



Kinetics of polymerization and co-polymerization of vinyl type monomers and their applications in the industry of textiles and paints

Thesis

**Submitted For the Requirements
of the Degree of Ph.D.**

By

(Waseem Abd El- Latif Abd El-Mawgood)

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List of abbreviations

Abbreviã	
A am	Acrylamide
AA	Acrylic acid
A N	Acrylonitrile
AIBN	Azobisisobutyronitrile
BP	benzoyl peroxide
bp.	Boiling point
BA	Butyl acrylate
DSC	Differential Scanning Colorimetry
EA	Ethyl acrylate
Glacial Ac.A	Glacial acetic acid
T _g	Glass transition temperature
HNMR	Hydrogen Nuclear Magnetic Resonance
IR.	Infra red Spectra.
Mp	Melting point
T _m .	Melting temperature
M.wt	Molecular weight
MAA	Methacrylic acid
MA	Methyl acrylate
MMA	Methyl methacrylate
Mn	Number average molecular weight
TGA	Thermo-gravimetric analysis
NaOH	Sodium hydroxide
η	Apparent viscosity
mpa.S	milipaschall.second
PAA	Plyacrylic acid
PMAA	Poly methacrylic acid

PAam	Poly acrylamide
PVA	Poly vinyl alcohol
Chelating agents	Are chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale.
Dispersing agents	Are chemicals that are added to a suspension, usually a colloid, to improve the separation of particles and to prevent settling or clumping.
Flocculants	Are substances that are used to optimize the separation of the solid phase from the liquid phase in aqueous suspensions.
Thickening agents	Are substances which increase the of a solution or liquid/solid mixture without substantially modifying its other properties.
Textile Sizing Agents	Are substances that are applied to the yarns to make it more resistant to the frictional processes that take place during weaving

Chemical structure of prepare homopolymers and copolymers

Abbreviation	Name	Chemical structure
PAA	Polyacrylic acid	$\left[\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right]_n$
PMAA	Poly methacrylic acid	$\left[\text{CH}_2 - \underset{\text{COOH}}{\text{C}(\text{CH}_3)} \right]_n$
PA am	poly acrylamid	$\left[\text{CH}_2 - \underset{\text{CONH}_2}{\text{CH}} \right]_n$
AA,MAAcopolymers	Acrylic acid, methacrylic acid copolymers	$\left[\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right]_n \left[\text{CH}_2 - \underset{\text{COOH}}{\text{C}(\text{CH}_3)} \right]_m$
MA,AN,MMA,AA,tetramer	Methyl acrylate, acrylonitril, methyl methacrylate, acrylic acid, tetramer	$\left[\text{CH}_2 - \underset{\text{COOCH}_3}{\text{CH}} \right]_a \left[\text{CH}_2 - \underset{\text{CN}}{\text{CH}} \right]_b \left[\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right]_c \left[\text{CH}_2 - \underset{\text{COOCH}_3}{\text{C}(\text{CH}_3)} \right]_d$

ABSTRACT

Waseem Abd –Elatif Abd El Mawgood

Kinetics of polymerization and co-polymerization of vinyl type monomers and their application in the industry of textiles and paints.

Unpublished Doctor in chemistry, Ain Shams University, ٢٠١٢.
This work is undertaken with.

١- Systematic study of the preparation of homopolymers of AA, MAA and Aam monomers, where the optimum conditions of the reactions, such as the concentration of monomer and initiator, method of their addition, overall reaction temperature and time of conducting the reactions were evaluated.

٢- Systematic study of preparation of different co- polymers suitable for producing sizing films on the fibers, using different ratios of selected monomers such as (MA, AN, MMA and AA) where MA, AA impart adhesive properties, and MMA and AN impart hardness properties.

٣- Synthesis of (AA-MAA) co-polymer for applications as dispersing agents and chelants.

٤- Study of the validity of PA.am as flocculating agent.

٥ Application of high M.wt PAA as a thickener for textile printing

٦- Estimation of the physical characteristics of the obtained polymers and co-polymers by using HNMR, DSC, TGA, FT-I.R and GPC analysis.

٧. Industrial application of the produced materials

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Chapter.I

Introduction

Vinyl polymers and copolymers, specially those of acrylic and methacrylic acids and their derivatives, cover a large range of applications such as hydro soluble dispersing agents, thickeners, flocculants, detergent auxiliaries, paints, varnishes, inks, dispersants for leather, textiles, non-woven fabrics, glues and adhesives, cleaning and waxing products, plastics and synthetic resins, synthetic rubbers and latex. [1]

Acrylamide monomer is applied as a chemical intermediate in the production of dam foundations, tunnel and sewers, and as additive for water treatment, enhance oil recovery, flocculants, paper making aids, thickeners, soil conditioning agent, sewage and waste treatment, ore processing, and pretreatment of press fabrics. PAam is water-soluble but being nonionic, the viscosity of its solution is less affected by alkali. This polymer softens at 110 °C. Some of the applications of its water solution are flocculation of ores, textiles sizes and retentions of paper filler. [2]

I - Polymers of acrylic acid and its derivatives

As is the case with other addition polymers, the polymerization of AA and its derivatives is an exothermic reaction. Whatever the initiating species, the heat liberated by the polymerization of each monomer is a definite and measurable value, called the heat of polymerization. Such values are listed in Table (1) which shows the amount of heat that must be accounted for in each polymerization. This heat may be allowed to dissipate slowly by controlling the rate

of polymerization, or the polymerization may be carried out in a medium not permitting a violent-or dangerous reaction.

Table (1) free radical polymerization data

Monomer	Heat of homopolymerization (J/K)
AA	1,09
Aam	13,8, 19,8

In order to avoid the premature polymerization of these monomers during storage and shipment, inhibitors or refrigerators are employed. A wide variety of inhibitors is available. Among those in common use for AA and its esters are hydroquinone and the methyl ether of hydroquinone. It is customary to inhibit the monomers to assure safe storage and handling, but it is possible to use minimal concentrations that allow subsequent polymerizations to be conducted without removing the inhibitor, thus avoiding an extra manipulative procedure. [3]

I –a. Preparation of polymers

Monomers of the AA series are generally polymerized with ease. Because of this ready polymerizability, the polymerization processes may require the separation of the inhibitor from the monomer in question by distillation, or by washing; in many cases, the process can be affected in the presence of the inhibitor.

Polymerizations may be carried out in bulk, in aqueous or organic solvent solution, in emulsion, or in aqueous dispersion. Derivatives of these polymers can also be prepared by chemical alteration of the

polymer functionality. In each case, the polymerization is affected by means of a suitable **initiator** system. The particular type of initiator system is governed by the polymerization method, and may include free radical initiation (produced by either thermal or oxidation-reduction operations, or by radiation techniques), anionic initiation, and organo-metallic initiation. The **molecular weight** may be controlled by the customary methods of choice of solvent or polymerization medium, concentration of monomer in solution, concentration of initiator, temperature of polymerization, the use of chain-transfer agents, such as mercaptans, alcohols, and chlorinated compounds, as well as by certain methods peculiar to individual polymerization processes, which are mentioned in subsequent sections. [१]

The solution polymerization of AA may be carried out in water by heating the aqueous monomer in the presence of an initiator, such as hydrogen peroxide, potassium persulfate, or acetyl peroxide, or by initiating a redox polymerization at reduced temperatures with a system composed of potassium persulfate and sodium thiosulfate as the oxidizing-reducing pair. The molecular weight may be controlled by the use of a special chain regulating system consisting of sodium hypophosphite, $\text{NaH}_2\text{PO}_3 \cdot \text{H}_2\text{O}$, and copper acetate, as well as by the conventional means. Polymer solutions in organic solvents, such as methanol and dioxane, may be prepared by the use of azobisisobutyronitrile initiator (AIBN) at elevated temperatures.

A solution of AA in such solvents as benzene and n-hexane may be polymerized with an initiator, such as benzoyl peroxide (BP). [२]

at elevated temperatures to produce an insoluble polymer, which may be removed from the reaction medium by filtration.