

CHAPTER I

INTRODUCTION

1.1 Introduction

Nowadays polymers are widely used in many applications instead of the natural products such as metal, wood, etc. due to their lighter weight, easier and cheaper to fabricate, and various properties offered dependent upon their chemical structure and physical characteristics. A single polymer or homopolymer, most of the time, has limited properties to meet the specific requirements acquired for specific applications. Polymer blend or polyblend, a mixture of at least two polymers, is an alternative material which have combination and sometimes synergistic properties of the individual polymers used for the blend. Besides the polymer blending, another alternative approach, copolymerization of at least two monomers yields a copolymer having different sequences of the monomer repeating units in the chain. The copolymerization has greatly allowed to produce the unlimited number of different “tailor-make” copolymers since the very first study in 1911 [1].

The tendency of each monomer to enter into copolymer chain being markedly difference was found in 1930's. This phenomena is so-called 'composition drift' which can cause the copolymer synthesized having the different sequence distribution of comonomer repeating units that directly results in different copolymer configurations, including random, block, alternate, periodic and grafted copolymers, which affect on the final properties. The composition drift has been attributed to the greater reactivity of one of the monomer in the mixture [2,3]. The monomer reactivity ratios are the ratios of the rate constant for the addition reaction of a given radical with its own monomer to the rate constant for that with the other monomer. They are important quantities since, for a given instantaneous comonomer composition, they control the overall composition of the copolymer formed at that instant and also the sequence

distribution of the different repeating units in the copolymer. Details of the influence of monomer reactivity ratios on the copolymeric structure can be found in many monographs [2,3]. In most cases, the presence of inhibitors, chain transfer agents or solvent cannot affect the monomer reactivity ratios. However, the difference mode of initiation, i.e., free radical or ionic polymerization, can cause a drastic change of the values of the monomer reactivity ratio [2].

Most experimental procedures for determination of the monomer reactivity ratios involved the polymerization of a variation of monomer feed compositions. The polymerizations were performed to low degree conversion as possible, e.g. less than 5%. The copolymer formed are isolated and analyzed their compositions by either direct or indirect method, such as radioisotopic labeling, spectroscopic techniques including IR, NMR and UV. The other alternative method is to measure the comonomer feed composition by the chromatographic techniques (HPLC, GPC or GC), which are more sensitive than those used for measurement of the copolymer compositions. Since the comonomer feed compositions are slightly changed, it is hardly to measure the small differences between large numbers [1]. The other weak point is that the monomer remained in the reaction can be absorbed on the polymer formed [4]. The techniques used to determine monomer reactivity ratios [1,5] are given in Section 2.4.3, Chapter 2.

There was not found in any literatures reported on utilization of DSC technique to determine the monomer reactivity ratio which, in this work, is the first time to employ such the useful technique.

1.2 Objectives

- 1) To study the kinetics of thermal-initiated free radical homopolymerizations of styrene and MMA and copolymerization of those monomers.
- 2) To determine the reactivity ratios of styrene and MMA using differential scanning calorimetric (DSC) technique.

1.3 Scope of the research

- 1) Literature survey
- 2) Studying the homopolymerization of styrene using DSC. The effect of initiator concentration and temperature were investigated.
- 3) Studying the homopolymerization of MMA using DSC. The initiator concentration and temperature were varied.
- 4) Determination of the propagation rate constant, overall rate constant, initial rate and activation energy.
- 5) Studying the copolymerization of styrene and MMA using DSC.
- 6) Determination of monomer reactivity ratio of styrene and MMA.
- 7) Confirmation of the reliability of the kinetic parameters using the well-known technique of gas chromatography which is normally used to study the kinetics of polymerization.
- 8) Summarizing the results.