

THE EFFECT OF POLYMERS ON DISPERSION PROPERTIES

edited by Th. F. Tadros



Academic Press

A Subsidiary of Harcourt Brace Jovanovich, Publishers

London New York

Paris San Diego San Francisco Sao Paulo

Sydney Tokyo Toronto



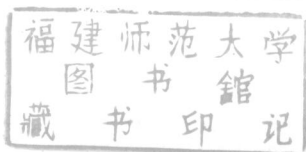
E027685

The Effect of Polymers on Dispersion Properties

Edited by

Th. F. TADROS

*ICI Plant Protection Division
Jealott's Hill Research Station
Bracknell, UK*



27685

1982



ACADEMIC PRESS

A Subsidiary of Harcourt Brace Jovanovich, Publishers

London New York

Paris San Diego San Francisco São Paulo

Sydney Tokyo Toronto

0648.2

T122

ACADEMIC PRESS INC. (LONDON) LTD.
24/28 Oval Road
London NW1

United States Edition published by
ACADEMIC PRESS INC.
111 Fifth Avenue
New York, New York 10003

Copyright © 1982 by
SOCIETY FOR CHEMICAL INDUSTRY

All Rights Reserved

No part of this book may be reproduced in any form by photostat, microfilm, or any other means without written permission from the publishers

British Library Cataloguing in Publication Data
The Effect of polymers on dispersion properties.

1. Polymers and polymerization—Congresses.
2. Suspensions (Chemistry)—Congresses.

I. Tadros, T.F.

660.2'9'93 TP156.P6

ISBN 0-12-682620-X

LCCCN 81-68982

Printed in Great Britain by
Whitstable Litho Ltd., Whitstable, Kent

The Effect of Polymers on Dispersion Properties



Based on the proceedings of an International Symposium of the Colloid and
Surface Chemistry Group of the Society for Chemical Industry held at
University College, London, from 21-23 September, 1981

PREFACE

The use of synthetic and natural polymers and polyelectrolytes to control the stability/flocculation behaviour of aqueous and non-aqueous dispersions and suspensions is of considerable technological importance. Only in the last thirty years or so has a clear understanding of the mechanism of stabilization of dispersions by polymers emerged. Extensive developments of theories of polymer adsorption and steric stabilization have appeared in the last few decades and there is still a need to develop these theories for real systems. It is perhaps fair to say that only recently have experimental techniques such as nuclear magnetic resonance, neutron scattering, etc., been developed to check these theories.

Due to the widespread use of polymers in many industrial applications and in view of the recent developments in the fundamental understanding of polymer adsorption and dispersion stability, the Colloid and Surface Chemistry Group of the Society of Chemical Industry together with the Pure and Applied Macro Molecular Chemistry Group decided to hold an International Symposium on the Effect of Polymers on Dispersion Properties, at University College, London. It was decided to run the Symposium as a general discussion. Invited and submitted papers were edited for style, clarity and wherever possible (by consultation with the author) for scientific content. Preprints of the papers were circulated two weeks before the Symposium. Presentations were then limited to fifteen minutes and ample time was given for discussion. This format was well received by the delegates and certainly led to lively discussion periods. Over 170 people participated in the meeting, of which about 70 were from overseas representing at least 14 different countries. Twenty papers and an Introductory lecture were presented; ten of the papers were presented by overseas participants.

The proceedings of the Symposium published in this book cover the recent advances in theory and experimental techniques used to study the effect of polymers on dispersion properties. After an introductory review paper on polymer

adsorption and dispersion stability, various papers are given on: (a) the adsorption and conformation of polymers at the solid/liquid interface, together with the implications of recent adsorption theories; (b) stability of dispersions in the presence of adsorbed polymers and polyelectrolytes; (c) destabilization of dispersions by polymers and polyelectrolytes. Some papers deal with the recent experimental techniques used to study polymer adsorption and conformation, polymer flocculation and direct measurement of interaction forces between macroscopic bodies with adsorbed polymer layers. Discussion remarks and their replies are given after each paper and the General Discussions are given at the end of the book.

We are very grateful to University College for hosting the meeting and in particular to Dr John Gregory for looking after the domestic arrangements at the University. I would like also to thank the rest of the organising committee for their help in selecting the papers. Thanks are due to the authors for submitting their manuscripts on time and for their cooperation while editing the manuscripts and also to those who contributed in the discussion. I am grateful to Academic Press for finishing the printing on time and producing an excellent set of preprints.

I would also like to thank my secretary, Mrs Irene Gallacher, for a first-class job in handling the administration of the Symposium and typing most of the discussion remarks during the Symposium. Last but not least I would like to thank my wife for her patience in coping with the situation and her voluntary help during very many weekends before the Symposium.

Th. F. Tadros
December, 1981

CONTENTS

Preface	v
Polymer Adsorption and Dispersion Stability <i>Th. F. Tadros</i>	1
Adsorption of AB Block Copolymers at the Silica- liquid Interface <i>J.V. Dawkins, M.J. Guest and G. Taylor</i>	39
Adsorption of Uncharged Water Soluble Polymers on Low Energy Solids: Wetting Studies <i>E.D. Goddard, M.P. Aronson and M.L. Gum</i>	59
Adsorption of Oligo- and Polypeptides on AgI, Their Effects on Double Layer and Colloid Stability <i>H.A. van der Schee and J. Lyklema</i>	81
Rheological Characteristics of Sterically Stabilized Nonaqueous Dispersions <i>M.D. Croucher and T.H. Milkie</i>	101
Polymers as Colloid Stabilizers <i>F.R. Eirich</i>	125
Some Implications of Recent Polymer Adsorption Theory <i>J.M.H.M. Scheutjens and G.J. Fleer</i>	145
Effect of Adsorption Forces on the Bridging of Surfaces by Polymers <i>A.T. Clark and M. Lal</i>	169
Neutron Scattering, Pulsed Nuclear Magnetic Resonance and Photon Correlation Studies of Partially-hydrolysed Poly(Vinyl Acetate) Adsorbed on a Polystyrene Latex Dispersion in Water <i>K. Barnett, T. Cosgrove, T.L. Crowley, Th. F. Tadros and B. Vincent</i>	183
Stabilisation of Colloids by Free Polymer <i>D.H. Napper</i>	199

The Properties of Polyvinyl Alcohol at the Silica Water Interface <i>H. Sonntag, B. Ehmke, R. Miller and L. Knapschinsky</i>	207
The Stability of Silica-(Aerosil)-Hydrosols Under the Influence of Polymer Adsorption <i>E. Killmann and J. Eisenlauer</i>	221
Stabilization of Platinum Particles by Polymers in Aqueous Solutions <i>J. Kiwi</i>	245
The Stability of Polystyrene Latices in the Presence of Poly(ethylene oxide) <i>C. Cowell and B. Vincent</i>	263
The Effect of Environmental Conditions on the Steric Stabilisation of Casein Micelles in Milk <i>D.F. Darling</i>	285
Polymer Flocculation in Flowing Dispersions <i>John Gregory</i>	301
Laser Optical Method for Dynamic Flocculation Testing in Flowing Dispersions <i>W. Ditter, J. Eisenlauer and D. Horn</i>	323
The Destabilisation of Anionic Polystyrene Latices by Vinyl Pyridine/Acrylamide Copolymers and Homopolymers <i>C.H. Ho and G.J. Howard</i>	343
The Relationship Between Polyelectrolyte Configuration and Colloid Stability <i>P.A. Williams, R. Harrop, G.O. Phillips, I.D. Robb and G. Pass</i>	361
Micro-Electrophoresis of Polyelectrolyte-coated Particles <i>R. Buscall, T. Corner and I.J. McGowan</i>	379
Heavy Metal Interactions with Adsorbing Proteins <i>David E. Graham, Heather S. Birch and Malcolm T. McKechnie</i>	397
General Discussion	415
Subject Index	419

POLYMER ADSORPTION AND DISPERSION STABILITY

Th. F. Tadros

*ICI Plant Protection Division,
Jealott's Hill Research Station,
Bracknell, Berkshire*

INTRODUCTION

The practical use of high molecular weight hydrophilic materials to stabilise aqueous hydrophobic colloidal dispersions is not new and was certainly applied by the ancient Egyptians and Chinese, who prepared dispersions of carbon black and other pigments using natural materials such as glue, gum arabic, resins, etc. This is what is nowadays known as "stabilisation of colloidal particles by adsorbed macromolecules". In the early decades of this century, this stabilisation by natural macromolecules was referred to as "protection", in the sense that the dispersion is protected from coagulation by addition of electrolytes, except at very high electrolyte concentrations. The term "steric stabilisation" was first introduced by Heller and Pugh (1954) and is now generally used to describe the stabilising action of layers of nonionic polymers and surface active agents.

The use of synthetic polymers and polyelectrolytes to control the stability/flocculation behaviour of colloidal dispersions and suspensions is of considerable technological importance. Polymeric additives find use as stabilisers in many industrial preparations, e.g. pharmaceuticals, cosmetics, foodstuffs, dyestuffs, pesticides, paper, paint and many allied industries. It is perhaps fair to say that polymers are especially useful in non-aqueous media where electrostatic stabilisation is less successful. However, even in aqueous systems, macromolecules are increasingly being used in many technological applications where stability is needed at high dispersed phase volume fraction and high electrolyte concentrations, as well as under extreme conditions of temperature and flow.

In spite of their wide applications for many years, it is only in the last thirty years or so that a clear understand-

ing of the mechanisms involved has emerged. During this period several theories have been developed to describe the adsorption and conformation of macromolecules at the solid/solution interface. At the same time theories have also been developed to describe the interaction of colloidal particles carrying adsorbed polymer layers. Several extensive reviews on the subject are available (Ash, 1973; Lipatov and Sergeeva, 1974; Vincent, 1974; Barrett, 1975; Vincent and Whittington, 1981) to which the reader should refer for detailed information.

In this introductory paper I will aim at summarising three main topics which cover the theme of this symposium: (i) the adsorption and conformation of macromolecules at the solid/liquid interface; (ii) the nature of the interaction forces that exist between particles containing adsorbed polymer layer; (iii) the stability of colloidal dispersions in the presence of adsorbed polymers.

As far as possible experimental techniques that are currently used to study each of these topics will be briefly mentioned. The papers which will follow in this meeting will deal in more detail with one or more of the above topics.

ADSORPTION AND CONFORMATION OF MACROMOLECULES AT THE SOLID/SOLUTION INTERFACE

This subject is obviously the key to understanding how polymers function as stabilisers and flocculants. The first theories on polymer adsorption were developed in the 1950's and the 1960's, with extensive development in the 1970's (see review articles mentioned above). A brief summary of the process of polymer adsorption and some of the available theories will be given below.

The process of polymer adsorption is fairly complicated. In addition to the usual adsorption considerations such as polymer-surface, polymer-solvent and solvent-surface interactions, one of the principal problems to be resolved is the conformation of the polymer molecule on the surface. This was recognised in 1951 by Jenckel and Rumbach who found that the amount of polymer adsorbed per unit area of the surface would correspond to a layer more than 10 molecules thick if all the segments of the chains are attached. They suggested a model in which each polymer molecule is attached in sequences separated by bridges which extend into solution. In other words not all the segments of a macromolecule are in contact with the surface. Those segments which are in direct contact with the surface are termed "trains"; those in between and extending into solution are termed "loops"; the free ends of the macromolecule also extending into solution are termed "tails"

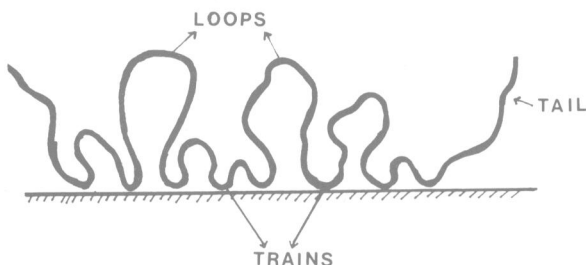


Fig. 1. Schematic representation of an adsorbed polymer molecule at a plane interface.

Theoretical Treatments of Polymer Adsorption

Different approaches to the theoretical treatment of polymer adsorption have been used by several authors. No single treatment has generally been accepted, partly because quantitative experimental verification is extremely difficult. Two general approaches have generally been adopted.

Random-Walk Approach. This is based on the random walk concept which was originally applied to the problem of diffusion and later adopted to deduce the conformations of macromolecules in solution (Flory, 1953). The earliest analysis was by Simha, Frisch and Eirich (1953) who neglected excluded volume effects and treated the polymer as a random walk. Basically the solution was represented by a three-dimensional lattice and the surface by a two-dimensional lattice. The polymer was represented by a realization of a random walk on the lattice. The probabilities of performing steps in different directions were considered to be the same except at the interface which acts as a reflecting barrier. The polymer molecules were therefore effectively assumed to be adsorbed with large loops protruding into the solvent and with few segments actually attached to the surface, unless the segment-surface attractive forces were very high. This theory predicts an isotherm for flexible macromolecules that is considerably different from the Langmuir-type isotherm. The number of attached segments per chain is proportional to $n^{1/2}$, where n is the total number of segments. Increasing the molecular weight results in increased adsorption, except for strong chain interaction with surface.

This approach has been criticised by many other investigators (Silberberg, 1962; DiMarzio 1965). One of the major problems was the use of a reflecting barrier as the boundary

condition, which meant overcounting of the number of distinguishable conformations. To overcome this problem, a Monte Carlo method was used (DiMarzio and McCrackin, 1965) to calculate the average number of contacts of the chain with the surface, the end-to-end length and the distribution of segments $\rho(Z)$ with respect to the distance Z from the surface, as a function of the chain length of the polymer and the attractive energy of the surface. The same method was also used by Clayfield and Lumb (1968).

Statistical Mechanical Approach. This approach was first used by Silberberg (1962) who treated separately the surface layer which contained adsorbed units (trains) and the adjacent layers in solution (loops or tails). The units in each layer were considered to be in two different energy states and partition functions were used to describe the system. The units close to the surface are adsorbed with an internal partition function determined by the short range forces between the segments and the surface, whereas the units in loops and tails were considered to have an internal partition function equivalent to that of segments in the bulk. By equating the chemical potential of the macromolecules in the adsorbed state and in bulk solution, the adsorption isotherm was determined. In this treatment, Silberberg (1962) assumed a narrow distribution of loop sizes and predicted small loops for all values of the adsorption energy. Later, the loop size distribution was introduced (Hoeve *et al.*, 1965) and this theory predicted large loops for small adsorption free energies and small loops and more units adsorbed for larger adsorption free energies when the chains are sufficiently flexible.

Most of the above theories considered the case of an isolated polymer molecule adsorbed at an interface, i.e. under conditions of low surface coverage, θ . These theories were extended (Silberberg, 1968; Hoeve, 1970, 1971) to take into account lateral interaction on the surface, i.e. high coverage. These theories also considered the excluded volume effect, which reduces the number of configurations available for interacting chains near the interface. Excluded volume effects are strongly dependent on the solvent as is the case for chains in solution. Some progress has also been made in the analysis of the problem of multilayer adsorption (Silberberg, 1972).

Very recently, a statistical theory for the adsorption of interacting chain molecules has been developed (Scheutjens and Fleer, 1979), using a quasi-crystalline lattice model. The partition function for a mixture of polymer chains and solvent near an interface was evaluated using the Bragg-

Williams approximation of random mixing within each layer. This implies that the polymer segments in each layer are considered to be randomly distributed over the lattice sites. In this derivation the partition function is maximised with respect to the number of chains in each conformation, i.e. with respect to the concentration of chains in each conformation. The interaction between segment and solvent molecules is taken into account by using the Flory-Huggins parameter χ , and that between segment and interface is described in terms of the differential adsorption energy parameter χ_s .

The partition function can be written as the product of configurational entropy term (combinatory factor) and an energy term, $\exp(-u/kT)$, i.e.

$$A(M, L, T, [n_c]) = \frac{\Omega}{\Omega^+} \exp(-u/kT) \quad (1)$$

where Ω is the number of ways of arranging n_c , n_d , n_e ... polymer molecules in specified conformations, and n^0 , n_1^0 , ... n_M^0 solvent molecules over M distinguishable layers of L lattice sites each. Ω^+ is the number of ways of arranging n polymer chains over n_r lattice sites in amorphous bulk polymer.

By differentiating the partition function with respect to the number of chains having a particular conformation, an expression can be obtained that gives the number of chains in each conformation in equilibrium. In this manner, train, loop and tail size distributions can be computed.

Segment Density Distribution

One feature of an adsorbed layer that is important in the theory of steric stabilisation is the actual segment distribution normal to the interface. Hoeve (1965, 1966) was the first to calculate this quantity for an adsorbed homopolymer of loops and trains, using random flight statistics. He showed that at a distance from the interface corresponding to the thickness of the trains, there was a discontinuity in the distribution. Beyond this the segment density fell exponentially with distance. This is shown schematically in Fig. 2. Similarly, Meier (1967) developed an equation for the segment density distribution of a single terminally adsorbed tail. Hesselink (1969, 1971) has developed Meier's theory and given the segment density distribution for single tails, single loops, homopolymers and random copolymers. These are shown in Fig. 3.

The recent analysis of Scheutjens and Fleer (1979) gives a more refined picture of the segment density distribution. Close to the surface the segment density decays roughly exponentially with increasing distance from the surface, but at

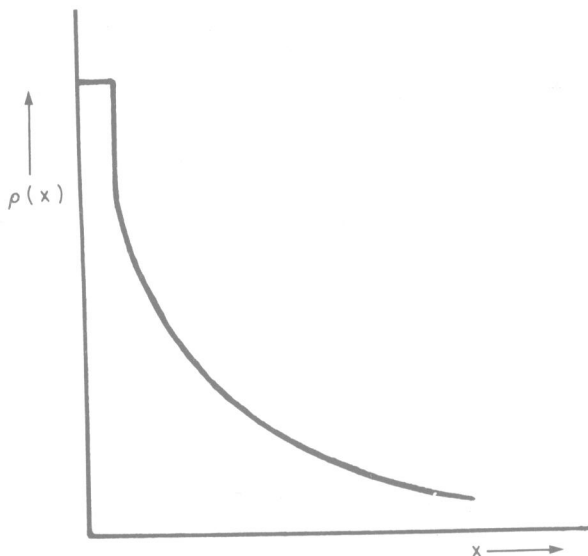


Fig. 2. Segment density - distance distribution.

larger distances the decay is much slower. This is related to the fact that a considerable fraction of the adsorbed segments is present in the form of long dangling tails. In previous theories the effect of tails was usually neglected. The occurrence of tails is important in many practical applications, particularly in relation to the stability (see paper by Sonntag *et al.*, in this symposium). The presence of long tails means that repulsion can occur at larger distances of separation than would be predicted if only loops are considered.

Experimental Quantities for Describing Polymer Adsorption

For a full description of the adsorption of polymers from solution it is necessary to measure three important quantities: the amount of adsorption per unit area of the surface (Γ); the fraction of segments in contact with the surface (p); and the distribution of segments in the vicinity of the surface ($\rho(z)$). It is also essential to know how these parameters change with the degree of polymerisation n (i.e. molecular weight), the monomer-surface interaction parameter, ($\lambda = \exp(-\epsilon/kT)$), where ϵ is the energy of adsorption per segment, surface coverage (θ) and the quality of the solvent as measured by the Flory-Huggins parameter (χ). A brief summary

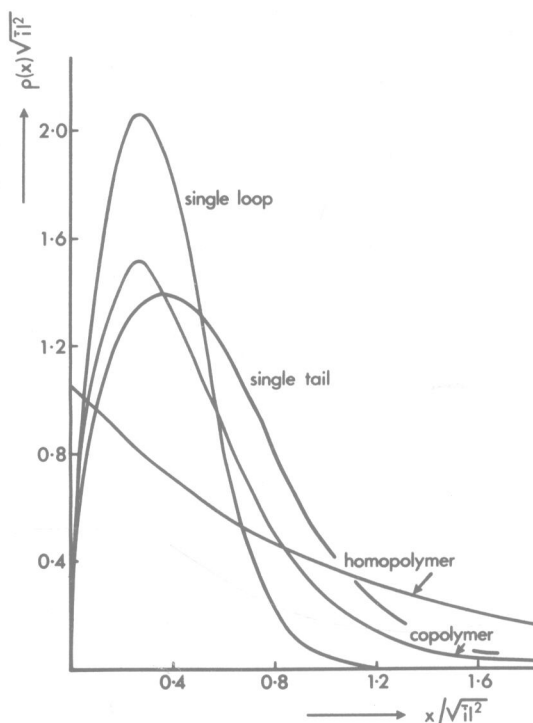


Fig. 3. Segment density distribution for single tails, single loops, homopolymers and random copolymers (Hesslink, 1969, 1970).

of how each of these quantities can be measured is given below; this is then followed by an example of a systematic study of the adsorption of a practical polymer in a model particulate dispersion.

Amount of Polymer Adsorbed The determination of polymer adsorption isotherms, i.e. Γ as a function of c_2 , the "equilibrium" concentration in solution is fairly well-established. Basically, one determines the change in polymer concentration Δc_2 , in the bulk solution phase, before and after, equilibration with the solid particles (of known surface area) in question. It is essential to develop analytical techniques that are capable of measuring low concentrations (p.p.m) in order to establish the initial steeply-rising part of the isotherm. Although simple in principle, in practice it requires some care to establish reliable isotherms. This has to do with the problem of "irreversibility" and the adsorption/desorption

kinetics. Irreversibility arises from the "multipoint" attachment to the surface and is a time-dependent phenomenon. This immediately raises the question of the validity of applying equilibrium thermodynamics*, (e.g. the Gibbs' adsorption isotherm). The attainment of equilibrium in studying polymer adsorption represents another problem. As a result of the low diffusion coefficient of polymer molecules in solution, and the finite time taken for a polymer molecule to adopt its steady state adsorbed conformation, long equilibration times (hours to days) are needed. This is particularly the case at high coverage, and when the polymer is polydisperse. The smaller molecules which have higher diffusion coefficients will adsorb first and these are gradually replaced by the preferentially adsorbed larger molecules.

Polymer Bound Fraction Several techniques now exist for measuring the fraction of segments of an adsorbed polymer that are in direct contact with the surface. The most direct methods for assessing p are probably spectroscopic techniques, namely, infra red (i.r.), electron spin resonance (e.s.r) and nuclear magnetic resonance (n.m.r). The i.r. method depends on measuring the shift in some absorption peak for a polymer adsorbed from solution (Fontana and Thomas, 1961; Killmann et al., 1977). E.s.r. and n.m.r. methods depend on the assumption that for an adsorbed homopolymer the segments in trains have a lower mobility, (i.e. a longer rotational correlation time) than those in loops. In the e.s.r. method (Robb and Smith, 1974), it is necessary to use a chemical spin label, e.g. a nitroxide group. The assumption is made that the introduction of a small number of such groups into the polymer chain does not affect the adsorption, particularly when such groups are randomly distributed. In this respect the n.m.r. method has a major advantage since it does not require attachment of a label and hence requires no such assumption. A pulsed n.m.r. technique has been recently applied by Barnett et al., (1981) for the estimation of p .

An indirect method for the estimate of p is microcalorimetry. Basically, one compares the measured enthalpy of adsorption per molecule with the enthalpy of adsorption per segment (Killmann, 1976). The ratio gives directly the number of segments per molecule in contact with the surface. The enthalpy of adsorption per segment is assumed to be equivalent to that

* Many authors attempt to analyse the data of polymer adsorption using Langmuir's theory, deriving quantities such as the free energy and enthalpy of adsorption. Clearly this is not valid and, therefore, the quantities obtained are of no value.