# Macromolecular Engineering by Controlled/Living Ionic and Radical Polymerizations

*Krzysztof Matyjaszewski*

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

SUMMARY: Various methods for the synthesis of well-defined (co)polymers with controlled dimension, polydispersity, topology, composition and functionality are discussed. They include controlled/living vinyl polymerization using anionic, cationic and radical intermediates being in equilibria with dormant species. Special emphasis is placed on the radical polymerization and on the needs for the comprehensive structure property correlation.

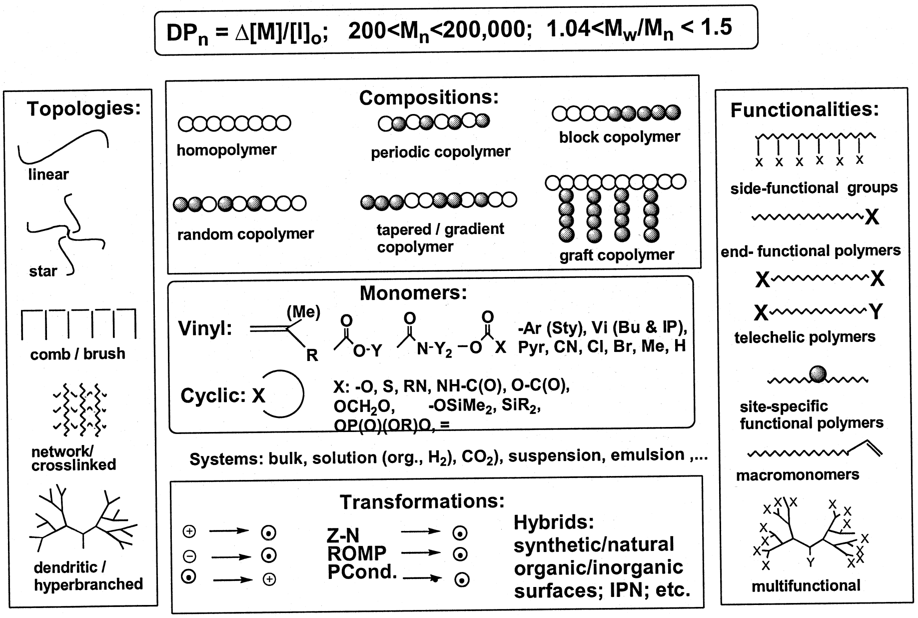
## Introduction

The control over macromolecular structure has always been one of the major goals of synthetic polymer chemistry. The ultimate target is to achieve the control found in biological systems that yields truly monodisperse polymeric chains. In organic chemistry, three major issues are important: chemoselectivity, regioselectivity and stereoselectivity; recently, supramolecular control has been added to that list. These four issues can be translated into synthetic polymer chemistry language as the "livingness" of a polymerization and /or the reactivity ratios in a copolymerization (chemoselectivity); the control over repeating unit structure via head-to-head and head-to-tail placement (regiochemistry), tacticity (stereoselectivity) and nanoscale (or microphase) separation (supramolecular control). In this short review, we will focus on the chemoselectivity aspect, which involves controlling the dimension, topology, composition and functionality of the polymer chains. Such control is possible in a chain-growth polymerization when nearly all the chains are initiated at the same time and the contribution of chain breaking reactions such as transfer and termination can be neglected in comparison to propagation. These systems have been defined as living or controlled polymerizations.1) Using this approach, it is possible to prepare polymers with precisely controlled molecular weights and designed polydispersities (which may approach a Poisson distribution); polymers that grow simultaneously in two and more directions and provide e.g. star-like or comb-like macromolecules; polymers with a smooth or abrupt change of composition along the chain such as gradient, block and graft copolymers; polymers with one, two or more functionalities that can be placed at the end or specific part of the macromolecule. Those macromolecules have been prepared using a single mechanism, for

CCC 1022-1360/00/$ 17.50+.50/0

example, the cationic, anionic, coordination or radical polymerization of vinyl monomers, as well as through either ionic or coordination ring-opening polymerizations.2) Additionally, it is possible to combine different techniques via a site transformation process to yield the corresponding hybrid structures.

Scheme 1 illustrates some examples of polymer chain topologies, compositions and functionalities which have been prepared using one or several of the aforementioned polymerization methods.



Scheme 1: Examples of systems prepared by controlled/living polymerizations.

This approach may be considered macromolecular engineering in the sense that every part of the macromolecule is first designed and then synthesized (engineered) to serve a special purpose. There are several driving forces behind macromolecular engineering, including improvement of properties of existing materials. This may encompass thermal properties, for example, by reducing the content of head-to-head units in poly(methyl methacrylates) or the mechanical properties of thermoplastic elastomers, which may be enhanced by synthesizing

ABA triblock copolymers with a lower content of contaminating diblocks. Lowering polydispersities of polymers may also improve the processing sequence.

Macromolecular engineering may also help to make polymeric materials more environmentally sound. Many thermosetts may be replaced by reversibly associating segmented copolymers. Thermoplastic elastomers that can replace irreversibly crosslinked rubbers is perhaps the best example. Other examples include solventless coatings, non-ionic surfactants, (bio)degradable polymers and polymers covalently attached to surfaces, which can reduce corrosion and improve lubrication.

Finally, macromolecular engineering may produce entirely new materials, applicable to such rapidly developing fields as drug delivery, tissue engineering and other biomedical materials; new photoresists, optoelectronic and conductive polymers; polymers for biomineralization and crystal engineering and many others. It is important to note that not only does macromolecular structure have to be controlled but processing as well to prepare materials with the targeted properties.

## Controlled/Living Polymerizations

Living polymerizations were originally defined as chain-growth processes without chain-breaking reactions.3) Additionally, to obtain good macromolecular control, it is necessary that all chains start growing at nearly the same time, i.e. ensure fast initiation. In reality, chain-breaking reactions do occur and cannot be completely avoided. Thus, some authors (including ourselves) introduced the term controlled polymerization.1) This applies to systems where the chain breaking reactions are present but macromolecular structure is still very well controlled. It has to be stressed that the quantitative assessment of the chain-breaking reactions under particular reaction conditions, is more important than nomenclature (living or controlled). We use here controlled/living polymerization to avoid any ambiguity.

There are several criteria, which help to assess the degree of the contribution of chain breaking reactions. They are shown schematically below and are related to the polymerization rate, the evolution of the molecular weight and polydispersity with conversion, and retention of chain-end functionality. Preservation of end-functionality may perhaps be the most important, especially for the synthesis of block copolymers and telechelics. Unfortunately, it is also the most difficult aspect to measure due to the small concentration of these groups.

Figure 1 presents schematic plots for the four discussed dependences. In a good controlled/living process, a linear plot for the change of monomer concentration with time should be obtained in semilogarithmic coordinates. The linear dependence indicates that the concentration of active species remains constant and that the contribution of termination is low. However, this criterion does not provide any information on the extent of transfer and is inapplicable to any polymerization with a steady state, like a conventional radical polymerization with slow initiation and termination. Moreover, it may happen that a significant curvature in the plot is observed but only a very small proportion of chains is terminated. This can happen in some catalyzed systems (like atom transfer radical polymerization) where the catalyst is destroyed but chain-end functionality preserved.

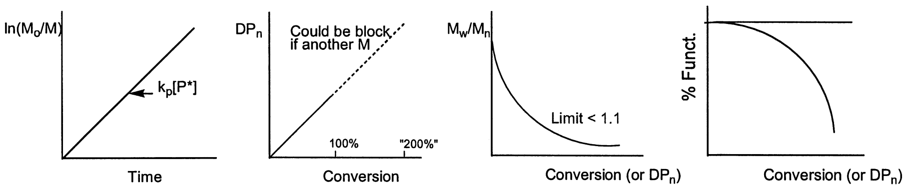


Fig. 1: Semilogarithmic kinetic plot and evolution of molecular weights, polydispersities and functionalities with conversion for controlled/living systems.

The second plot correlates molecular weight with monomer conversion. A straight line indicates there is a constant number of chains in the system but gives no information about the state of these chains, i.e., whether they are active or terminated. Thus, in the case of (pseudo)unimolecular termination or termination by disproportionation no deviation from linearity will be observed. Non-linearity in the plot indicates either slow initiation or transfer is occurring.

The third plot describes the evolution of polydispersity with conversion. In an ideal living process with fast initiation, this evolution should follow a Poisson distribution ($M_w/M_n=1 + 1/DP_n$). However, in systems with multiple active sites which slowly exchange, much higher polydispersities can be observed, although nearly all the polymer chains may retain their activity and ability to grow.

The last plot describes the evolution of chain end functionality. In the presence of termination and transfer, some chains will loose their functionality and the ability to grow. For the synthesis of block copolymers or telechelic materials, preservation of chain end functionality is vital and may seriously affect the properties of the final products. Thus, the remaining functionality should be precisely measured. Loss of functionality may be especially significant at high conversion, because the propagation rate decreases substantially but the rate of chain-breaking reactions may not, since they are not affected by the diminishing monomer concentration.

## Living Anionic Polymerization of Non-Polar Vinyl Monomers and Other Systems

Living anionic polymerization of styrene and dienes initiated by alkyl lithium is the first, and perhaps still the best example of a polymerization with a minimal contribution of chain-breaking reactions.3) This method was successfully applied to the synthesis of the first block copolymers, which have been commercialized to yield thermoplastic elastomers.4) Anionic polymerization has several unique features, which can not be matched by either cationic or radical processes. First, butyl lithium (and other alkyl lithium compounds) is a stable but reactive initiator. This is mostly due to the aggregation of alkyl lithium compounds, which is a rapid and reversible process, providing the needed reactive species. This results in relatively rapid initiation. Since alkyl lithium compounds are stable, termination is negligible if sufficiently pure and dry systems are used. On the other hand, aggregation reduces the overall polymerization rate, due to the predominant formation of the less reactive ion-pairs. In this system, the exchange between free ions and ion pairs is fast, yielding polymers with nearly Poisson distributions.

The success of anionic polymerization of dienes and styrenes could not be matched by other systems for nearly thirty years. Some authors even questioned whether carbocationic polymerization would ever provide a living system. The same was true for radical vinyl polymerization. Both processes require essentially ppm quantities of active species, carbocationic because of the very large propagation rate constants and radical due to diffusion controlled termination. Thus, it was not possible to ensure fast initiation and adventitious moisture often acted as a part of the carbocationic initiating system, which was dominated by transfer processes. Radical polymerization has evolved into the major preparative technique for commodity and specialty polymers using continuously initiating systems. Unfortunately, this process can not provide routes to block, grafts and end –functional polymers.

The situation was significantly better in ring-opening polymerizations. Both cationic and anionic processes were successfully used because the rate constants of propagation with onium and olate active centers were relatively low, enabling a high concentration of active species, which was well above the level of adventitious impurities. Ring-opening metathesis polymerization yielded similar results. However, all three techniques are limited to a relatively small number of monomers in comparison with the plethora of vinyl monomers accessible for conventional radical or carbocationic polymerization. It must be also noted that living anionic vinyl polymerization is limited to styrenes and dienes. Polymerization of (meth)acrylates with alkyl lithiums was very poorly controlled with a large contribution of side reactions.

## Systems with Equilibria between Active and Dormant Species

Perhaps the first system with a dormant species could again be traced back to the living anionic polymerizations. Ion pairs and ionic aggregates are much less reactive than free carbanions and were considered dormant. Formally, these species have the same chemical structure but differing degrees of physical ionic aggregation.

Another system was analyzed in 1974, in which isomerization between ionic and non-ionic species was observed and quantified by NMR.[5] In the polymerization of tetrahydrofuran (THF) initiated by triflate esters, oxonium ions were in equilibrium with the corresponding covalent esters.

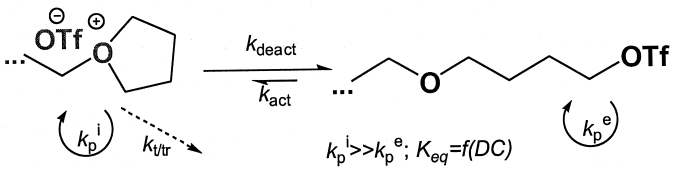


Fig. 2: Schematic representation of equilibria in THF polymerization.

The proportion of ions and esters depended strongly on the solvent, the temperature and the counterion (perchlorates and fluorosulfonates were also used). In non-polar $CCl_4$ only a few % of the ions were present, whereas in polar $CH_3NO_2$ only a few % of the covalent esters were found. Ionization was exothermic and the rates of exchange were similar to the propagation rates. Thus, a system with a controlled proportion of active and dormant species was discovered which allowed for a fine tuning of the reaction rates and also allowed macromolecular engineering by using multifunctional initiators, terminators, block and copolymer synthesis, etc.[6]

This type of system was eventually extended to many radical and ionic vinyl polymerizations in which a tiny proportion of propagating ions remains in a dynamic equilibration with the predominant unreactive dormant species.

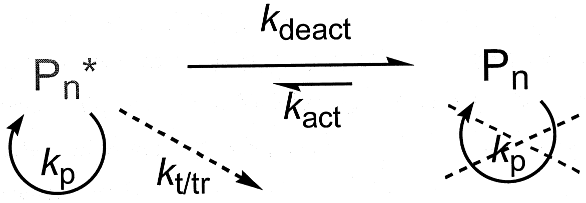


Fig. 3: Schematic representation of systems with equilibrium between active and dormant species.

The control of the polymer structure depends strongly on position of the equilibrium (rates).but also on the dynamics of exchange (molecular weights and polydispersities).

We will analyze these systems based on three mechanisms of exchange and structure of the active/dormant species: spontaneous or catalyzed activation of covalent species, degenerative transfer and systems with preserved spin/charge. Examples will be provided for each of these systems from anionic, cationic and radical vinyl polymerization, to show the similarities of the mechanistic features for all three systems.

## Reversible Activation of Covalent Species

A covalent species may contain a group or atom X which can either spontaneously (thermally) or, in the presence of a catalyst (Y), be activated with the rate constant of activation, $k_a$, to form a propagating species, whether a radical, anion or cation. This growing species is accompanied by the corresponding counter-ion or a counter-radical (X or Y-X), which can reversibly deactivate the growing center with the rate constant of deactivation, $k_d$.

The first, and perhaps the most famous, example of this system is group transfer polymerization (GTP).7) In the polymerization of methacrylates, silyl ketene acetals play the role of the dormant covalent species which can be reversibly activated by some silylophilic reagents to form propagating enolate anions. The bifluoride-based catalysts originally used yielded enolates irreversibly, resulting in degenerative transfer (cf. infra). However, weaker nucleophiles, such as bibenzoates, lead to the reversible formation of enolates.

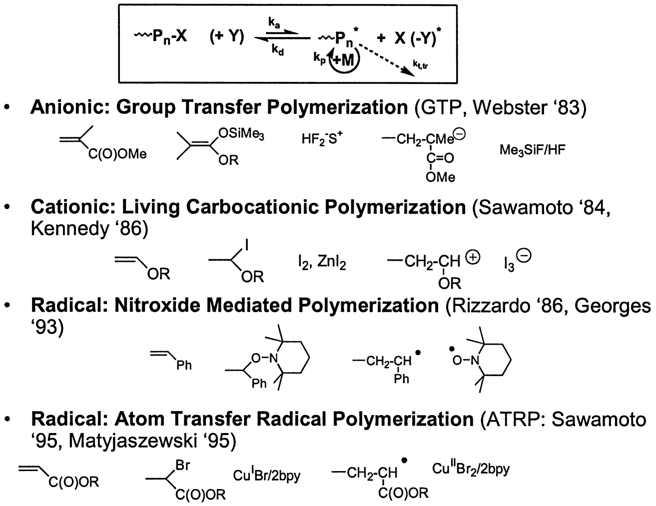
Then came the carbocationic system in which covalent alkyl halides were reversibly activated in the presence of Lewis acids to yield carbocations. In this way, the polymerization of vinyl ethers and isobutene was controlled.8-10)

Finally, radical polymerizations began to be controlled at a level approaching that of the ionic processes. Two examples can be cited here, the reversible thermal generation of radicals from alkoxyamines11, 12) and atom transfer radical polymerization (ATRP).13, 14)

These four methods are illustrated in the Scheme 2 below, together with the structures of monomers, dormant species, catalysts, active centers and the scavenging species.

## Degenerative Transfer

Degenerative transfer is based on a different principle. The dormant species reacts in a bimolecular way with the propagating species, deactivating it and simultaneously becoming active. The equilibrium constant is unity and the driving force for the process is randomization of the distribution of group or atom X among the chains. If exchange is fast, in comparison with propagation, then polymers with low polydispersities can be formed.



Scheme 2: Systems based on reversible activation of covalent species (spontaneous and catalyzed).

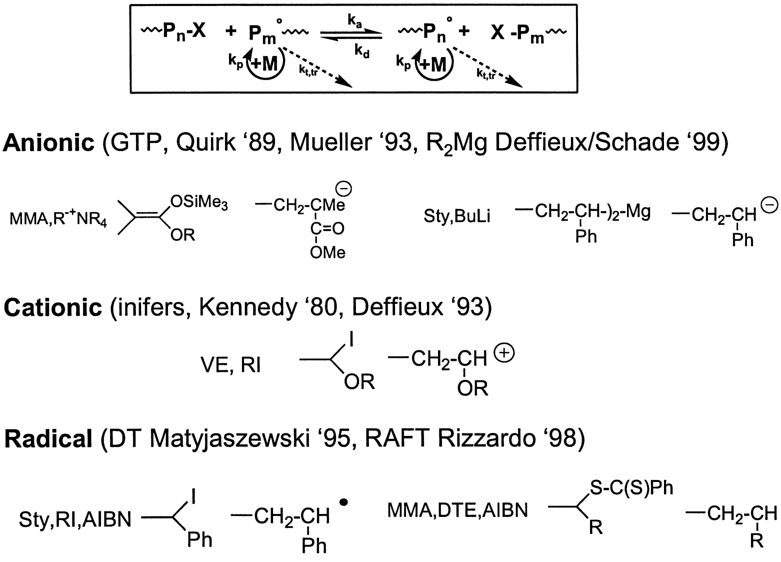
Degenerative transfer may operate in some GTPs, as deduced from the anionic polymerization of MMA in the presence of silyl ketene acetals.15) More recently, degenerative transfer was applied to slow down the styrene anionic polymerization in the presence of organomagnesium reagents.16)

The degenerative transfer process may also occur in carbocationic systems using the inifer approach as well as in the polymerization of some vinyl ether with alkyl iodides.17, 18)

The conventional radical polymerization of styrene and butyl acrylate initiated by AIBN in the presence of the corresponding alkyl iodides provided polymers and block copolymers with low polydispersities.19) However, much better control was observed in the presence of dithioesters20) that accelerated the exchange process by addition-fragmentation chemistry as shown in Scheme 3.

### Systems with Preserved Charge/Spin

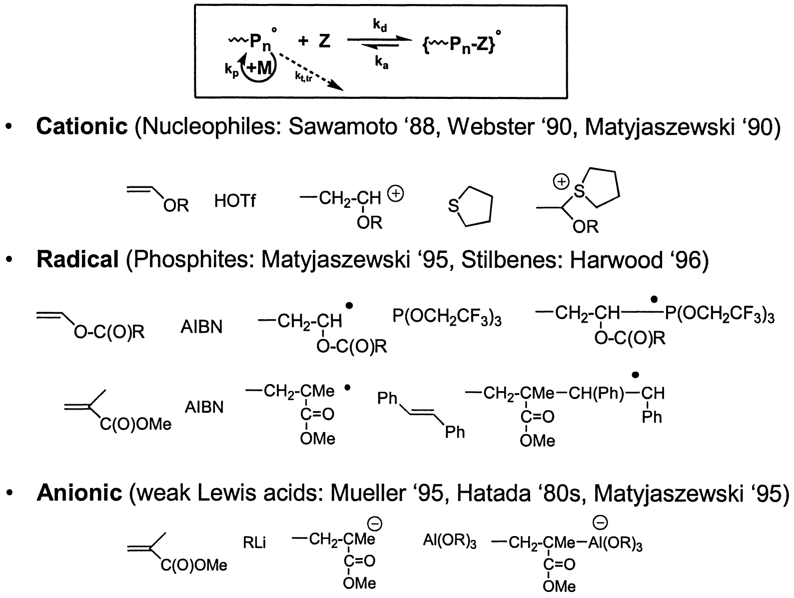
The third approach to controlling the polymerization using an equilibrium approach converts propagating carbocations/carbanions/radicals to species with preserved charge/spin but with a much lower reactivity towards monomer (i.e. dormant species). This approach still remains the least explored. The first convincing examples came from the use of nucleophiles in polymerization of vinyl ethers.[21-23]



Scheme 3: Systems based on degenerative transfer.

In radical polymerization, the use of phosphates and non-polymerizable monomers improved the control but not yet to a level achieved by other techniques.[24, 25]

In anionic polymerization of (meth)acrylates carried out in the presence of various metal compounds, the reversible formation of adducts was proposed as shown in Scheme 4.[26, 27]



- **Cationic** (Nucleophiles: Sawamoto '88, Webster '90, Matyjaszewski '90)
- **Radical** (Phosphites: Matyjaszewski '95, Stilbenes: Harwood '96)
- **Anionic** (weak Lewis acids: Mueller '95, Hatada '80s, Matyjaszewski '95)

Scheme 4: Systems based on preservation of charge/spin.

## Advantages of New Controlled/Living Systems

The new controlled/living systems can not suppress chain-breaking reactions at the same level as living anionic polymerization. Termination does occur in all radical processes and it is not possible to entirely suppress β-proton elimination from carbocationic systems, unless the reaction is run at very low temperatures.28) However, by keeping the concentration of growing species sufficiently low, it is possible to significantly reduce the contribution of termination in radical polymerizations and extend the reaction time in carbocationic systems to levels where macromolecular engineering becomes possible, i.e. from seconds to hours.29) The same can now be accomplished in the anionic polymerization of methacrylates. In many polymerizations, bicomponent initiating systems were used which generated initiating sites only upon mixing. This initiating system mimics the structure and reactivity of the growing centers, enabling fast initiation in one, two or several directions, giving access to star and comb polymers. Since the rate of the reaction depends on the concentration of the catalyst, it is possible to obtain relatively low molar mass functional polymers at reasonable rates when small amounts of catalyst are used. Due to the high concentration of chain ends, the effect of impurities is diminished, enabling high tolerance to moisture, protic impurities and oxygen.

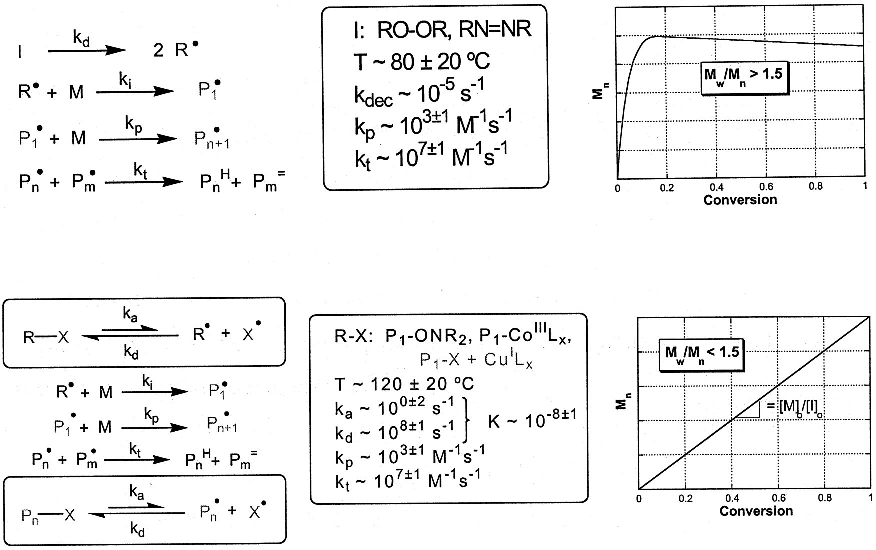
Many of these new systems are quite complex and contain several components which affect the polymerization rate and may also lead to side reactions. Their role should be precisely understood. They affect rates, polydispersities and end functionalities. Although new mechanisms were originally proposed, these new controlled/living systems most likely employ the same old basic propagation steps of electrophilic, nucleophilic or radical addition to a double bond; however, supplemented by the dynamic exchange process such as atom, group transfer, reversible ionization, etc.

## Controlled/Living Radical Polymerization

The new controlled/living methodology may have the biggest impact on radical polymerization, especially from the point of view of commercial processes. This can be witnessed by over 1,000 papers and over 100 patent applications published in this field since 1995. Through July 2000, 536 papers and 72 patent applications were devoted alone to ATRP systems.

The great expectations for the controlled/living radical polymerization (CRP) have their origins in the dominating position of the free radical technique, by far the most common method of making polymeric materials (nearly 50% of all polymers are made this way). This is due to the large number of available vinyl monomers (e.g., there are nearly 300 different methacrylates available commercially) which can easily homo and copolymerize. Reaction conditions are not demanding and only require moderate heating, deoxygenation and are tolerant to moisture and any protic impurities. However, in contrast to many ionic reactions, it has not yet been possible to make well-defined polymers through a conventional radical process. The advent of 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 (potentially for crystal engineering), gels and hydrogels, lubricants and additives, surface modifiers, hybrids with natural and inorganic polymers, various biomaterials and electronic materials. 30-32)

Mechanistically, new controlled/living systems are quite similar to conventional radical polymerization, as shown in Scheme 5.33)



$$I \xrightarrow{k_d} 2R^\bullet$$
$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet$$
$$P_1^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$$
$$P_n^\bullet + P_m^\bullet \xrightarrow{k_t} P_n^H + P_m^=$$

$$R{-}X \underset{k_d}{\overset{k_a}{\rightleftharpoons}} R^\bullet + X^\bullet$$
$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet$$
$$P_1^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$$
$$P_n^\bullet + P_m^\bullet \xrightarrow{k_t} P_n^H + P_m^=$$
$$P_n{-}X \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P_n^\bullet + X^\bullet$$

Scheme 5: Comparison of conventional and controlled radical polymerization.

Primary radicals react with the monomer to induce propagation. Polymeric radicals grow and terminate with similar rate constants. The main difference between the two systems is only how the radicals are generated. They are generated slowly and irreversibly in the conventional processes through dissociation of peroxides or diazo compounds which typically have a half-lifetime in the range of 10 hours. Thus, a lot of unreacted initiator remains even at high monomer conversions. Propagation is rapid with an approximate frequency of monomer addition of ~1 ms. This means that within 1s, a polymer chain with the DP~1000 is typically formed. Within approximately the same time, chains terminate by either coupling or disproportionation. During such a short time, it is not possible to perform any kind of macromolecular engineering by adding another monomer, functionalizing reagent, etc.

The controlled/living reactions 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.

Thus, perhaps the most important difference between the two approaches is the lifetime of the propagating chains, which is extended from ~1s to more than 1h. The second major difference is the very significant increase in the initiation rate, which enables simultaneous growth of all the polymer chains. Both parameters allow various macromolecular engineering techniques to be applied, such as making well-defined star polymers, block and grafts, end functional polymers and many other well-defined materials.

The key feature of the controlled/living radical polymerization is the dynamic equilibration between the active radicals and various types of dormant species. Currently three systems seem to be most efficient: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes such as RAFT, as discussed previously.[31)]

## Limitations of Controlled/Living Radical Polymerizations

Termination processes cannot be avoided in CRPs. Thus, CRP is generally less precise than the anionic polymerization. Also, since propagating species are free radicals, chemo-, regio- and stereoselectivities are similar to those found in conventional radical polymerizations. This means that similar reactivity ratios, similar sensitivity to transfer reagents and similar tacticities are observed.

Termination is the most dangerous chain breaking reaction in CRPs. Since it is a bimolecular process, increasing the polymerization rate increases concentration of radicals and enhances the termination process. Termination also becomes more significant for longer chains and at higher conversion, however, this process is somehow self tuned, since termination is chain length dependent.[34)]

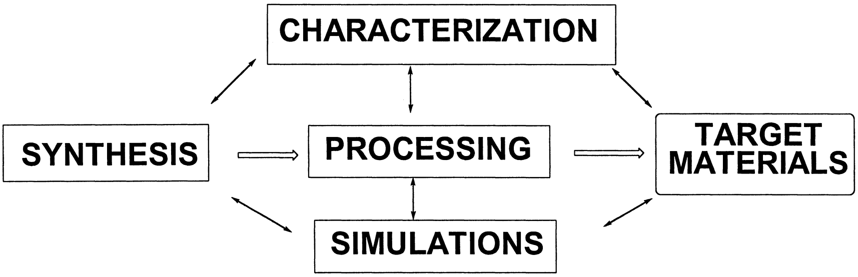
Thus, polymers prepared by CRPs will never have 100% functionality and 100% blocking efficiency. For slowly propagating monomers such as dienes, styrenes and methacrylates, it is necessary to slow down the polymerization rate to avoid excessive termination; for acrylates this is less important.

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 is limited 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. 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.

RAFT can be applied to the polymerization of many unreactive monomers, such as vinyl acetate.

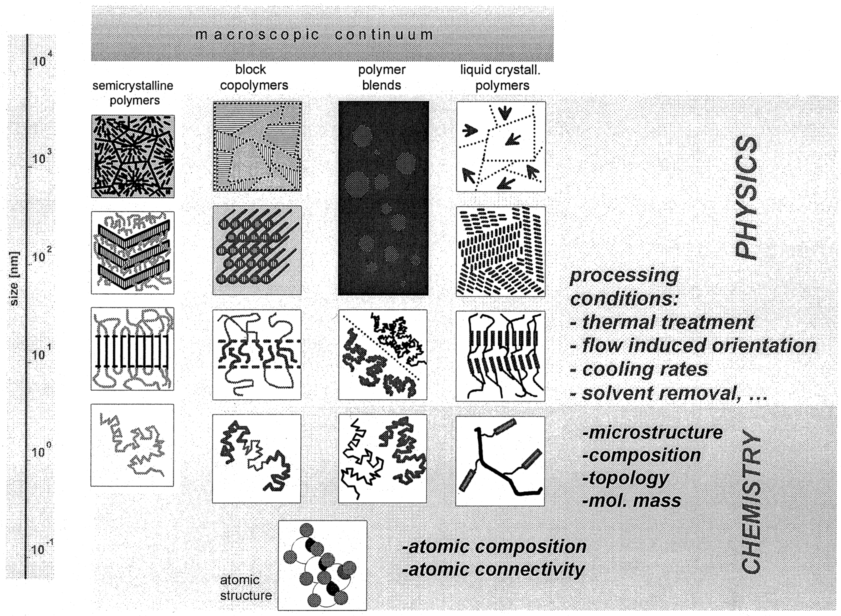
## Towards Comprehensive Structure-Property Correlation

Perhaps the most important feature of all CRPs is that they can be used for the preparation of many well-defined (co)polymers under mild conditions, requiring essentially only deoxygenation of the reaction mixture. Thus, many new materials can easily be prepared with precisely controlled topologies, compositions and functionalities. Therefore, it becomes possible, and also very attractive, to make a comprehensive structure-property correlation. However, this approach requires not only precise control and characterization of molecular structure of the obtained polymers (MW, MWD, microstructure) but also control over the processing, which includes variation of the temperature profiles, mechanical stresses, solvent removal, etc. The latter will also affect morphology, thermal and mechanical properties as well as many others. It is anticipated that computer simulations may help to predict and correlate properties of the final materials with molecular structure and processing methods. This will require combining methods for various sizes and time scales and simulating the complete routes including the synthesis, the processing and the characterization. Currently, the most feasible approach is a semiempirical one that relies on the preparation and the characterization of molecularly well-defined systems. A cooperative motion algorithm approach has been very efficient at simulating many properties of various stars, blocks, gradients, blends, etc.35)



Scheme 6:Interrelations between synthesis, processing, characterization and simulations to reach final properties of targeted materials.

Building a comprehensive structure property correlation requires many collaborative efforts between organic chemists, polymer synthetic chemists, physical chemists, physicists and process engineers. Organic chemists typically consider the structures, which are smaller than 1nm and focus on compositional, structural and stereo-isomers. Synthetic polymer chemists typically focus on the 1 to 10 nm scale caring about topologies, compositions and functionalities as well as the uniformity of the polymer chains.



Scheme7: Macroscopic continuum bridging polymer chemistry with polymer physics.

Physical polymer chemists would approach size of 100 nm to study various mesophases, semicrystalline structures and chain folded crystals. Polymer physicists center on even larger dimensions, approaching 1000 nm such as spherulites, domains and grains, whereas processing engineers care about the final microscopic objects and their thermal, mechanical and surface properties. Nevertheless, there is a real macroscopic continuum that must be comprehensively studied in order to bridge the gap between molecular structures, processing and final material properties

It is anticipated that the new controlled/living techniques will help to bridge this gap by providing many new well-defined polymers via macromolecular engineering.

**Acknowledgments:** Partial support from the National Science Foundation and ATRP Consortium is acknowledged.

## References

1) K. Matyjaszewski, *J. Phys. Org. Chem.*, 8, 197 (1995).
2) O. Webster, *Science*, 251, 887 (1991).
3) M. Szwarc, *Nature*, 176, 1168 (1956).
4) M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Processes*, Interscience Publishers, New York (1968).
5) K. Matyjaszewski, P. Kubisa and S. Penczek, *J. Polym. Sci., Polym. Chem. Ed.*, 12, 1333 (1974).
6) S. Penczek and K. Matyjaszewski, *J. Polym. Sci., Polym. Symp.*, 56, 255 (1976).
7) O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. RajanBabu, *J. Am. Chem. Soc.*, 105, 5706 (1983).
8) T. Higashimura, M. Miyamoto and M. Sawamoto, *Macromolecules*, 18, 611 (1985).
9) J. P. Kennedy and B. Ivan, *Designed Polymers by Carbocationic Macromolecular Engineering. Theory and Practice*, Hanser, Munich (1992).
10) K. Matyjaszewski, *Cationic Polymerizations: Mechanisms, Synthesis and Applications*, Marcel Dekker, New York (1996).
11) D. H. Solomon, E. Rizzardo and P. Cacioli, *U. S. Pat. 4, 581, 429*, 1986.
12) M. K. Georges, R. P. N. Veregin, P. M. Kazmaier and G. K. Hamer, *Macromolecules*, 26, 2987 (1993).
13) M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 28, 1721 (1995).
14) J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 117, 5614 (1995).
15) R. P. Quirk and G. P. Bidinger, *Polymer Bull.*, 22, 63 (1989).
16) P. Desbois, M. Fontanille, A. Defieux, V. Werzelhan, S. Latsch and C. Schade, *Macromol. Chem. Phys.*, 200, 621 (1999).
17) J. P. Kennedy and R. A. Smith, *J. Polym. Sci., Polym. Chem. Ed.*, 18, 1539 (1980).
18) H. Cramail, A. Deffieux and O. Nuyken, *Makromol. Chem., Rapid Commun.*, 14, 17 (1993).
19) S. Gaynor, J. S. Wang and K. Matyjaszewski, *Macromolecules*, 28, 8051 (1995).
20) J. Chiefari, Y. K. B. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 31, 5559 (1998).
21) M. Sawamoto, S. Aoshima and T. Higashimura, *Makromol. Chem., Macromol. Symp.*, 13/14, 513 (1988).
22) C. G. Cho, B. A. Feit and O. W. Webster, *Macromolecules*, 23., 1918 (1990).
23) C.-H. Lin and K. Matyjaszewski, *Polym. Prepr., Div. Polym. Chem., Am. Chem. Soc.*, 31(1), 599 (1990).
24) H. J. Harwood, L. Christov, M. Guo, T. V. Holland, A. Y. Huckstep, D. H. Jones, R. E. Medsker, P. L. Rinaldi, T. Soito and D. S. Tung, *Macromol. Symp.*, 111, 25 (1996).
25) D. Greszta, D. Mardare and K. Matyjaszewski, *ACS Polym. Preprints*, 35(1), 466 (1994).
26) H. Schlaad, B. Schmitt, A. H. E. Müller, S. Jüngling and H. Weiss, *Macromolecules*, 31, 573 (1998).
27) D. Mardare and K. Matyjaszewski, *Polym. Prepr.*, 35(1), 468 (1994).
28) K. Matyjaszewski and P. Sigwalt, *Polymer Intern.*, 35, 1 (1994).

29) D. Greszta, D. Mardare and K. Matyjaszewski, *Macromolecules*, 27, 638 (1994).

30) K. Matyjaszewski (Editor), *Controlled Radical Polymerization*, ACS, Washington, D.C., 1998.

31) K. Matyjaszewski (Editor), *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*, ACS, Washington, D.C., 2000.

32) T. E. Patten and K. Matyjaszewski, *Adv. Mat.*, 10, 901 (1998).

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

34) D. A. Shipp and K. Matyjaszewski, *Macromolecules*, 32, 2948 (1999).

35) T. Pakula and S. Gayler, *Macromolecules*, 21, 1665 (1988).