Macromol. Symp. ***195***, *25–31 (2003)*

Controlling Polymer Structures by Atom Transfer Radical Polymerization and Other Controlled/Living Radical Polymerizations

Krzysztof Matyjaszewski

Carnegie Mellon University, Department of Chemistry
4400 Fifth Ave., Pittsburgh, PA 15213, U.S.A.

Summary: Fundamentals of controlled/living radical polymerization (CRP) and Atom Transfer Radical Polymerization (ATRP), relevant to the synthesis of controlled polymer structures are described. Macromolecular brushes with star like structure are used as an example to illustrate synthetic power of ATRP.

Keywords: Atom transfer radical polymerization (ATRP); controlled/living radical polymerization; CRP; molecular brushes; star polymers

Introduction

The advent of controlled/living radical polymerization (CRP) enables preparation of many new materials such as well-defined components of coatings (with narrow MWD, precisely controlled functionalities and reduced VOCs), non ionic surfactants, polar thermoplastic elastomers, entirely water soluble block copolymers (agents for crystal engineering), gels and hydrogels, lubricants and additives, surface modifiers, hybrids with natural and inorganic polymers, various biomaterials and electronic materials. This is very important since free radical polymerization is the most common method of making polymeric materials (nearly 50% of all polymers are made this way). [1] This is due to the large number of available vinyl monomers which can be easily homopolymerized and copolymerized. Reaction conditions are undemanding and only

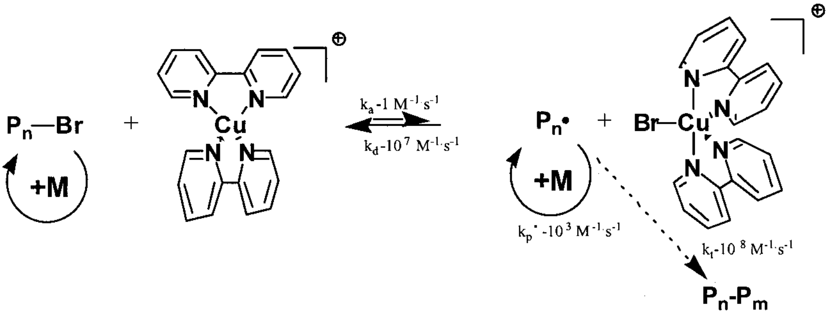
CCC 1022-1360/00/$ 17,50+.50/0

require moderate heating, deoxygenation and are tolerant to moisture and any protic impurities.

The controlled/living systems are quite similar to the conventional ones, however, the radical formation is reversible. Similar values for the equilibrium constants during initiation and propagation, ensure that the initiator is consumed at the early stages of the polymerization, generating chains which slowly and continuously grow, like in a living process. Currently three systems seem to be most efficient: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes such as RAFT.[2] Each of the CRPs has some limitations and some special advantages and it is expected that each technique may find special areas where it would be best synthetically suited. For example, NMP carried out in the presence of bulky nitroxides cannot be applied to the polymerization of methacrylates due to fast β-H abstraction. ATRP can not yet be used for the polymerization of acidic monomers, which can protonate the ligands and complex with copper. RAFT is very slow for the synthesis of low MW polymers due to retardation effects and may provide branching due to trapping of growing radicals by the intermediate radicals. At the same time, each technique has some special advantages. Terminal alkoxyamines may act as additional stabilizers for some polymers. ATRP enables the synthesis of special block copolymers by utilizing a halogen exchange and has an inexpensive halogen at the chain end.[3] RAFT can be applied to the polymerization of many unreactive monomers, such as vinyl acetate.[4]

Fundamentals of ATRP

ATRP is based on the reversible transfer of an atom or group from a dormant polymer chain (R-X) to a transition metal (M_t^n/Ligand) to form a radical ($R^\cdot$), which can initiate the polymerization, and a metal-halide whose oxidation state has increased by one ($X\text{-}M_t^{n+1}$/Ligand); the transferred atom or group is covalently bound to the transition metal. A catalytic system employing copper (I) halides (M_t^n/Ligand) complexed with substituted 2,2'-bipyridines (bpy) has proven to be quite robust, successfully polymerizing styrenes, various (meth)acrylates, acrylonitrile and other monomers.[5, 6] Other metal centers have been used, such as ruthenium, nickel and iron based systems.[7, 8] Copper salts with various anions and polydentate complexing ligands were used, such as substituted bpys, pyridines, and linear polyamines. The rate constants of the exchange process, propagation and termination shown below refer to bulk styrene polymerization at 110 °C.

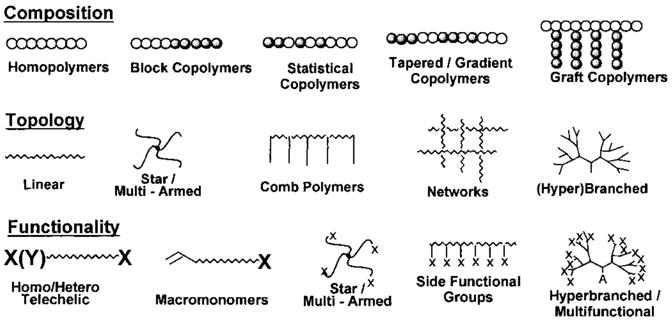


The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, Cu(I), and negative first order with respect to deactivator, XCu(II). However, the kinetics may be more complex due to the formation of XCu(II) species via PRE. The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variations of their structures and reactivities with concentrations and composition of the reaction medium. It should be also noted that the contribution of PRE at the initial stages might be affected by the mixing method, crystallinity of the metal compound and ligand, etc.

One of the most important parameters in ATRP is the dynamics of exchange, and especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [XCu(II)]. They, however, increase with the propagation rate constant, k_p, and the concentration of initiator, $[RX]_0$. This means that more uniform polymers are obtained at higher conversions, when the concentration of deactivator in solution is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive (e.g. copper(II) complexed by 2,2'-bipyridine or pentamethyldiethylenetriamine rather than by water) and monomer propagates slowly (styrene rather than acrylate).

Materials Made by ATRP and Other CRP Techniques

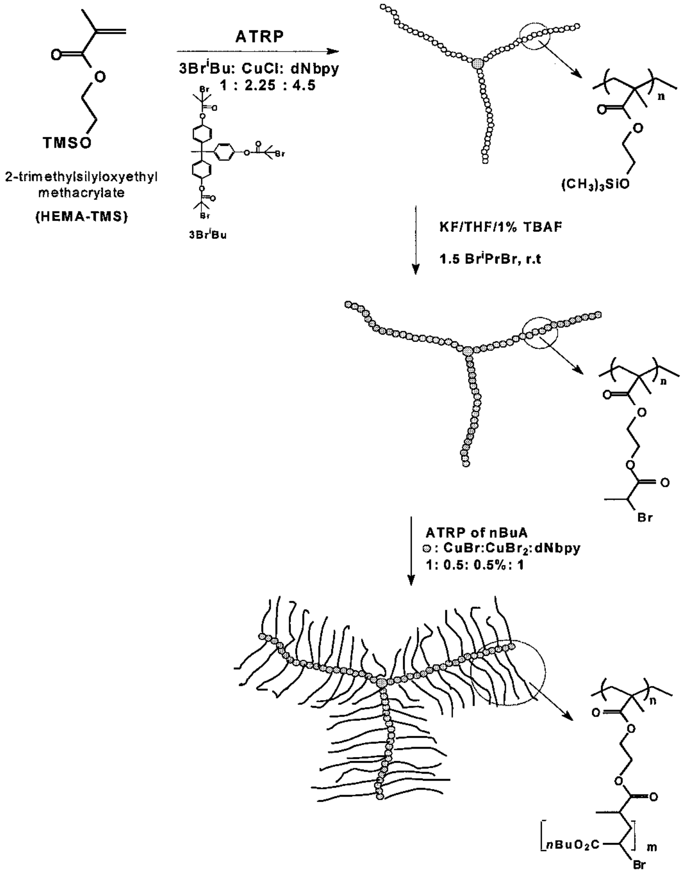
The most important benefit of controlled/"living" polymerizations is that they allow to prepare new macromolecules with novel topologies (linear, star, comb, (hyper)branched, networks, etc.), varying compositions (homopolymers, random, periodic, block, graft and gradient copolymers), and functionalities placed at different parts of macromolecules or various combinations of these.[9] Some of the possibilities are depicted below.



Star-Shaped Molecular Brushes by ATRP

Atom transfer radical polymerization (ATRP) is among the most efficient CRP methods and has been successfully applied to the synthesis of polymers with complex architectures such as stars[10, 11] and molecular brushes.[12, 13] Densely grafted molecular brushes are among the most intriguing macromolecular structures. These very large macromolecules can be prepared by grafting from, through and onto. ATRP has been successfully used to prepare molecular brushes with methacrylate backbones and polystyrene, various polyacrylates and polymethacrylate and poly(ethylene oxide) side chains. In addition, side chains with block copolymer structures and with a gradient density of grafting have been prepared.[14, 15] The length of the main chain has been varied from $DP_{MC}=100$ to 4,000 and side chains from $DP_{SC}<10$ to ~100. The molecular brushes are so large that they can be visualized as single molecules by AFM and in addition they are subject to various phase transitions induced by external stimuli, such as pressure.[16]

Non-linear brushes with a shape of three-arm stars may serve as an example of quite sophisticated molecular architecture. They have been prepared using the star-like backbone made by ATRP and subsequent grafting-from poly(n-butyl acrylate) by ATRP as shown below.



The SEC analysis of the functionalized backbone indicate M_n=83,000 and M_w/M_n=1.16. The former value is lower than the theoretical molecular weight assuming quantitative initiation for a controlled/living process. This may be due to a more compact structure of the three-arm star than the linear polymer. The value M_n=480,000 for the brush measured by SEC using liner polystyrene standards is obviously smaller than the value obtained by light scattering which agrees with the theoretical value, based on three-arm stars with average DP_{arm}=310 and average poly(n-butyl acrylate)side chain length DP_{sc}=30 (M_n= 3,600,000).

We subsequently visualized the star molecular brushes by AFM on mica surfaces. The tapping mode AFM detects easily brush backbones with the side chains filling the space between them. As seen in Figure 1, nearly all molecular brushes have star-like structure.

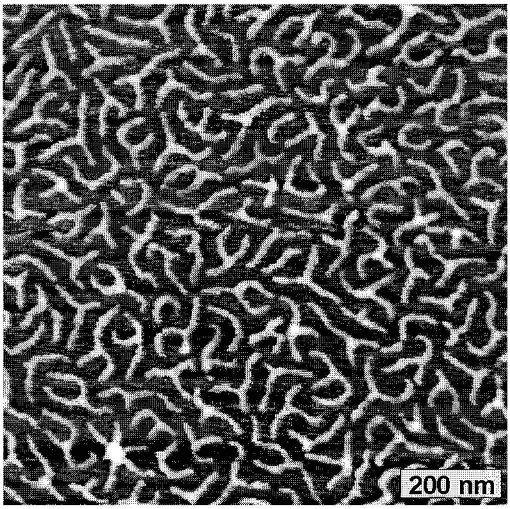


Figure 1. AFM tapping mode image of the three-arm star brush macromolecules with $DP_{n,arm}=310$, $DP_{n,star}=930$.

The results demonstrate very good agreement between the theoretical degrees of polymerization predicted for controlled/living ATRP and AFM dimensions of stars which assume nearly fully extended backbone. The contour length per repeating unit is~ 0.2 nm, as compared to a value for a planar zig-zag chain 0.25 nm. Nevertheless, it is relatively easy to detect many imperfections. Not all arms are of the same length and some arms are missing. The statistical analysis of both entire stars and constituting arms yield the following results: Arm: $L_w=72$ nm, $L_n=62$ nm, PDI=1.161; star: $L_w=196$ nm, $L_n=186$ nm, PDI=1.054.

The length distribution of individual arms is much broader than that of the assembled three arm stars. The early treatment of the statistics of chain coupling by Schulz and Flory, correlates the polydispersity of the individual chains with polydispersity of the n coupled stars:[17, 18]

$$(M_w/M_n-1)_{star} = (M_w/M_n-1)_{arm}/n$$

Taking the value M_w/M_n=1.161 of the polydispersity of the arm length and n=3 for three-arm stars, the predicted polydispersity of the lengths of entire stars should be M_w/M_n=1.054. The calculated value from AFM is M_w/M_n=1.054, confirming the agreement with Schulz-Flory predictions is very good.

Nearly all synthetic polymer chemists would be quite satisfied with the product of polydispersity $M_w/M_n<1.05$ (stars) or 1.16 (arms), especially for polymers with molecular weights as large as $M_n>1{,}000{,}000$, but they have to realize that the chains are very far from being monodispersed. The logarithmic scale used for PDI representations from SEC does not allow to notice the variation of chain lengths, which is especially striking in the star systems when chains are nearly fully extended.

Acknowledgements. Financial support from the National Science Foundation (ECS 01-03307) is gratefully appreciated. AFM analysis has been performed by Prof. S. Sheiko (University of North Carolina, Chapel Hill). Three-arm stars have been prepared by Dr. Shuhui Qin.

[1] K. Matyjaszewski, T. P. Davis, *Handbook of Radical Polymerization*, Wiley-Interscience, New York, **2002**.
[2] K. Matyjaszewski, Ed. *ACS Symposium Series, Vol. 768*, American Chemical Society, Washington, DC, **2000**,
[3] K. Matyjaszewski, D. A. Shipp, J.-L. Wang, T. Grimaud, T. E. Patten, *Macromolecules* **1998**, *31*, 6836.
[4] M. Destarac, D. Charmot, X. Franck, S. Z. Zard, *Macromol. Rapid Comm.* **2000**, *21*, 1035.
[5] J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614.
[6] J.-S. Wang, K. Matyjaszewski, *Macromolecules* **1995**, *28*, 7901.
[7] M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev. (Washington, D. C.)* **2001**, *101*, 3689.
[8] K. Matyjaszewski, J. Xia, *Chem. Rev. (Washington, D. C.)* **2001**, *101*, 2921.
[9] T. E. Patten, K. Matyjaszewski, *Adv. Mater.* **1998**, *10*, 901.
[10] K. Matyjaszewski, P. J. Miller, J. Pyun, G. Kickelbick, S. Diamanti, *Macromolecules* **1999**, *32*, 6526.
[11] X. Zhang, K. Matyjaszewski, *Macromolecules* **1999**, *32*, 7349.
[12] K. L. Beers, S. G. Gaynor, K. Matyjaszewski, S. S. Sheiko, M. Möller, *Macromolecules* **1998**, *31*, 9413.
[13] H. G. Boerner, K. Matyjaszewski, *Macromolecular Symposia* **2002**, *177*, 1.
[14] H. G. Boerner, K. Beers, K. Matyjaszewski, S. S. Sheiko, M. Moller, *Macromolecules* **2001**, *34*, 4375.
[15] H. G. Boerner, D. Duran, K. Matyjaszewski, M. da Silva, S. S. Sheiko, *Macromolecules* **2002**, *35*, 3387.
[16] S. S. Sheiko, S. A. Prokhorova, K. L. Beers, K. Matyjaszewski, I. I. Potemkin, A. R. Khokhlov, M. Moeller, *Macromolecules* **2001**, *34*, 8354.
[17] J. R. Schaefgen, P. J. Flory, *J. Am. Chem. Soc.* **1948**, *70*, 2709.
[18] G. V. Schulz, *Z. Phys. Chem. (Leipzig)* **1939**, *B43*, 25.