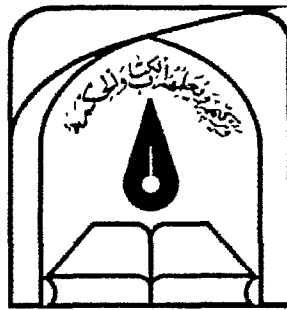


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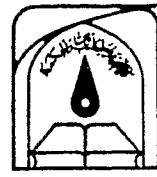
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**KINETICS OF FREE RADICAL COPOLYMERIZATION
OF ISOBUTYL METHACRYLATE AND LAURYL
METHACRYLATE**

By: Ali Habibi

Supervisor: E. Vashegani Farahani

۳۵۷۷۳



دانشگاه تربیت مدرس

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ماده ۳ به منظور جبران بخشی از هزینه های انتشارات دانشگاه، تعداد یک درصد شمارگان کتاب (در هر نوبت چاپ) را به «دفتر نشر آثار علمی» دانشگاه اهدا کند. دانشگاه می تواند مازاد نیاز خود را به نفع مرکز نشر در معرض فروش قرار دهد.

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تاریخ و امضا:

**Kinetics of Free Radical Copolymerization
of iso-butylmethacrylate and laurylmethacrylate**

**Dissertation Submitted to the Faculty of Engineering
of Tarbiat Modares University (TMU) in Partial Fulfillment
of The Requirements for The Degree of Doctor of Philosophy**

Chemical Engineering Department

By: Ali Habibi

Supervisor: Dr. E. Vasheghani-Farahani

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ABSTRACT:

Copolymers of isobutyl methacrylate (i-BMA), and lauryl methacrylate (LMA), were prepared by bulk and solution free radical polymerization. Synthesis of these copolymers was investigated over a wide composition range both at low and high conversion levels. The monomer reactivity ratios as well as 95% confidence intervals were calculated by "ordinary least square" (OLS), "generalized least square" (GLS), NLLS and monte carlo (MC) methods. "Bootstrap" and "Preferential adsorption models" which explain anomalous behavior in free-radical copolymerization, was also presented. Maximum likelihood function with error-in-variable model (EVM), was used to estimate the initiator decomposition and coupled propagation-termination rate constants. A two-step procedure based on Marquardt and Interval Newton/Bisection algorithm was used to estimate the individual rate parameters. This technique was used, with mathematical and computational guarantees of certainty, to find the global optimum. Statistical analysis indicates that although copolymer composition is well described by terminal unit model, but rate data are well represented by the "Implicit Penultimate Unit Effect" model of Fukuda and co-workers. The kinetic and thermodynamic parameters of initiation, overall reaction and thermal degradation of copolymer was also determined using TGA/DTGA and DSC data. The model-free and model-fitting kinetic approaches were applied to these data for retrieval of kinetic parameters. Finally a systematic, full conversion range study of copolymerization is being conducted in solution. The polymers produced were characterized for conversion, copolymer composition and molecular weight distribution. The experimental trails were of the two-level factorial type and were designed optimally using a D-optimal criteria. This design procedure with two levels of temperature, initiator concentration, chain transfer agent concentration, monomer feed composition and agitator rotational speed led to the identification of significant effects and interactions on cumulative copolymer composition, molecular weight distribution, batch time and the onset of gelation.

KEY WORDS: Methacrylates, Kinetics, Reactivity Ratios, Monte Carlo, Thermal Analysis, D-optimal

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CHAPTER 1

SCOPE AND OUTLINE OF THE THESIS

SCOPE AND OUTLINE OF THIS THESIS

SYNOPSIS. This chapter starts with a general introduction to the work described in this thesis, followed by some general theory concerning free radical copolymerization kinetics. The concept of intramolecular composition drift is discussed and the investigated lines of research are validated. Hereafter, the outline of the thesis is given in detail. Finally, the remainder of this thesis is outlined.

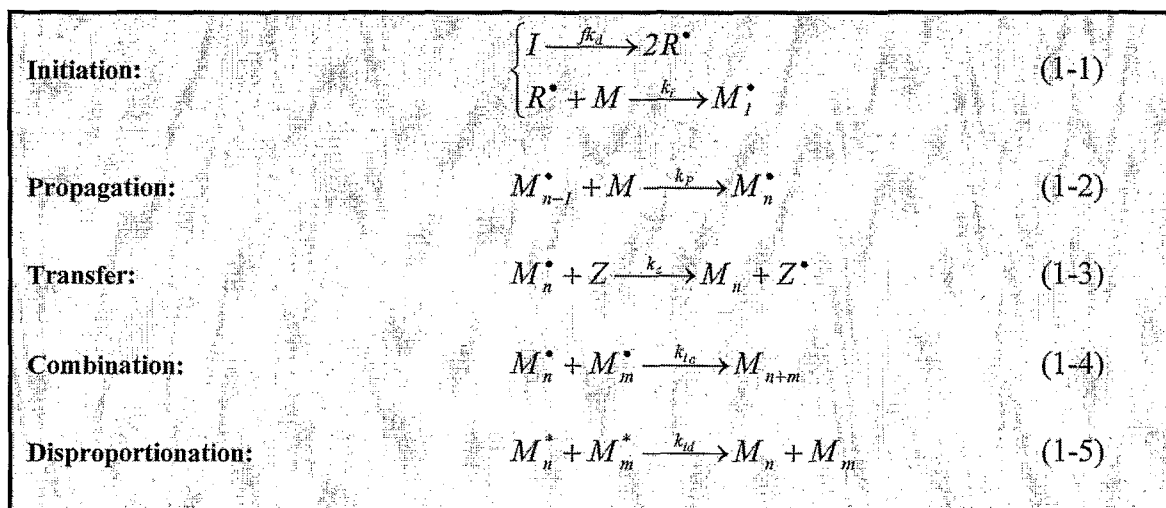
1.1 INTRODUCTION

The growing interest in multicomponent polymerizations from both industry and academia has uncovered the need for a more systematic approach to the study of such systems. The systematic accumulation of reliable kinetic data will be useful for the purposes of parameters estimation, thus aiding further the modeling efforts. Also a good working knowledge of the mechanism and an appreciation of the effects the process variables on the properties of interest are required for optimization and control of polymerization process. The approach which utilized in this work, consist of using experimental kinetics and mathematical modeling to examine all levels of multicomponent polymerization.

1.1.1 Free-Radical Polymerization

One of the most convenient ways to produce polymeric material on an industrial scale is through free-radical polymerization¹. It allows the synthesis of a wide gamut of homopolymers, while at the same time virtually any combination of monomers can be employed to produce copolymers. Moreover, the technique is relatively insensitive towards all kinds of impurities, notably water, and only requires the absence of oxygen. Free-radical polymerization comprises essentially three distinguishable

features; initiation, propagation and termination¹. The general scheme for free-radical homopolymerization is depicted in the following scheme:



Generally, in the initiation step a primary radical is formed by dissociation of an initiator, usually a peroxide or an azo-compound. This primary radical can react with monomer to yield a carbon-centered radical. The carbon-centered radical can now add monomer until it undergoes bimolecular termination, which can occur either by combination or by disproportionation. It should be noted that growing polymeric radicals can also be terminated by transfer reactions with a transfer agent, solvent or even a polymeric chain. In this case, the radical will be transferred from the growing polymeric radical to the transfer agent, which, in turn, can re-initiate polymerization. Two features characterize the conventional free-radical polymerization system.

First, chains grow very fast and the average lifetime of the growing radical chains is in the order of only a second or even less (0.1-1 s).

Second, the addition of monomer to the polymeric radical most often occurs without any selectivity, i.e. stereoregular incorporation of monomer is only claimed in special cases.

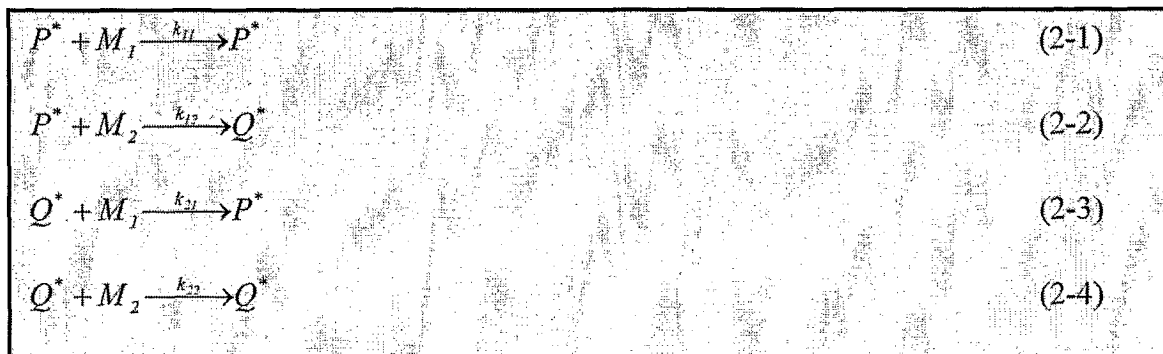
Because the microscopic polymer properties, such as chemical composition distribution, molecular-weight distribution and tacticity, are key parameters that determine the macroscopic behavior of the polymer, the control of these parameters is essential. The absence of control of the incorporation of monomer into the polymeric chain implies that many macroscopic properties cannot be influenced to a large extent.

It is evident that the characteristics of the polymeric chain are determined by all fundamental reaction steps in the polymerization process. Since transfer and termination events only account for a very small part of the polymeric chain, the kinetic behavior of free-radical polymerization in this work will be focused mainly on the initiation and propagation steps.

1.1.2 Free Radical Copolymerization

The situation becomes slightly more complicated when two different monomers are copolymerized. In this case, two monomers participate in the propagation steps and, as a result, polymeric radicals with different chain ends exist. In general, these radicals will not exhibit the same affinities towards both monomer species. In addition, interactions between monomer and solvent, monomer and copolymer, monomer and growing polymeric radicals and even between both monomers may exist. These interactions affect the intrinsic reactivities of the radicals and, therefore, have a strong influence on the composition of the resulting copolymer and its macroscopic properties. In order to describe the copolymerization and to explain copolymer compositions, sequence distributions and average propagation rate coefficients, several models have been proposed. The simplest one is the terminal unit model^{2,3} that disregards any of the physical interactions stated above and, beside the two monomer species, only takes into

account two growing radicals with different monomer units at their chain ends. The terminal unit model (TUM) thus considers the following four propagation reactions:



where P^* and Q^* represents the growing polymer chain with M_1 and M_2 monomer linked to a primary radical of initiator. The expressions derived from the TUM may give only a qualitative description and do not quantitatively describe the experimentally observed data very well. In these cases more complicated models, such as the penultimate unit model^{4,5} or monomer complex participation model⁶ could be considered to derive the corresponding expressions. Obviously, a better description of the system is gained, but additional parameters need to be introduced. Copolymerization models have been extensively discussed in many literature reviews⁷⁻⁹.

1.1.2.1 Chemical Composition Distribution: Intramolecular Composition Drift

The chemical composition distribution is a result of the different reactivities of the monomers in the polymerization process, the different sequence of incorporation into the polymer chain, and different chain termination reactions. The determination of the microstructure of copolymers (monomer sequencing and tacticity in the polymer chain) is important in obtaining more detailed information on the different macromolecules. It gives information on the mechanism of the polymerization reaction and helps to establish structure-property relationships. The way both monomers are distributed in a copolymer determines in great part its physical properties. Two copolymers can have