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**Controlled Synthesis
of Functional Polymers**



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*Invited lectures presented at the
39th Microsymposium
of the Prague Meetings on Macromolecules
held in Prague, Czech Republic
July 12–15, 1999*

Symposium Editor

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Preface

The microsymposium "Advances in Polymerization Methods. Controlled Synthesis of Functionalized Polymers" was the 39th in the series of the Prague Meetings on Macromolecules organized since 1967. The microsymposium devoted to the tailoring of polymers tried to bring together experts dealing with controlled polymerizations of all kinds regardless of the character of the growing chain-end. Thus, anionic, cationic, and radical processes were discussed leading to polymers with tailored structure and properties and bearing reactive groups. The main topics covered were: (i) Tailoring of polymers by ionic living systems, (ii) Controlled free-radical polymerization, (iii) Synthesis of functionalized polymers by initiation and termination methods and by chemical modification of polymers, and (iv) Characterization and application of functionalized polymers. It was shown that both the ionic (R.P. Quirk) and radical (K. Matyjaszewski) methods can offer the desired products; none of them, however, is generally applicable and each method has its advantages and drawbacks (P. Lutz). Several lecturers presented the utilization of appropriate combinations of polymerization methods giving polymers and copolymers of new structures, thus demonstrating potentials of controlled polymerization and stimulating new research initiatives.

An effort was made to include specialists from various parts of the world (127 participants from 29 countries); also young scientists were encouraged to participate in the meeting. The scientific program consisted of 9 invited (main) lectures presented by top experts in various fields, 23 short (special) presentations and 61 posters. Most of the oral contributions are included in the present volume reflecting both the quality and diversity of the meeting and giving a brief overview for those interested in the field.

The organizers of the microsymposium wish to express their gratitude to the sponsoring companies: Unipetrol, Inc., Czech Republic; Sigma-Aldrich Ltd., Czech Republic; Eastman Chemical Europe, B.V., United Kingdom; Bayer A.G., Germany; and Exxon Chemical Europe, Belgium.

Petr Vlček

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Advances in Polymerization Methods. Controlled Synthesis of Functionalized
Polymers
Prague, Czech Republic, 1999**

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Molecular Events in Atom Transfer Radical Polymerization of Styrene and Methyl Acrylate

Krzysztof Matyjaszewski

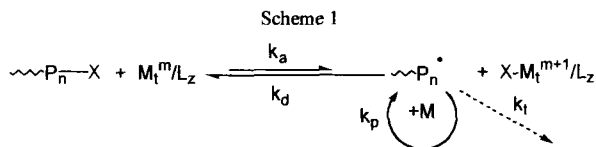
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SUMMARY: Typical reactions involved in the atom transfer radical polymerization (ATRP) are discussed and expressed as their frequencies in polymerization of styrene and methyl acrylate. In polymerization of styrene, several activation-deactivation cycles occur before one monomer unit is incorporated and termination between growing radicals occurs 800 times slower than propagation. In methyl acrylate polymerization, several monomer molecules are incorporated during each activation step resulting in broader molecular weight distribution than in styrene ATRP. Radical termination in methyl acrylate is even slower and occurs after 400 000 monomer additions.

Introduction

Atom transfer radical polymerization (ATRP) is one of the most efficient controlled radical polymerization (CRP) systems.¹⁾ ATRP employs a reversible transfer of the halogen atom between growing chains and a redox-active transition metal catalyst.²⁻⁴⁾ In the key reaction, macromolecular alkyl halides are activated (k_a) by reduction to the free radicals and transition metal complexes (M_t^m/L_z) are simultaneously oxidized by accepting halogen atom to its inner coordination sphere. The generated free radicals are involved in three major reactions shown in Scheme 1 (other reactions such as transfer are neglected to simplify the analysis):

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



The relative proportion of these three processes determines the degree of control of ATRP process and of the obtained polymers.^{5,6)}

A variety of monomers have been polymerized successfully by ATRP. They include substituted styrenes,⁷⁾ acrylates,⁸⁾ methacrylates,⁹⁾ acrylonitrile,¹⁰⁾ vinylpyridine¹¹⁾ and many others. As initiators, typically alkyl halides and pseudohalides are used.⁵⁾ A list of suitable transition metals includes Cu, Fe, Ru, Ni, Pd and some others.⁵⁾ Most often, transition metal halides are used but other salts and organometallic derivatives have been also successfully applied.¹⁾ The ligands play a crucial role in ATRP because they strongly affect thermodynamics and dynamics of the ATRP equilibrium and assure proper solubility of metal complexes.¹¹⁾

Bulk ATRP of Styrene at 110 °C

The results of bulk ATRP of styrene initiated with 1-phenylethyl bromide are depicted in Figs 1 and 2.

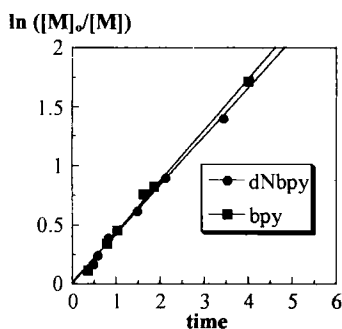


Fig. 1. Kinetics of bulk ATRP of styrene at 110 °C with 1 mol-% of 1-phenylethyl bromide and 1 mol-% of CuBr/2dNbpy or CuBr/2bpy.

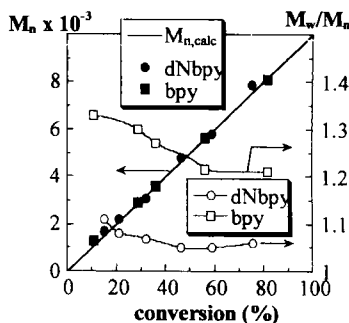


Fig. 2. Evolution of molecular weights and polydispersities with conversion for bulk ATRP of styrene. (For conditions, see Fig. 1.)

This polymerization catalyzed by CuBr/2dNbpy (dNbpy = 4,4'-di(nonan-5-yl)-2,2'-bipyridine) is perhaps the most carefully studied ATRP system.¹²⁾ 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 ($M_{n,calc} = \Delta[M]/[I]_0$), indicating quantitative initiation and insignificant transfer; polymers with polydispersities close to the Poisson distribution $M_w/M_n = 1.04$ are obtained.¹³⁾ All of these facts indicate satisfactory control of polymerization.

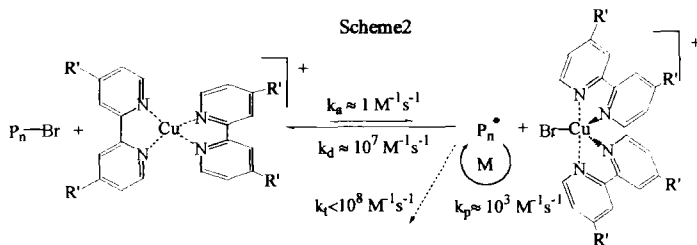
It has to be noticed that under these conditions, approximately 5 % of initiator chains have been involved in termination as evidenced by the spontaneous formation of 5 % of Cu(II) species. This species has been directly observed by EPR.¹⁴⁾ The presence of the small amount

of Cu(II) species is necessary in order to reduce the concentration of radicals and accelerate the deactivation process.

When unsubstituted 2,2'-bipyridine was used instead of dNbpy, higher polydispersities were observed due to the limited solubility and lower concentration of Cu(II) species in solution¹⁵⁾.

Kinetics of Styrene ATRP

Scheme 2 presents the plausible mechanistic steps involved in ATRP of styrene with the CuBr/dNbpy catalytic system. The role of the dormant species is played initially by the 1-phenylethyl bromide as initiator and subsequently by the corresponding macromolecular alkyl halides. The active species are presumably free radicals: 1-phenylethyl and polystyryl, respectively. 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.¹⁶⁾ It is, however, possible that in solution, the structure of the activator may be more complex. The deactivator may be best 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 non-polar media may be different, as already discussed before.^{8,17)} The rate constants of the elementary reactions depicted in Scheme 2 have been determined in the following way:

1. *Monomer addition.* The rate constants of addition of benzyl and cumyl (and presumably 1-phenylethyl) radicals to styrene have been measured and they are approximately 10 times higher than the propagation rate constant.¹⁸⁾ The latter has been measured by pulse laser polymerization, EPR and also by the rotating sector techniques and can be extrapolated to 110 °C giving $k_p = 1.6 \cdot 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$ (ref.¹⁹⁾). This value should not be strongly chain-length-dependent. It is assumed here that propagation in ATRP and other CRPs involves free radicals.

2. *Termination.* Two benzyl and 1-phenylethyl radicals terminate with diffusion-controlled rates ($k_t > 10^9 \text{ mol}^{-1}\text{Ls}^{-1}$).²⁰⁾ However, with the reaction progressing, the termination rate coefficient (perhaps a better term than the rate constant, since it continuously changes) is strongly reduced due to increasing chain length and increasing viscosity (less monomer acting as a solvent, more polymer of high molecular weight). The value of the termination rate coefficient drops continuously but it reaches a level around $k_t = 10^8 \text{ mol}^{-1}\text{Ls}^{-1}$ at 30 % conversion.²¹⁾ It is worth noting that in ATRP, after a certain conversion, only termination between long chains can happen. This is in contrast to conventional radical polymerization where short-short and long-short terminations predominate, meaning that growing chains are terminated by continuously generated initiating and oligomeric radicals.

3. *Activation.* The rate constant of activation has been directly measured by conversion of the low-molecular-weight bromine-terminated polystyrene to high-molecular-weight polymer in the presence of CuBr/2dNbpy under conditions where concentration of deactivator was very low. At 110 °C, the bimolecular rate constant of activation was $k_a = 4.5 \cdot 10^{-1} \text{ mol}^{-1}\text{Ls}^{-1}$ (ref.²²⁾).

4. *Deactivation.* The rate constant k_d can be calculated from either the evolution of polydispersities with conversion or the overall rate of polymerization, provided that the concentration of Cu(II) species is known. The latter has been measured directly by EPR or an excess Cu(II) has been added in the amount which exceeded that formed spontaneously via persistent radical effect.

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

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

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 $[\text{RX}]_0$).

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

$$R_p = (k_p [\text{M}] [\text{RX}]_0 k_a [\text{Cu}^{\text{I}}]) / (k_d [\text{X-Cu}^{\text{II}}]) \quad (2)$$

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

The values of the deactivation rate constant calculated using both methods were in a fairly good agreement providing a value $k_d = 1.1 \cdot 10^7 \text{ mol}^{-1}\text{Ls}^{-1}$ at 110 °C. This value is very large but significantly smaller than the diffusion-controlled one.²²⁾

Molecular Events in Styrene ATRP

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

Because in polymerization, concentration of monomer continuously decreases and concentration of deactivator slightly increases, we will take a "snap-shot" at approximately 30 % monomer conversion when $[M] \approx 5 \text{ M}$, $[P_n\text{-Br}] \approx 0.1 \text{ M}$, $[Cu^I\text{Br}/2dNbpy] \approx 0.1 \text{ M}$, $[Cu^{II}Br_2/2dNbpy] \approx 0.005 \text{ M}$, $[P_n^*] \approx 10^{-7} \text{ M}$.

The concentrations of alkyl halide and Cu(I) do not change much during the reaction. The concentration of Cu(II) has been measured directly by EPR. The concentration of growing radicals is easily accessible from the overall propagation rate and k_p ($[P_n^*] = \ln[M]/k_p dt$). Using these concentrations and the rate constants presented in the previous section, the frequency or time intervals of the following events can be calculated:

1. *Activation.* The periodicity of activation is the reciprocal of the product of the activation rate constant and the concentration of the activator: $\tau_a = 1 / (k_a [Cu^I\text{Br}/2dNbpy]) = 22 \text{ s}$.

2. *Deactivation.* The periodicity of deactivation is the reciprocal of the product of the deactivation rate constant and the concentration of the activator: $\tau_d = 1 / (k_d [Cu^{II}Br_2/2dNbpy]) = 0.018 \text{ ms}$.

3. *Propagation.* The periodicity of propagation is the reciprocal of the product of the propagation rate constant and the concentration of the monomer: $\tau_p = 1 / (k_p [M]) = 0.12 \text{ ms}$.

Propagation is six times slower than deactivation, meaning that six activation-deactivation cycles are necessary for the incorporation of one monomer unit and indicating that every chain will grow with a time interval of 2 min per unit. This value progressively increases with conversion, since $[M]$ will be reduced.

4. *Termination.* The periodicity of termination is the reciprocal of the product of the termination rate coefficient and the concentration of the radicals: $\tau_t = 1 / (k_t [P^*]) = 0.1 \text{ s}$. Termination is 800 times slower than propagation, meaning that, on average, chains will die after 30 h. This value should extend 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 the time at which half of all chains would die. The real time when half of chains would die will be even longer, due to a build-up of Cu(II) species and decrease in the concentration of dormant/growing chains. Clearly, chains will be terminating continuously.

Thus, a typical picture of the ATRP of styrene can be briefly described as follows. At the very beginning of polymerization, many 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 initial Cu(I) species. This build-up of Cu(II) species leads to very fast deactivation and the significant reduction of termination rate. When 30 % monomer conversion is reached, then an average chain is activated ("wakes up") every 20 s. However, it is nearly immediately deactivated ("goes back to sleep") after 0.018 ms. Since propagation is six times slower than deactivation (0.12 ms vs. 0.018 ms), six activation-deactivation cycles are required for the average addition of 1 monomer unit. Thus, effective monomer addition occurs every 2 min, meaning that 2 h would be needed for the formation of a polymer with $DP = 100$. In fact, longer times are needed to reach such DP, because the rate of propagation decreases with monomer conversion. Termination between two growing radicals occurs every 0.1 s, i.e., 800 times slower than propagation. Thus, an average chain will die after 30 h, meaning that at that time approximately half of all chains would terminate. 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 in viscosity, a build-up of Cu(II) species and reduction of the concentrations of dormant/growing chains.

This picture is obviously oversimplified and does not take into account other chain-breaking reactions such as transfer to monomer and some additional termination reactions which limit the chain growth.

Polymerization of Methyl Acrylate

ATRP of methyl acrylate has not yet been as precisely studied as that of styrene. It also appeared to be much more dependent on the structure of counterion, solvent and temperature.⁸⁾ Nevertheless, one can attempt to estimate the periodicity of similar molecular events as discussed above for styrene:

1. *Monomer addition.* Neither the rate constants of addition for propionate radicals nor the propagation rate constants are precisely known. However, we can reasonably assume that the propagation rate constant for methyl acrylate should be similar to that for butyl acrylate, the latter can be extrapolated to 90 °C giving $k_p = 5 \cdot 10^4 \text{ mol}^{-1} \text{Ls}^{-1}$.²³⁾ The similarities of the

propagation rate constants of all methacrylates, and in particular methyl and butyl esters have been reported before²⁴⁾.

2. *Termination.* It can be assumed that the termination rate coefficients for styrene and methyl acrylate will be decreasing with conversion continuously and they both may reach a level $k_t \approx 10^8 \text{ mol}^{-1}\text{Ls}^{-1}$ at 30 % conversion.²¹⁾

3. *Deactivation.* The rate constant can be calculated from evolution of polydispersities with conversion if the concentration of Cu(II) species is known. The latter has been measured directly by EPR to be in the range of 3 mol-% from initial Cu(I) species.²⁵⁾ Values of k_d for MA were evaluated from the dependence of polydispersities on conversion reported in ref.⁸⁾, and using the above values of [Cu(II)] species and reported k_p for butyl acrylate. The experiment with concentrations of [methyl 2-bromopropanoate] = [CuBr/2dNbpy] = 0.028 M was analyzed. Using Eq. (1), the estimated value of $k_d \approx 2 \cdot 10^7 \text{ mol}^{-1}\text{Ls}^{-1}$ was obtained. It is slightly higher than for styrene in spite of lower temperature.

4. *Activation.* The rate constant of activation for MA has not yet been directly measured. However, it can be estimated from the value of the deactivation rate constant and the equilibrium constant:

$$K = k_a/k_d = ([P^*] [Cu(II)]) / ([P-X] [Cu(I)]) \quad (3)$$

The concentration of propagating radicals $[P^*]$ has been calculated to be equal to $\approx 0.7 \cdot 10^8 \text{ M}$, leading to the equilibrium constant $K \approx 7 \cdot 10^9$. Using this value and the deactivation rate constant $k_d \approx 2 \cdot 10^7 \text{ mol}^{-1}\text{Ls}^{-1}$, the rate constant of activation was estimated as $k_a \approx 1.5 \cdot 10^{-1} \text{ mol}^{-1}\text{Ls}^{-1}$, three times smaller than in styrene polymerization. It has to be mentioned that EPR measurements were performed under similar concentrations but in 50% solution in diphenyl ether. Apparently, experiments done in bulk MA, in the presence of the added excess of Cu(II) species lead to a smaller value of the equilibrium constant and, consequently, would result in a smaller values of $k_a \approx 0.3 \cdot 10^{-1} \text{ mol}^{-1}\text{Ls}^{-1}$. Because these values have not yet been measured directly, we use a value $k_a \approx 1 \cdot 10^{-1} \text{ mol}^{-1}\text{Ls}^{-1}$.

Molecular Events in ATRP of Methyl Acrylate

Using a similar approach to that for styrene ATRP, we may evaluate the frequencies of all molecular events in ATRP of methyl acrylate. The following concentrations are used:

$[M] \approx 5 \text{ M}$, $[P_n\text{-Br}] \approx 0.03 \text{ M}$, $[\text{Cu}^{\text{I}}\text{Br}/2\text{dNbpy}] \approx 0.03 \text{ M}$, $[\text{Cu}^{\text{II}}\text{Br}_2/2\text{dNbpy}] \approx 0.0009 \text{ M}$,
 $[P_n^*] \approx 7 \cdot 10^{-9} \text{ M}$.

1. *Activation*. $\tau_a = 1 / (k_a [\text{Cu}^{\text{I}}\text{Br}/2\text{dNbpy}]) = 330 \text{ s}$.

2. *Deactivation*. $\tau_d = 1 / (k_d [\text{Cu}^{\text{II}}\text{Br}_2/2\text{dNbpy}]) = 0.05 \text{ ms}$.

3. *Propagation*. $\tau_p = 1 / (k_p [M]) = 0.004 \text{ ms}$. Propagation for MA is 14 times *faster* than deactivation, in contrast to styrene ATRP. This is due to both larger k_p and smaller $[\text{Cu(II)}]$.

4. *Termination*. $\tau_t = 1 / (k_t [P^*]) = 1.4 \text{ s}$. Termination is 350 000 times slower than propagation, meaning that an average chain will die after 100 days.

Thus, a typical picture of the ATRP of methyl acrylate can be briefly described as follows. At the very beginning of polymerization, radicals terminate very fast resulting in the loss of approximately 2-3 % of chains and formation of 2-3 % of Cu(II) species from the initial Cu(I) species. This leads to faster deactivation and reduction in radical concentrations and, consequently, to a slower termination rate. When the 50 % monomer conversion is reached, then an average chain is activated every 300 s (15 times slower than for styrene). It is deactivated after 0.05 ms (three times slower than in styrene). Now propagation is 14 times faster than deactivation (0.004 ms vs. 0.05 ms). Thus, 14 monomer units are added during each activation-deactivation cycle. This value is 80 times larger than for styrene and explains larger polydispersities observed for acrylates at low conversions. Termination between two growing radicals occurs every 1.4 s, i.e., 350 000 times slower than propagation. This indicates that most Cu(II) species must be formed during early stages when termination coefficients are much larger.²⁵⁾ Therefore, termination in acrylate polymerization can be largely neglected at least for growing macromolecular chains, enabling synthesis of well-defined stars, densely grafted brushes and other well-defined macromolecular structures.²⁶⁻²⁸⁾

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