COPOLYMERIZATION OF SOME VINYL MONOMERS

A THESIS

SUBMITTED TO THE UNIVERSITY COLLEGE FOR WOMEN
AIN SHAMS UNIVERSITY
CAIRO

By

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(B.Sc.)

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

Of

MASTER OF SCIENCE

AIN SHAMS UNIVERSITY
UNIVERSITY COLLEGE FOR WOMEN
CAIRO

1978

Copolymerization of Some Vinyl Monomers.

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NOTE

Beside the work carried out in this thesis, the candidate attended postgraduate course for one year in Physical and Inorganic Chemistry covering the following topics :

(1) Techniques of Inorganic Chemistry.

(2) Structure and Symmetry of Inorganic Compounds.

(3) Nuclear and Magneto Chemistry.

(4) Surface Chemistry.

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ACKNOWLEDGEMENT

The auther wishes to express her gratitude to Prof. Dr. Saleh Ahmed Awad Professor of Physical Chemistry, University College for Women, for his interest in this work ,and for his helpful in discussion.

I am also much indebted to Dr. Abo El Khair B. Mostafa Assistant Professor of Physical Chemistry for suggesting the problem, sincere help and close supervision during this work.

Best thanks are also delicated to my colleagues for kind experimental facilities.

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INTRODUCTION

INTRODUCTION

Chemistry of high polymers has been developed enormously during the last few years. As examples of such macromolecules are the polymers of acrylonitrile which have been accepted in a broad array of applications and industries because of their unique properties. For example, the acrylic fibers, containing at least 85 percent acrylonitrile, exhibit the properties of high strength, stiffness, toughness, and abrasion resistance. They are relatively insensitive to moisture and have good resistance to stains, chemicals, insects and fungi. However, the commercialization of polyacrylonitrile fibers was delayed by their inherent resistance to solvents and dyes. Thus, other monomers are often used in small amounts to make the polymer amenable to dyeing with conventional textile dyes. Common comonomers are vinyl acetate, acrylic esters, and vinyl pyrrolidone. The side chain interrupts the regularity of the polyacrylonitrile skeleton; thus opening up the structure and improving accessibility to solvents and dyes.

Despite considerable study of the chemistry of polymerization, as mentioned above, various laboratories continue to differ in the quantitative details of polymerization mechanisms. The quantitative details are highly important because the properties of the polymer depend upon the polymerization conditions.

The aim of this work is to study the effect of zinc chloride as a modificator on the polymerization mechanism of acrylonitrile (AN) and ethylmethacrylate (EMA) in different media. This was performed by :

a- Studying the kinetics of homo- and copolymerization of acrylonitrile and ethyl methacrylate at different concentrations of $ZnCl_2$. The study of polymerization kinetics is considered as the most important step for the production of polymers and copolymers with required properties.

b- Determining the reactivity ratios of AN and EMA monomers in bulk and in solution media at different molar ratios of $ZnCl_2$. Such investigations give very useful information about the relationship between structure and reactivity of monomers.

LITERATURE SURVEY

A- Homopolymerization of Acrylonitrile

It is well known that the choice of any polymerization technique depends upon the solubility characteristics of the obtained polymer, the application to which it will be put, and the scale of operation. The polymerization of acrylonitrile (AN) is most commonly carried out in solution, bulk, emulsion or suspension systems. The polymerization of acrylonitrile in solution to low conversion has been examined by numerous authors[1,2]. The most complete work seems to have been conducted either in dimethylformamide (DMF), in ethylene carbonate or in dimethyl sulfoxide solvent. Bulk polymerization of pure acrylonitrile occurs quite readily but is limited to small scale experiments, because of the large heat of polymerization (17 Kcal/mole) and the autocatalytic nature of the process[1,3]. One explanation for this phenomenon is that growing polymer precipitates early in the reaction, thus physically trapping the radical in the solid mass. An alternate explanation for autocatalysis of acrylonitrile polymerization has been offered by Ham$^{3)}$.

The mechanism of bulk polymerization of acrylonitrile at conversion $\leqslant$ 15 was studied, using dilatometric method$^{4)}$. It was suggested that the polymer growth in the heterogeneous state where bimolecular terminations could be neglected. Induction periods for the polymerization were not caused by monomer impurities, since they were reproducible and depend on initial initiator concentration. Since bulk homopolymerization of acrylonitrile is not suitable for commercial preparations, bulk copolymerizations may be practicable$^{5)}$.

In the preparation of a polymer insoluble in its monomer or in polymerization in the presence of a non-solvent for the polymer, marked deviations from the kinetics of homogeneous radical polymerization may occur. An example is the preparation of polyacrylonitrile (PAN), which is insoluble in its own monomer.

In this case, the polymer precipitates from the reaction medium; this is followed by centrifugation or filteration, and washing and drying before it can be used. In fact, the polymer tends to precipitate when the growing chain has ten or less monomer units in it6). Thus it may be suggested that, the heterogeneous polymerization of acrylonitrile is highly influenced by the presence of the precipitated particle.

In the absence of precipitated material, when only homogeneous polymerization occurs, the kinetics and mechanism of polymerization are straight forward. It is when the polymer starts to precipitate that the unusual features occur. It was suggested that polymerization occurs in the following three different loci :

a- in the monomer - diluent solution;

b- at the solution - particle interface, and

c- in the interior of the particle.

Dalton and Roberts7) assumed that in the solution phase, the rate of polymerization should be controlled by the viscosity of the medium, similar to the case of methylmethacrylate (MMA) polymerization and the kinetic method of Benson and North[8]. Since they observed that the rate of acrylonitrile polymerization is independent of viscosity of the medium. They concluded that all polymerization occurred at the solution - particle interface, i.e. on the surface, or in the interior of the particles, rather than by solution polymerization. Their results showed that the rate of polymerization of acrylonitrile in solution is independent of viscosity[9], implying that polymerization is not necessarily restricted to the polymer particle. Even at high conversion in ethylene carbonate solution, the rate of polymerization remains proportional to the first power of monomer concentration, and independent of the viscosity of the medium[9]. Dalton and Roberts[7] had also found that the rate of polymerization is independent of the viscosity of the medium.

Thomas[1] had presented electronphotomicrographs which show that the precipitated polyacrylonitrile particles, prepared under different conditions do have different bulk densities. The presence of cracks and crevices can be seen, indicating that a very open structure can occur which would influence accessibility to the particle interior and hence the amount of interior polymerization. Nagao and Uchida[10)] had correlated the rate and degree of polymerization with particle size; the larger the particle, the slower the rate of polymerization. Thus, it would be possible to separate the three loci of polymerization by varying both the adsorption power of the diluent and the temperature of polymerization. The characterization of polyacrylonitrile samples obtained by different polymerization mechanisms was examined by Stein[11)].

A study of molecular weight data obtained by different methods, such as asmometry and light scattering, and data obtained from intrinsic viscosity measurements, indicated a strong branching in a polyacrylonitrile