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CHARACTERIZATION OF POLYMER SORBERS PRODUCED BY CATALYTIC INITIATION AND GAMMA IRRADIATION

B7644

A thesis
Presented in candidature for the degree
of Doctor of philosophy
in Chemistry

by

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Submitted to
Department of Chemistry, Ain Shams University
(1995)

DEDICATION

To my family

CURRICULUM VITAE

Aiman Mohamady Atta was born on September 27, 1965, in Monofia, Egypt. He attended El-Said El-Badwy Secondary School. After graduating in 1982, he was enrolled at the Faculty of Science, Monofia University and got the B.Sc. Degree with grade "Very Good" in May 1986, and now he is working in the Department of Petroleum Applications, Egyptian Petroleum Research Institute.

He obtained his M. Sc degree in Chemistry from Faculty of Science, Ain Shams University, Cairo at 1992. He registered this thesis in February 1993 under the direct supervision of Asso. Prof. Abdel-Azim A. Abdel-Azim, Assoc. Prof. of Polymer Chemistry, Egyptian Petroleum Research Institute and under attention of Prof. Salah A. Hassan, Prof. of Physical Chemistry, Faculty of Science, Ain Shams University and Prof. Maher A. El-Sockary, Head of the Petroleum Application, Egyptian Petroleum Research Institute.

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ABSTRACT

The thesis deals with the study of the molecular characteristics of some water soluble polymers. A great attention on the flow properties of the solution of poly(vinylpyrrolidone), PVP has been exerted. The viscosity-molecular mass relationship, the effect of solvent on the unperturbed dimensions of PVP in a series of mixed solvents exhibiting a synergistic effect, the applicability of some extrapolation procedures for deriving the unperturbed polymer dimensions from measurements of $[\eta]$ in non-ideal solvents were studied. A new empirical equation for calculating the unperturbed dimensions was suggested. The equilibrium flexibility and hydrodynamic properties of PVP in water/ACT binary mixtures were premeditated. The dependence of the excluded volume, Z , on the composition of the solvent and molecular weight was, also, illustrated

Various types of crosslinked homopolymers and copolymers were prepared and their efficiency as water sorbing polymers was investigated. Different monomer combinations comprised 2-Acrylamide-2-methylpropane sulphonic acid (AMPS) acrylamide (AM), acrylic acid (AA), N-vinylpyrrolidone (VP), butyl acrylate (BA) and 2-Hydroxyethylmethacrylate (HEMA) were used. The polymerization reactions were initiated either by chemical initiator or γ -irradiation. Two types of crosslinking agents, namely, 1,1,1-Trimethylolpropanone trimethacrylate (TPT) and Methylene bisacrylamide (MBA), were utilized for obtaining the crosslinked hydrogels. The structure of the produced polymers was confirmed by the aid of Perkin Elmer 1500 Fourier Transform spectrometer (FTIR). The swelling behavior and the network parameters of the prepared crosslinked polymer were deliberated.

Aim of the work

In the last decades, water soluble polymers have found increasing commercial applications in mineral processing, pharmaceuticals, detergents, cosmetics, textile production, enhanced oil recovery, and for separation of protein mixtures .

PVP, as one of the most important water soluble polymer is considered in the present investigation because it is a widely applied polymer. It has many interesting properties from both physical and biological aspects.

The molecular characteristics of PVP have been described in many papers. However, little attention was given to the flow properties of this water-soluble polymer solution, despite of its importance. Moreover, the reported viscosity-molecular mass relationship for PVP vary greatly. Consequently, chapter three in the present investigation aims to study:

- 1) The effect of solvent on the unperturbed dimensions of PVP in a series of mixed solvents exhibiting a synergistic effect.
- 2) The applicability of some extrapolation procedures for deriving the unperturbed polymer dimensions from measurements of $[\eta]$ in non-ideal solvents.
- 3) The equilibrium flexibility and hydrodynamic properties of PVP in water/ACT binary mixtures.

Various types of crosslinked homopolymers and copolymers are used in many applications such as micro capsules, water absorbing polymers and polyelectrolytes. A further aim of this work is the preparation of crosslinked water soluble polymers and measuring their swelling properties. Because of high

deformation and inferior mechanical properties of many crosslinked homopolymers, it is of interest to utilize different monomer combinations to overcome this problem. Such combinations may comprised AMPS, AM, AA, VP, BA and HEMA for the sake of synthesize the crosslinked copolymers. Accordingly, it is desired to study the parameters which influence the swelling behavior of the prepared crosslinked polymers. These parameters such as

- 1) the effect of the type and percentage of the components incorporated in the copolymer network,
- 2) type and percentage of crosslinker,
- 3) effect of the type and concentration of the chemical initiator used for activating the monomers, and
- 4) the effect of using the advantages of ionizing radiation such as γ -irradiation as an effective method for polymerization initiation.

LIST OF ABBREVIATIONS

Acrylic acid	AA
Acrylamide	AM
2-Acrylamide-2-methylpropane sulphonic acid	AMPS
butyl acrylate	BA
Equilibrium water contents	EWC
Extension ratio	ER
Fourier Transform Spectrometer	FTIR
2-Hydroxyethylmethacrylate	HEMA
Inagaki, Suzuki and Kurata	I-S-K
Kuhn-Mark- Houwink-Sakurada	KMHS
Kamide and Moore	K-M
Linear expansion	LE
Length of the chains between the crosslinks	M_c
Methylene bisacrylamide	MBA
Munk and Halbrook	M-H
Poly(vinylpyrrolidone)	PVP
Stockmayer-Fixman	S-F
Sol fraction	SF
Standard deviation	SD
1,1,1-Trimethylolpropanone trimethacrylate	TPT
Unperturbed Dimensions	UD
Ueda and Kajitani	U-K
N-vinylpyrrolidone	VP

LIST OF SYMBOLS

Bond angle	θ
Bond length	ℓ
Characteristic number of segments	N_0
Conformational ratio	σ
Characteristic ratio	C_{∞}
Crosslinking density	ν_e
Degree of polymerization	n
Density of water	ρ_w
Density of polymer	ρ_p
Disc diameter before swelling	d_0
Disc diameter after swelling	d
Degree of swelling	γ
Expansion factor	α
Effective radius	R_e
Effective length	b
Excluded Volume	Z
Flory constant	Φ_0
Freely-rotating dimension	$\langle r_{of}^2 \rangle^{1/2}$
Hydrodynamic radius of the monomeric unit	r_0
Intrinsic viscosity	$[\eta]$
Kuhn-Mark- Houwink-Sakurada exponent	ν
Mean square end-to-end distance	$\langle r^2 \rangle_0$
persistence length	a_p
Polymer-solvent interaction parameter	χ

Relative viscosity	η_{rel}
swelling ratio	q
Thickness of the disc after swelling	b
Thickness of the disc before swelling	b_0
Unperturbed dimensions	$(\langle r^2 \rangle_0 / M)^{1/2}$
Volume fraction of acetone	ϕ_{ACT}
Volume fraction of water	ϕ_{water}
Volume fraction of polymer	ϕ_{P}