective monomer addition on the average occurs every 2 min, meaning that more than 3 h would be needed for the formation of a polymer with DP = 100. In fact, longer times are needed to reach such a DP because the frequency of propagation decreases with monomer conversion. It has to be recognized that although six activation deactivation cycles occur between two propagation acts, during 0.018 ms a radical collides many times with solvent or monomer molecules. It may recombine not with the same deactivator molecule it was formed with but with another one, as evidenced by the efficient halogen exchange reactions.[20] Therefore, polymerization proceeds via free radicals and not via insertion mode and chemo-, regio-, and stereoselectivities are close to those in free radical polymerization.[4] Termination between two growing radicals on the average occurs every 0.1 s, i.e., 800 times slower than propagation. Thus, an average chain would die after 30 h, meaning that at that time approximately half of all chains would terminate. Again, this time should increase with the progress of the reaction due to the reduction of the termination rate coefficient with the length of growing chains, increase of viscosity, a buildup of Cu(II) species, and reduction of the concentrations of dormant/growing chains.

Similar calculations for polymerization of methyl acrylate based on the kinetic data, the evolution of polydispersities with conversion,[12] and the concentrations of Cu(II) species measured by EPR[21] lead to an entirely different picture due to much higher values of the propagation rate constants.[22] In this case, at [M] = 5 M, approximately 14 monomer molecules are incorporated during one activation/deactivation cycle.

The presented picture is obviously oversimplified and does not take into account other chain-breaking reactions such as transfer to monomer and some additional termination reactions that limit the chain growth. However, it describes in a simple fashion the dynamics of ATRP process and provides a feeling for the extent and significance of the basic reactions that occur during polymerization for those not directly in the field.

Acknowledgment. Partial support from the National Science Foundation and ATRP Consortium is acknowledged.

References and Notes

(1) Matyjaszewski, K. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998; Vol. 685, p 258.

(2) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(4) Matyjaszewski, K. *Macromolecules* **1998**, *31*, 4710.

(5) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.

(6) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.

(7) Matyjaszewski, K. *Chem.—Eur. J.* **1999**, *5*, 3095.

(8) Matyjaszewski, K.; Patten, T.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

(9) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(10) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McClaverty, J. A., Eds; Pergamon: Oxford, England, 1987; Vol. 5, p 533.

(11) Wang, J. L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 6507.

(12) Davis, K. A.; Paik, H. J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 1767.

(13) Kickelbick, G.; Reinohl, U.; Ertel, T. S.; Bertagnolli, H.; Matyjaszewski, K. *ACS Polym. Prepr.* **1999**, *40* (2), 334. EXAFS studies indicate that in nonpolar solvents the Cu(I)/bpy$_2$ cation is accompanied by a Cu^{I}X$_2$ anion. In such a case the rate constant of activation may be twice as large as that reported in ref 14, and the amount of activator twice as small as the [Cu(I)] species originally used. Nevertheless, under such conditions the rate of activation and lifetimes remain the same. Reactivity of the anion is much lower than that of the cation which can be solely responsible for the activation process (cf. ref 8).

(14) Ohno, K.; Goto, A.; Fukuda, T.; Xia, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 2699.

(15) Kajiwara, A.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 548.

(16) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.

(17) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.

(18) Shipp, D. A.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2948.

(19) Russell, G. T. *Macromol. Theory Simul.* **1994**, *3*, 439.

(20) Shipp, D. A.; Wang, J.-L.; Grimaud, T.; Matyjaszewski, K. *Polym. Prepr.* **1998**, *39* (2), 504.

(21) Kajiwara, A.; Matyjaszewski, K. *Polym. J.* **1999**, *31* (1), 70.

(22) Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 9, 1918.

MA991145X