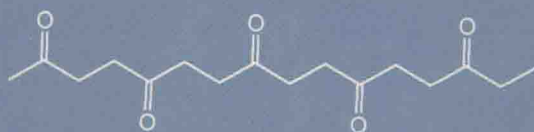


ACS SYMPOSIUM SERIES 760

Transition Metal Catalysis in Macromolecular Design



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Lisa Saunders Boffa and Bruce M. Novak

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Transition Metal Catalysis in Macromolecular Design

Lisa Saunders Doffa, EDITOR
Exxon Research & Engineering Company

Bruce M. Novak, EDITOR
North Carolina State University



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Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded in order to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

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Preface

The use of organometallic catalysis as a tool for producing well-defined macromolecules has advanced rapidly since the development of metallocene and “living” transition metal-mediated polymerizations. In addition to the continued understanding and development of controlled addition and condensation polymerizations, recent years have seen the discovery of new catalytic chain-building mechanisms and the achievement of greater levels of control of polymer architecture. Catalytic reactions involving polymers as substrates have produced many new macromolecules, and advances in catalyst design have allowed controlled polymerization techniques to be applied under a wider range of conditions.

This book examines several themes in the area of transition metal-mediated polymer synthesis, with the special intent to demonstrate how this field has moved beyond the use of single-site catalysts to new applications and advanced techniques for architectural control. It is based on a symposium that took place at the 217th National American Chemical Society (ACS) Meeting in Anaheim, California, April 1999, entitled “Advanced Catalysis: New Polymer Syntheses and Modifications”. We hope this book will serve as a useful introduction and tutorial to readers interested in polymer design through catalysis.

The book contains 16 chapters, beginning with an overview chapter designed to illustrate how organometallic techniques have advanced the design of one particular type of polymer (polyacrylates and -methacrylates). The remainder of the book is divided into four sections representing current areas of relevant research: New Chain-Building Mechanisms, Polymer Modification Using Transition Metals, Olefin-Alkyne Addition Polymerization, and Controlled Radical Polymerization. Each section begins with a brief description of the chapters to follow. We have attempted to include a balance of review, synthetic, mechanistic, and applied papers to fully represent the progress being made in organometallic polymer synthesis. We have also included two papers featuring unusual non-transition-metal-based polymerizations, which are in keeping with the spirit of this book.

Acknowledgments

We thank all of the chapter authors, primarily for their excellent contributions, but also for their cooperation and timeliness regarding manuscript submission. We are also grateful for the excellent support of Teresa Henline (North Carolina State University) and Pat Kocian (Exxon) with chapter reviews and submissions. Anne Wilson and Kelly Dennis at ACS were critical in helping this book take shape. Finally, we appreciate the patience of our colleagues, particularly Joe Sissano and Don Schulz at Exxon, during the preparation of the Advanced Catalysis symposium and this volume. Financial support for the Advanced

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LISA SAUNDERS BOFFA
Corporate Research Laboratory
Exxon Research & Engineering Company
Route 22 East
Annandale, NJ 08801

BRUCE M. NOVAK
Department of Chemistry
North Carolina State University
Raleigh, NC 27695

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Chapter 1

The Organometallic Polymerization of (Meth)acrylates: An Overview

Lisa Saunders Boffa

Corporate Research Laboratory, Exxon Research and Engineering Company,
Route 22 East, Clinton Township, Annandale, NJ 08801

Metal-mediated (meth)acrylate polymerizations provide a good example of the versatility and importance of transition metal catalysis in polymer design. This chapter surveys several of these processes with respect to “living” behavior, experimental condition and monomer restrictions, and types of polymer architectures available. In addition to anionic methods, Group Transfer Polymerization (GTP) with silyl enolates or zirconocenes, organolanthanide- and aluminum porphyrin-initiated polymerization, and Atom Transfer Radical Polymerization (ATRP) are discussed.

Polymethacrylate and polyacrylate materials play an important role in our society. Almost two billion pounds of polymer products based on acrylic esters are produced each year for applications such as window plastics, dental materials, paints, contact lenses, fibers, and viscosity modifiers. Polymethacrylates--particularly poly(methyl methacrylate) (PMMA)--possess high strength, high impact resistance, excellent heat and chemical stability, and a highly amorphous nature which results in excellent optical clarity. For these reasons, they are used widely as building plastics (*Plexiglas*, *Lucite*). Polyacrylates are less rigid due to their lower glass transition temperatures, and as latex emulsions form the basis for durable automobile and house paints and coatings. Random copolymers of (meth)acrylates with vinylidene chloride (*Saran*), acrylonitrile, and ethylene find applications as clothing fibers, tubing, gaskets, disposable gloves, and heat- and oil-resistant automotive elastomers.

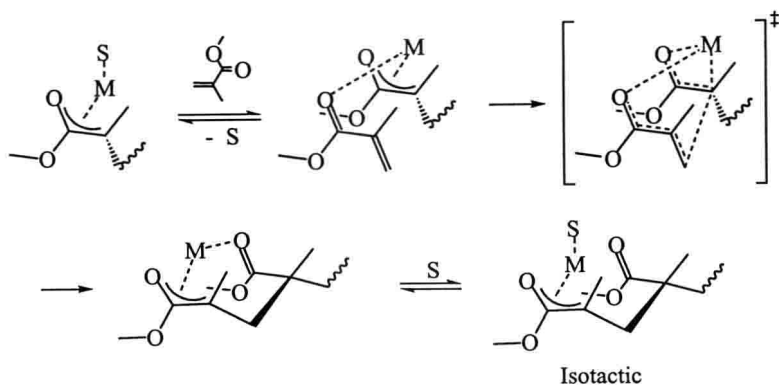
Despite the commercial utility of polymethacrylates and polyacrylates, refinements in synthetic methodology these macromolecules have lagged behind that of other polymers. The great majority of acrylic ester products in use today are still produced by radical polymerization, which allows little if any control over the fine points of the polymerization process. This is the result of the traditionally ill-controlled nature of acrylate polymerization. While chain termination and transfer side reactions may be largely eliminated for other monomers, such as styrene and dienes, through the use of controlled anionic polymerization, the (meth)acrylate ester

group can participate in a number of side reactions during polymerization. For this reason the control necessary to produce well-defined acrylic macromolecules has been an elusive goal, and comparatively fewer special-architecture poly(meth)acrylate materials have been prepared.

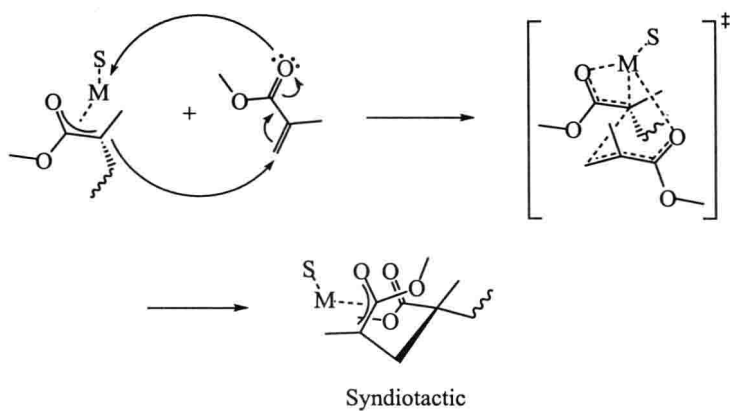
The instances in which special-architecture acrylics have been studied indicate that these materials are both scientifically and technologically appealing. For example, telechelic polymethacrylates and -acrylates are useful toughening agents (1) and chain extenders (2) and are known to act as self-assembling rheo-thickeners (3). Diene-methyl methacrylate (MMA) diblock copolymers are excellent emulsifiers for filler blends, liquid dispersions, and high-impact polymeric matrices (4). Acrylics are predicted to be ideal components for styrene-butadiene-styrene-type triblock thermoplastic elastomers (5), and new copolymer combinations of (meth)acrylates and nonpolar monomers should produce interesting amphiphilic materials. A great deal of effort has thus been expended in the last two decades to develop polymerization techniques with the control necessary to produce well-defined poly(meth)acrylates of varying architectures. In addition to modified anionic methods, well-controlled or "living" pseudoanionic polymerizations (6-9) of (meth)acrylates based on organometallic initiators have provided a number of complimentary strategies for the synthesis of useful and novel materials. These processes, along with a discussion of the difficulties associated with traditional anionic polymerization, are discussed in this chapter.

Anionic Polymerization

Methacrylates and acrylates may be polymerized by traditional anionic initiators, including alkali metal alkyls and enolates, Grignard reagents, α -methylstyrene tetramer, and electron-transfer agents (sodium naphthalide, etc.). This process is extremely sensitive to both oxygen and active-hydrogen impurities. Two mechanisms are known to be operative (10). In weak or noncoordinating solvents such as toluene, the propagating enolate endgroup exists as an ion pair, and monomer precoordination to the counterion through the carbonyl group is favored. This requires a same-side configuration of the chain end and monomer ester groups, giving an isotactic unit upon addition (Scheme 1). In highly coordinating solvents--particularly chelating solvents such as dimethoxyethane (DME)--the incoming monomer unit is not able to displace the solvent molecule and addition takes place via a concerted process (Scheme 2). An opposite-side configuration of the monomer and endgroup esters is preferred for steric reasons and the resultant linkage is syndiotactic. This mechanism is most highly favored for lithium counterions, which interact very strongly with the solvent and chain end due to orbital overlap. When mixed solvents or larger, more weakly interacting cations are used, a mixture of both mechanisms results, giving largely atactic polymer. A concerted mechanism is also operable with cryptated cations, which cannot undergo monomer precoordination prior to addition, and in cases where free ions rather than ion pairs are the active species.



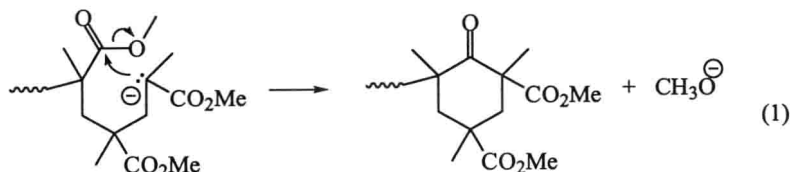
Scheme 1. Precoordination mechanism for anionic methacrylate polymerization (weakly coordinating solvents).



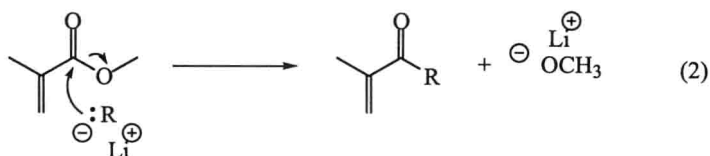
Scheme 2. Concerted mechanism for methacrylate polymerization (strongly coordinating solvents).

Side Reactions

Side reactions involving nucleophilic attack at the ester group render anionic (meth)acrylate polymerization nonliving under typical conditions (11-15). The most common process is intramolecular "backbiting" of the active endgroup to the antepenultimate ester unit of the polymer chain (Equation 1) (13, 16-18). This produces



a nonreactive cyclic ketone endgroup and an alkoxide ion and results in lowered initiator efficiency and inflated molecular weights. Backbiting occurs mainly at the trimer stage of polymerization since additional chain units sterically inhibit attack at the carbonyl group (19). The alkoxide eliminated during cyclization may act as a weak initiator, and secondary polymerization of MMA by this species contributes to a lowering and broadening of the molecular weight distribution through chain transfer. The extent of initiation by alkoxide byproducts appears to be dependent on the identity of the counterion (10, 11, 20). A second side reaction occurring during early stages of the polymerization has been observed for alkyllithium and Grignard initiators (15, 21-26); this process involves 1,2- rather than 1,4-attack of the initiator on monomer, giving alkoxide and a vinyl ketone which may be added to a growing chain as a comonomer (Equation 2). The propagating enolate endgroup of the ketone



is not as reactive as the enolate anion of the (meth)acrylate, and also gives lowered and broadened molecular weight distributions since the overall polymerization rate is slowed. Schreiber (15) and Korotkov (27) and Löhr et al. (28) have proposed similar termination steps involving 1,2-addition at either the monomer or backbone carbonyl groups by the enolate propagating species; however, no evidence has been found for the existence of these mechanisms. Extremely bulky methacrylates, such as *tert*-butyl methacrylate (*t*BMA), are the only monomers which have been thought to be immune to terminating side reactions (29-31). However, recent evidence indicates that even

for *t*BMA, oligomers resulting from side reactions are found in the polymerization mixture (32).

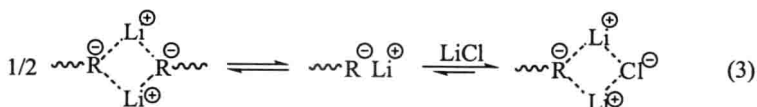
Side reactions involving chain transfer (other than secondary initiation from alkoxide byproducts) are not problematic for methacrylate polymerization. In contrast, chain transfer is facile for acrylates due to the presence of an acidic proton at the carbonyl α -position (10, 13, 33-36). Again, only bulky monomers such as isopropyl and *t*-butyl acrylate (*t*BuA), may be polymerized anionically to high conversion with even moderate degrees of control. Additionally, polymerizations of both methacrylates and acrylates carried out in noncoordinating solvents involve multiple active species due to the formation of chain end aggregates (10). Very broad, multimodal molecular weight distribution are obtained under these conditions, with polydispersities of up to 80 being reported for MMA polymerization.

Strategies for Living Polymerization

Several "ligated anionic polymerization" (LAP) approaches have been employed to suppress termination in anionic (meth)acrylate polymerization with the goal of obtaining "living" behavior (3, 37). Low temperatures (≤ -75 °C), polar solvents (THF, DME), and large counterions are known to minimize terminating side reactions (10, 38, 39). The use of these conditions in conjunction with bulky, less nucleophilic initiators, such as alkali metal 1,1-diphenylalkanes (40, 41) and aromatics (42) and branched Grignard reagents (43), has allowed the preparation of relatively monodisperse PMMA ($PDI < 1.20$) with good molecular weight control. Alkali metal enolates, which mimic the active endgroup of the polymerization, are especially effective in this regard (18).

tert-Butylmagnesium bromide may be used to synthesize highly isotactic PMMA in noncoordinating solvents at low temperatures (44-46). The unusual control imparted by this reagent is thought to arise from an interaction between the initiating species, which has been postulated to exist as a complex aggregate bearing multiple *tert*-butyl groups due to the Schlenk equilibrium, and the active endgroup (47). This hypothesis is supported by the fact that the viscosity of the polymerization medium decreases upon termination. Similarly, the preparation of monodisperse, highly isotactic poly(isopropyl acrylate) was reported with a mesitylmagnesium bromide initiator in toluene (48).

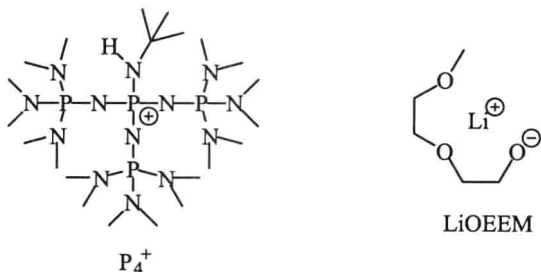
A second strategy for imparting control in anionic methacrylate polymerization involves the addition of common-ion salts (49). In the absence of these additives, the active enolate chain ends exist in a slow equilibrium between free and associated species, which have differing activities and thus form polymer at different rates (10). When lithium chloride is added to the polymerization medium, a new, more rapid equilibrium involving μ -bridged endgroup-salt adducts results (Equation 3) (50-52). The faster interchange between active species results in a lowered polydispersity for



the resultant polymer, and "protection" of the active center by the bridging groups serves to lessen side reactions. Interestingly, the addition of LiCl does not affect tacticity. Lithium *tert*-butoxide is also used as a μ -bridging additive although it is not as effective at promoting fast interchange as LiCl (53-55). Aluminum alkyls and phenoxides have also been employed as additives (46, 56). Recently, Zundel, Teyssié, and Jérôme have used lithium silanolates as μ -ligands with butyllithium initiators (57, 58). The resultant $\text{Bu}(\text{Me}_2)\text{SiOLi}$ -stabilized alkylolithium species can produce high molecular weight, monodisperse, $\geq 90\%$ isotactic PMMA in toluene at 0°C . Well-defined poly(*n*-butyl acrylate) and PMMA-*Pn*BA block copolymers can also be prepared at lower temperatures.

The use of a hindered lithium alkyl or enolate complex as an initiator, in conjunction with LiCl as an additive, has allowed Jérôme and Teyssié and coworkers to prepare PMMA with polydispersities as low as 1.02 and to achieve initiator efficiencies of over 95% at -78°C in THF (51). Since the polymerization of *t*-butyl acrylate is also greatly improved by the addition of LiCl ($\text{PDI} \approx 1.2$) (59), this methodology has been used to synthesize relatively monodisperse MMA-*t*BuA and styrene-*t*BuA block copolymers (60, 61).

A complementary approach, disruption of aggregation by complexation of the counterion rather than the anionic endgroup, has also been employed. Crown ethers, amine cryptands, and pyridine all promote the formation of narrow-PDI poly(meth)acrylates by eliminating chain-end aggregation and promoting the formation of monomeric, highly reactive species (2, 62-67). Large "metal free" organic counterions, including tetraalkylammoniums (68-70), tetraphenylphosphonium, and ' P_4^+ ' (71) have also been employed to control polymerization at



higher temperatures (0 – 20°C) with reasonable success. Lithium 2-(2-methoxyethoxy)ethoxide (LiOEEM), which incorporates both cation-complexing and endgroup-bridging moieties, has recently been used as an additive to prepare monodisperse poly(*n*-butyl acrylate) ($\text{PDI} = 1.15$) and poly(2-ethylhexyl acrylate) ($\text{PDI} = 1.07$) and related block copolymers (72-74). Unfortunately, the presence of chain transfer prevents the synthesis of similarly well-defined polyacrylates with shorter primary ester chains.

Group Transfer Polymerization

Silyl Group Transfer Polymerization

The first strategy for achieving “living” (meth)acrylate polymerization through modification of the ionic nature of the endgroup was group transfer polymerization (GTP), developed by Webster and Sogah et al. at DuPont in 1983 (75-80). This process involves initiation with a silyl ketene acetal or related compound, producing a silyl enolate propagating species. GTP proceeds without significant interference from chain termination and transfer steps and is thus a “living” process. Since no highly charged species are involved, it is much more robust than anionic (meth)acrylate polymerization, and may be carried out at room temperature and in the presence of oxygen, although protic compounds still must be excluded. Solvents such as dimethylformamide (DMF) and chlorinated hydrocarbons, which are incompatible with anionic initiators, may also be used.

The mechanism of GTP monomer addition was originally postulated as associative, i.e. the silyl group remains attached to one particular polymer chain throughout the course of the polymerization and is simply “transferred” to each new monomer unit as it is added (Scheme 3) (81). However, studies by Quirk involving silyl endgroup exchange processes for “living” oligomers have indicated that a dissociative mechanism is more consistent (Scheme 4) (82-84). Viewed in this light, GTP is actually an anionic polymerization carried out via ester enolates, which are stabilized by rapid and reversible “termination” with silyl ketene acetals. Based on kinetic data, Müller has subsequently proposed an associative mechanism, at least for cases involving certain GTP catalyst components (see below) (85).

A small amount of either a nucleophilic or Lewis acid catalyst is needed in addition to the initiator to activate (or cleave, depending on which mechanism is actually operative) the silyl enolate endgroup for monomer addition. Nucleophilic catalysts function by promoting displacement at the silyl group through a hexavalent intermediate (for an associative process) and are needed only in low concentrations (< 0.1 mol % of initiator). A wide range of nucleophiles may be used, including fluoride, bifluoride (HF_2^-), azide, cyanide, cyanate, nitrite, carboxylates, phenolates, sulfonates, and sulfonamides (75-77, 86-89). Lewis acid catalysts function by coordinating to the monomer carbonyl group and are thus needed in higher concentrations (≥ 10 mol % of initiator). Zinc dihalides, dialkylaluminum halides, tetraalkylaluminoxanes, and more recently lanthanide triflates and HgI_2 have been used in this capacity (85, 90, 91). Lewis acid catalysts are preferred for acrylate polymerization, as nucleophilic catalysts have been found to give broader molecular weight distributions. GTP may also be performed without added catalysts under conditions of high pressure (1000-3000 atm) (92).

With the correct choices of initiator and catalyst, both methacrylates and acrylates may be polymerized quantitatively with GTP to give polymers with low polydispersities ($1.03 \leq \text{PDI} \leq 1.4$). Good control of molecular weight through the monomer to initiator ratio is achieved. However, the synthesis of polymers with molecular weights in excess of 60 000 is difficult, especially with acrylates; it is thought that the silyl group possesses the ability to migrate to other locations along the polyacrylate backbone. Most reported examples of poly(meth)acrylates synthesized by GTP are of $M_n < 20\,000$. Additionally, GTP does not produce