

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-94-1-0101

R&T CODE 31321075

Technical Report #50

KINETIC STUDIES OF ATOM TRANSFER RADICAL
POLYMERIZATION OF METHYL ACRYLATE

by

H. Paik, K. Matyjaszewski

Published

in the

ACS Polymer Preprints, in press

Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

June 12, 1996

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale;
its distribution is unlimited.

19960621 015

DTIC QUALITY INSPECTED 1

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Technical Report #50	
4. TITLE AND SUBTITLE Kinetic Studies of Atom Transfer Radical Polymerization of Methyl Acrylate		5. FUNDING NUMBERS N0004-94-1-0101	
6. AUTHOR(S) H. Paik, K. Matyjaszewski			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Carnegie Mellon University Department of Chemistry 4400 Fifth Avenue Pittsburgh, PA 15213-2683		8. PERFORMING ORGANIZATION REPORT NUMBER N0004-94-1-0101	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER Technical Report #50	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Kinetic aspects of Atom Transfer Radical Polymerization of methyl acrylate [MA] were studied. The results showed the characteristic features of living polymerization up to Mn (80,000, e.g. constant concentration of propagating species, a linear relation between conversion and molecular weight and narrow polydispersities (Mw/Mn (1.2). As an initiation system, 2-bromomethyl propionate and CuBr complexed by 4,4'-Di-tert-butyl-2,2'-bipyridine [dTbipy] or 4,4'-di-(5-nonyl)-2,2'-bipyridine [dNbipy] were employed. Kinetic studies showed that the propagation rate is first order in relation to the monomer and initiator. For the homogeneous catalyst system (copper(I) / dNbipy), the propagation rate is first order with respect to the initial concentration of catalyst and inverse first order with respect to the initial concentration of Cu(II)Br ₂ . The propagation rate in non-homogeneous system (copper(I) / dTbipy) less depends on the on the initial concentration of catalyst and Cu(II)Br ₂ . These results can be explained by the reversible formation of growing polyacrylate radicals by the reaction of dormant bromo-terminated chains with copper halide.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
17. SECURITY CLASSIFICATION OF REPORT		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to *stay within the lines* to meet optical scanning requirements.

Block 1. Agency Use Only (Leave blank).

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. (if known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."

DOE - See authorities.

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave blank.

DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.

NASA - Leave blank.

NTIS - Leave blank.

Block 13. Abstract. Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (*NTIS only*).

Blocks 17 - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

Kinetic Studies of Atom Transfer Radical Polymerization of Methyl Acrylate

Hyun-joong Paik and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh, PA 15213

Introduction

The perfect control over polymerization, including chain architecture, end groups, molecular weight and its distribution, is one of the most important goals for synthetic polymer chemists. This control can broaden the realm to new materials without using new monomers.¹ After Szwarc first reported living polymerizations,^{2,3} e.g. polymerization in which chain termination and chain transfer are absent, it has been regarded as the most promising method for control.

In radical polymerization, it is impossible to achieve a truly living process due to bimolecular termination reactions such as coupling and disproportionation which are absent in ionic polymerization. Therefore, instead of a living process in true meaning, approaches to the controlled or "living" polymerization in which chain breaking reactions exist, but in tolerable and controllable proportions, have been proposed by various means.⁴ Radical polymerization has many advantages over ionic polymerization, such as a large variety of polymerizable and copolymerizable monomers and less stringent reaction conditions compared to ionic polymerization.

Atom Transfer Radical Polymerization (ATRP), whose concept came from Atom Transfer Radical Addition,^{5,6} was recently reported as a route to the synthesis of well defined polymers of such monomers as styrene, acrylates and methyl methacrylates.^{7,8}

In this report, the kinetic studies of the polymerization of methyl acrylate with a homogeneous and heterogeneous catalytic system will be described. Also, the evolution of molecular weights and polydispersities with conversion will be discussed.

Experimental Materials

Methyl acrylate [MA] was stirred over CaH₂ overnight and distilled under vacuum before polymerization. Methyl 2-bromopropionate [MBP] was used as received from Aldrich without purification. 4,4'-Di-*tert*-butyl-2,2'-bipyridine [dTbipy] was prepared according to the known procedure⁹ and 4,4'-di-(5-nonyl)-2,2'-bipyridine [dNbipy] was obtained from Reilly Industries. CuBr was purified according to the literature.¹⁰ CuBr₂ was used without further purification.

Polymerization

The general procedure for the polymerization was as follows: to a glass tube, CuBr, ligand, initiator and monomer were added. The solution was degassed two times by the "freeze-pump-thaw" method and sealed under vacuum. The tube was placed in an oil bath thermostatted at desired temperature. At timed schedule, the tube was removed from the oil bath and opened. The mixture was dissolved in a known amount of THF and analyzed.

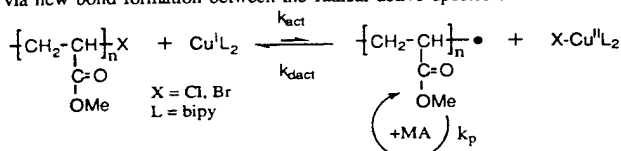
Characterization

The monomer conversion was determined by Gas Chromatography using a Shimadzu GC-14A with DB-WAX column. Molecular weights and polydispersities were measured using Phenogel GPC columns (guard, linear, 1000 Å and 100 Å) and 410 refractive index detector. Narrow polystyrene standards were used to calibrate the columns.

Results and Discussion

General Features

The key point in controlled radical polymerization is the establishment of a rapid equilibrium between dormant and active species. The equilibrium should lie towards the dormant species to lower the stationary concentration of active species, thus minimizing the termination reactions. In ATRP, this is accomplished by cleavage and formation of halogen-carbon bond by copper / bipy complex. The propagation proceeds via new bond formation between the radical active species and monomer.



Mechanistic Studies

According to the proposed mechanism, the rate of propagation can be described by the following equations.

$$R_p = k_p^* [M][P^*] = k_p^* K_e [M][P-X] \frac{[\text{Cu}^{\text{I}}\text{L}_2]}{[\text{X-Cu}^{\text{II}}\text{L}_2]} = k_p^{\text{app}} [M] \quad \text{eq. 1}$$

$$K_e = \frac{k_{\text{act}}}{k_{\text{dact}}} = \frac{[P^*][\text{X-Cu}^{\text{II}}\text{L}_2]}{[\text{Cu}^{\text{I}}\text{L}_2][P-X]} \quad \text{eq. 2}$$

$$k_p^{\text{app}} = k_p^* [P^*] = - \frac{d \ln [M]}{dt} \quad \text{eq. 3}$$

In order to support the proposed mechanism of propagation, basic kinetic studies were performed. The internal order in monomer and external order in initiator, copper(I) complex and copper(II) complex.

To satisfy the requirement¹¹ for controlled radical polymerization, e.g. fast initiation comparable to propagation, methyl 2-bromopropionate, which has a very similar structure to the end group of dormant polymer, was used. A complex of CuBr / dTbipy or dNbipy (1:2 mole ratio) was used as the catalyst. The reaction mixture was not completely homogeneous with the copper(I) / dTbipy complex, but it was homogeneous with dNbipy. The first order kinetic plot was linear which indicated that the number of active species was constant during the polymerization. (Fig 1) The rate has first order dependence on the initiator concentration (slope = 0.89). (Fig 2)

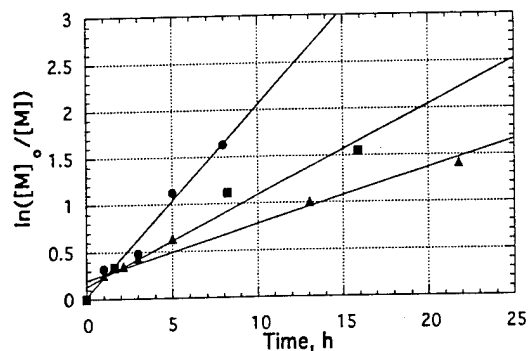


Figure 1. Effects of various concentration of initiator on polymerization kinetics, [MA]₀ = 11.2 M; [MBP]₀ = 0.112 M (●), 0.056 M (■), 0.028 M (▲); [CuBr]₀ = 0.056 M; [dTbipy]₀ = 0.112 M; Temp = 90 °C

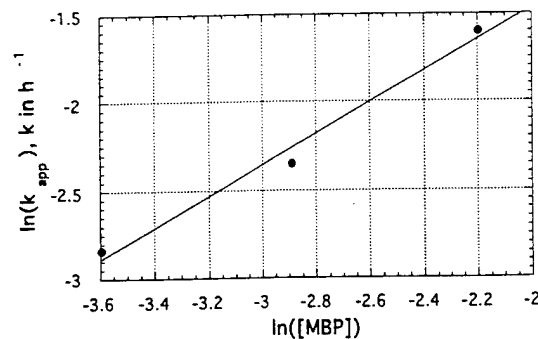


Figure 2. Dependence of apparent rate coefficient (k_{app}) on the initiator concentration in the polymerization of MA, [MA]₀ = 11.2 M; [CuBr]₀ = 0.056 M; [dTbipy]₀ = 0.112 M; Temp = 90 °C

The linear increase of molecular weights versus conversion was observed with good correlation to predicted values, $DP = \Delta[M]/[I]_0$ and the molecular weight distribution was narrow, $M_w/M_n = 1.2$. These results indicate that the chain breaking processes could be neglected leading to a controlled polymerization. (Fig 3).

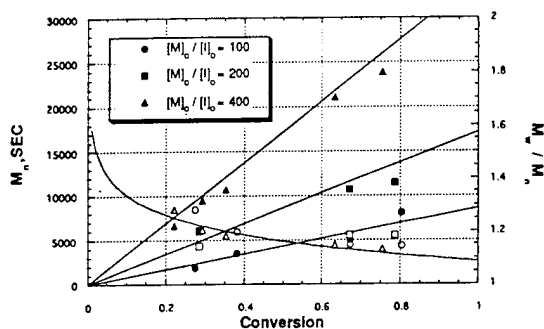


Figure 3. M_n and M_w / M_n dependence on conversion for different $[\text{monomer}]_0 / [\text{initiator}]_0$ ratios for bulk ATRP of methyl acrylate $[\text{MA}]_0 = 11.2 \text{ M}$; $[\text{MBP}]_0 = 0.112 \text{ M}$; (●,○), 0.056 M (■,□), 0.028 M (▲,△); $[\text{CuBr}]_0 = 0.056 \text{ M}$; $[\text{dTbipy}]_0 = 0.112 \text{ M}$; Temp = 90°C

Figure 4 shows that the dependence of the rate constant on the initial catalyst concentration is first order for the homogeneous catalyst system (copper(I) / dNbipy). The changes in concentration of non-homogeneous catalyst system (copper(I) / dTbipy) showed little effect on the propagation rate, presumably due to the solubility limit. The slightly negative slope ordered for dTbipy may be due to additional solubility limitations of the deactivator Cu(II). (vide infra)

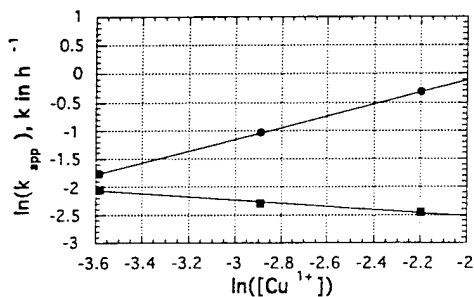


Figure 4. Effects of various concentrations of catalyst on polymerization rate $[\text{MA}]_0 = 11.2 \text{ M}$; $[\text{MBP}]_0 = 0.056 \text{ M}$ with CuBr / dNbipy (1:2, ●) and CuBr / dTbipy (1:2, ■); Temp = 90°C

As expected, the apparent rate constant for copper(I) / dNbipy system had inverse first order on the concentration of copper(II) bromide. (Fig 5) The slope of the $\ln(k_{\text{app}})$ versus $\ln(1 / [\text{Cu}^{2+}])$ for copper(I) / dTbipy system (0.43) means that the propagation rate is less affected by the concentration of copper(II)bromide in non-homogeneous system.

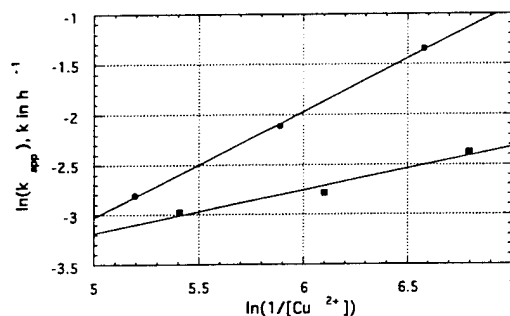


Figure 5. Effects of various concentration of copper(II) bromide on polymerization rate with CuBr_2 ; $[\text{MA}]_0 = 11.2 \text{ M}$; $[\text{MBN}]_0 = 0.056 \text{ M}$; $[\text{CuBr}]_0 = 0.056 \text{ M}$; $[\text{dNbipy}]_0 = 0.112 \text{ M}$ (●), $[\text{dTbipy}]_0 = 0.112 \text{ M}$ (■); Temp = 90°C

Synthesis of High Molecular Weight Polymer.

The synthesis of polymers with molecular weights up to 10^5 was attempted. The experimental molecular weight had good correlation with the theoretical values up to $M_n \approx 80,000$ and molecular weight distribution was narrow ($M_w / M_n = 1.2$). (Fig 6)

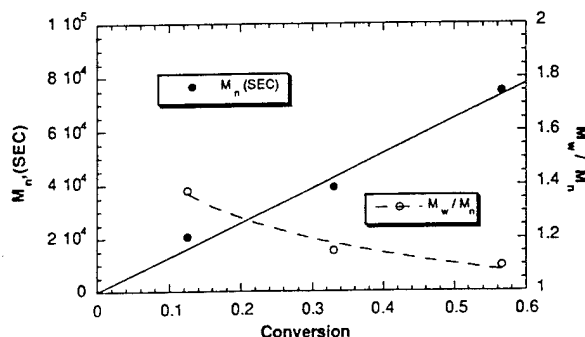


Figure 6. M_n and M_w / M_n dependence on conversion for ATRP of methyl acrylate $[\text{MA}]_0 = 11.2 \text{ M}$; $[\text{MBP}]_0 = 0.0074 \text{ M}$ ($[\text{M}]_0 / [\text{I}]_0 = 1500$); $[\text{CuBr}]_0 = 0.0074 \text{ M}$; $[\text{dTbipy}]_0 = 0.0148 \text{ M}$

Acknowledgments This work was partially supported by the Office of Naval Research.

References

- O. Webster, *Science* **251**, 887 (1991).
- M. Szwarc, *Carbanions, Living Polymers, and Electron transfer Processes*; Wiley; New York (1968).
- M. Szwarc, *Nature* **178**, 1168 (1956).
- D. Greszta, D. Mardare, K. Matyjaszewski, *Macromolecules* **27**, 638 (1994).
- D.P. Curran, in *Comprehensive Organic Synthesis*; B.M.Trost, I.Fleming Eds.; Vol. 4, Pergamon; Oxford, 1991; p 715
- P. Martin, E. Steiner, J. Streith, T. Winkler, D. Bellus, *Tetrahedron* **41**, 4057 (1985)
- J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **117**, 5614 (1995).
- J. S. Wang, K. Matyjaszewski, *Macromolecules* **28**, 7901 (1995).
- T. B. Hadda, H. L. Bozoc, *Polyhedron* **7**, 575 (1988).
- R. N. Keller, H. D. Wycoff, *Inorg. Synth.* **2**, 1 (1946)
- K. Matyjaszewski, *J. Phys. Org. Chem.* **8**, 197 (1995)