
CHAPTER 5

LIVING AND / OR CONTROLLED RADICAL POLYMERIZATION

5.1 INTRODUCTION

The term living polymerization was initially used to describe a chain polymerization in which chain-breaking reactions were absent. In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer and termination. Thus, in the ideal living polymerization each chain should retain its ability to react with monomer infinitely. However transfer and termination often occur in real systems. Thus, living polymerizations (no chain-breaking reactions) and controlled polymerization (formation of well-defined polymers) are two separate and not necessarily overlapping terms which should be distinguished and should not be confused.

A controlled polymerization is defined here as a synthetic method for preparing polymers with predetermined molecular weights ($DP = \Delta[M] / [I]_0$), low polydispersity and controlled functionality.

Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected. On the other hand, living polymerizations will lead to well defined polymers only if the following additional prerequisites are fulfilled: initiation is fast in comparison with propagation; exchange between species of different reactivities is fast in comparison with propagation; the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of the availability of active centers and mixing.

Systems with reversible transfer or reversible termination deserve special comment, since they have often been called pseudo-living or quasi-living. In these systems various active species coexists, including ions, ion pairs of various structures and reactivities and their aggregates. Reactivities of ions are sometimes much higher than those of ion pairs ($k_p^- / k_p^\pm \approx 10^5$ in the polymerization of styrene with Li^+ counter ion in dioxane at 20 °C), and in some cases ionic aggregates are much less reactive than ion pairs. This observation indicates that growing species with different reactivity exchange rapidly enough to give the same probability of growth for all chains. This also implies that the temporary decrease in activity (or temporary deactivation) does not interfere with the concept of a living polymerization. Thus, temporary deactivation is not considered as termination.

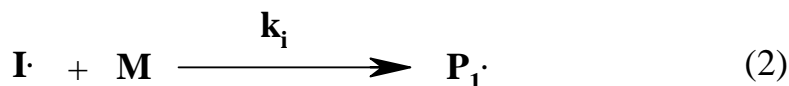
5.1.1 FIVE ELEMENTARY REACTIONS OF RADICAL POLYMERIZATION

Slow homolytic cleavage of a initiator (such as diazo, peroxide, or other similar compounds)

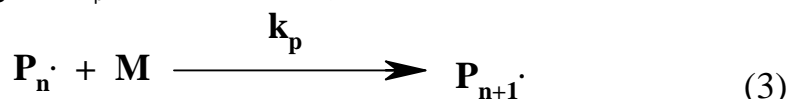
$$k_d < 10^{-5 \pm 1} \text{ s}^{-1},$$



relatively fast reaction of primary radicals with monomer to generate the first growing species, because $k_d < k_o[\text{M}]$, the decomposition is the rate determining step in the initiation process.



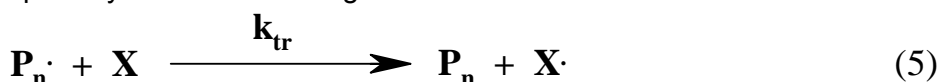
fast propagation $k_p \approx 10^{3\pm 1} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$,



very fast termination between growing radicals via coupling or disproportionation;
 $k_t \approx 10^{7\pm 1} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$,

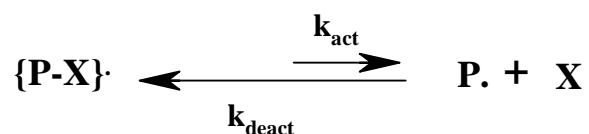


transfer reactions including transfer to monomer, initiator, solvent, polymer, and specially added transfer agents.



Ratio of the rate of propagation to that of termination (livingness) decreases with $[\text{P}\cdot]$, because propagation is first order but termination is second order in respect to $[\text{P}\cdot]$. the proportion of chains marked by termination increases with chain length. Therefore, well- defined polymers may be formed in radical polymerization only if chains are relatively short and concentration of free radicals is low enough. ($[\text{P}\cdot] \approx 10^{-7\pm 1} \text{ mol/L}$). There is apparent contradiction between these two requirements because usually a decrease of the concentration of radicals leads to higher molecular weights. However, the two conditions can be accommodated in systems with reversible deactivation of growing radicals. The controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weights sufficiently low. This necessitates a relatively high concentration of the initiator or, in other words, low $[\text{M}]_0/[\text{I}]_0$ ratios. However, because termination is bimolecular, the contribution of termination becomes more significant at high $[\text{I}]_0$, when a large concentration of radicals, $[\text{P}\cdot]$, is generated. In order to solve the discrepancy between high $[\text{I}]_0$ and low $[\text{P}\cdot]$, it is necessary to establish an exchange between dormant and active species. The concentration of the dormant species can be equal to $[\text{I}]_0$, and the momentarily growing species to $[\text{P}\cdot]$. The total number of growing chains will be equal to $[\text{I}]_0 (\approx [\text{P-R}]_0 + [\text{P}\cdot])$, and radicals would be present at a very low stationary concentration. The covalent species P-R can reversibly and homolytically cleave to produce the growing radical $\text{P}\cdot$ capable of propagation and the dormant radical (scavenging radical) $\text{R}\cdot$ which ideally should react only with $\text{P}\cdot$ but not with monomer or itself to form inactive dimers. $\text{P}\cdot$ can react with M and $\text{R}\cdot$ but also with another $\text{P}\cdot$, leading to termination. Because termination rate is proportional to $[\text{P}\cdot]^2$, and propagation rate to $[\text{P}\cdot]$, the contribution of termination and the proportion of deactivated chains increase with $\text{P}\cdot$. This case is probably most frequently postulated in controlled radical polymerizations. As example of $\text{R}\cdot$: dithiocarbamate radicals, nitroxyl radicals and also bulky organic radicals such as triarylmethyl and substituted diarylmethyl species can be used. Another approach for controlled radical polymerization is to use persistent radical $\{\text{P-X}\}\cdot$. The persistent radical should only cleave homolytically to form $\text{P}\cdot$ and the specie X. X should be an inert compound capable only of reacting with $\text{P}\cdot$ (reversible

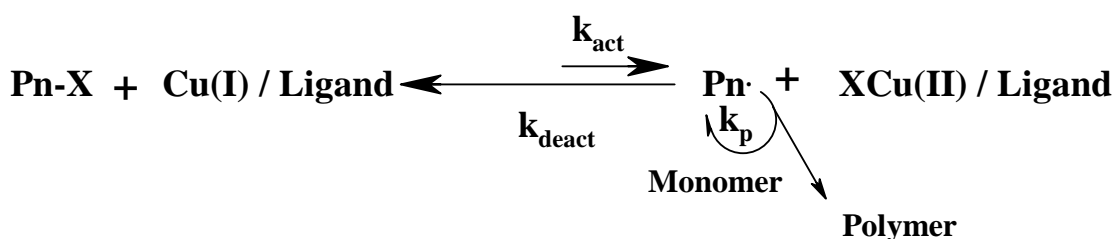
deactivation of a growing radical with a non-radical species through the formation of a dormant persistent radical).



X can be some elementoorganic or organometallic species with an even number of electrons. Some success has been reported with group XIII and XV elements such as aluminum and phosphorus as well as with organometallic derivatives of Co, Cr, and other transition metals.

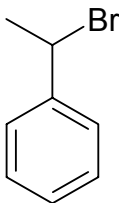
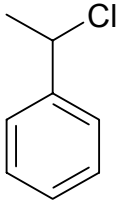
5.1.2 MECHANISM OF ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

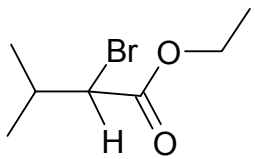
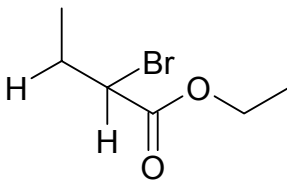
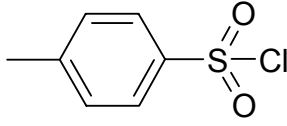
An ATRP system consist of an initiator, a copper(I) halide complexed with some ligand(s), and of course, monomer. ATRP occurs as a repetitive addition of a monomer to a growing radicals generated from dormant alkyl (pseudo) halides by a reversible redox process catalyzed by transition metal compounds complexed by amine ligand.



5.1.2.1 Initiators

The initiator (organic halides) usually, but not always, should have a structure homologous to the corresponding polymer end group.

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene

 <p>2-Bromo ethyl isobutyrate</p>	Methylmethacrylate
 <p>2-Bromo ethyl propionate</p>	Methylacrylate and other acrylates
 <p>chloride <i>p</i>-toluene sulphonyl</p>	Methylmethacrylate

5.1.2.2 Transition metals used in ATRP

Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting $X-M_t^{n+1}$ species (higher oxidation state of metal). The metal should participate in an one-electron process which would result in oxidative addition / reductive elimination but not in atom transfer process. Additionally, the metal should have a high affinity for atom / group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β - hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control (livingness) of process. The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle M_t^n / M_t^{n+1} but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus, the inner coordination sphere of M_t^n must expand to accommodate a new X (halide) ligand. Expansion from tetra to pentacoordinated structure $Cu(I) / 2 \text{ ligand} \Rightarrow X-Cu(II) / 2 \text{ ligand}$ or pentacoordinated structure $X_2Fe(II) / 3PR_3 \Rightarrow X_3Fe(III) / 3PR_3$ must be possible. The most important catalysts used in ATRP are given below;

$Cu(I)Cl$, $Cu(I)Br$, $Ni(II)$, $Ru(II)$ / $Al(OR)_3$, and $Fe(II)$ / $3PR_3$.

5.1.2.3 Ligand

The role of ligands is three-fold. They affect the redox chemistry by their electronic effects. They control the selectivity by steric /electronic effects and they also solublize catalytic systems. The most effective ligands for ATRP are derivatives of 2,2-bipyridine. Other nitrogen based ligands such as N,N,N',N'',N''pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10- hexamethyltriethylenetetraamine (HMTETA), Tris[2-(dimethylamino)ethyl]amine (Me_6 -TREN), and Alkylpyrldylmethanimines are also used.

5.1.2.4 Monomers

ATRP can be used for many vinyl monomers including Styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyrrolidinone, N-vinylpyridine and dienes.

5.1.2.5 Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction usually negative first order with respect to the deactivator (CuX_2 / Ligand).

$$R_p = k_{\text{app}}[M] = k_p[P\cdot][M] = k_p K_{\text{eq}}[I]_0 \frac{[\text{Cu(I)}]}{[\text{Cu(II)X}]} [M]$$

The equilibrium constant (K_{eq}) depends on the monomer used, for example, in the bulk polymerization of styrene at 110 °C using R-Br and CuBr / dNbipy the equilibrium constant is approximately $K_{\text{eq}} = k_{\text{act}}/k_{\text{deact}} = 4 \times 10^{-8}$.

5.2 EXPERIMENTS

5.2.1 PREPARATION OF POLYMETHYLMETHACRYLATE BY ATRP

To a 100-ml three neck flask equipped with nitrogen inlet and magnetic stirring bar which was flame dried under vacuum, methylmethacrylate (3 ml; 28.3 mmol), diphenylether (3 ml), CuCl (14 mg; 0.142 mmol), pentamethyldiethylenetriamine [24.5 mg. (30 μ l); 0.142 mmol], and p-toluenesulphonylchloride (27 mg; 0.142 mmol) were added in the order mentioned. The reaction solution was bubbled by nitrogen (10 min.) to remove dissolved gases and then flask was immersed in an oil bath and held by a thermostat at 90 °C., with rigorous stirring. The polymerization of methylmethacrylate was performed for 90 min. and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF (approx. 30 ml of THF). The THF solution was passed through a short alumina column to remove copper complex and then concentrated by rotavaporator under vacuum at room temperature. The polymer was precipitated from excess of methanol and filtered. The polymer was dried at 50 °C under vacuum. The conversion was determined by gravimetrically.

5.2.2 PREPARATION OF POLYSTYRENE BY ATRP

To a 100-ml three neck flask equipped with nitrogen inlet and magnetic stirring bar which was flame dried under vacuum, styrene (3 ml; 26.1 mmol), CuBr (19 mg; 0.13 mmol), pentamethyldiethylenetriamine [23 mg. (27 μ l); 0.142 mmol], and 1-bromo-1-phenylethane (24 mg; 0.13 mmol) were added in the order mentioned. The reaction solution was bubbled by nitrogen (10 min.) to remove dissolved gases and then flask was immersed in an oil bath and held by a thermostat at 110 °C., with rigorous stirring. The polymerization of styrene was performed for 90 min. and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF (approx. 30 ml of THF). The THF solution was passed through a short alumina column to remove copper complex and then concentrated by rotavaporator under vacuum at room temperature. The polymer was precipitated from excess of methanol and filtered. The polymer was dried at 50 °C under vacuum. The conversion was determined by gravimetrically.

5.2.3 MATERIALS REQUIRED

100-ml three -necked round bottomed flask
Magnetic stirring bar
Three-way gase valf
Rubber septum
3 x 10 ml pipet
Termostated oil bath with stirring unit
400 ml beaker
Column 20 or 30 cm x 1.5-2 cm HxD
Aluminium Oxide neutral (Brockman I)
Styrene 3 ml
Methylmethacrylate 3 ml
Diphenylether 3 ml
Methanol 250 – 300 ml

REFERENCES

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2. K. Matyjaszewski, J. phys. Org. chem., 8, 197 (1995).