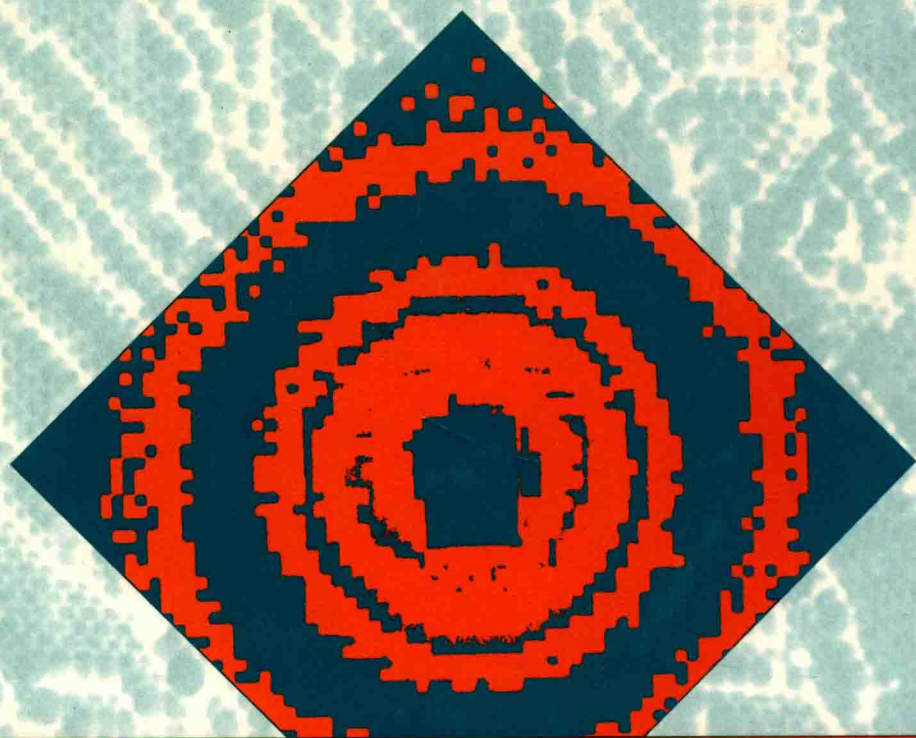


EDITED BY J.W. GOODWIN AND R.BUSCALL



# COLLOIDAL POLYMER PARTICLES



A C A D E M I C P R E S S

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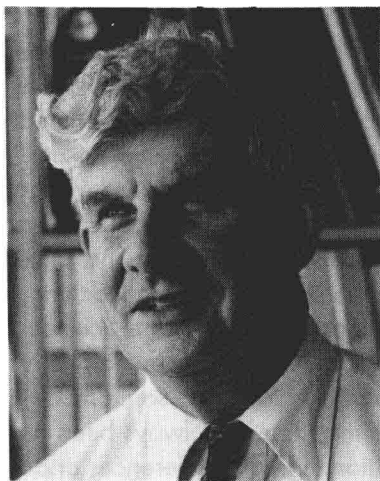
## PREFACE

During the past thirty years the field of polymer colloids has been a particularly fertile one with more and more interest changing from natural rubber latex to a wide variety of synthetic latices reflecting the increasing use of these materials in an increasing number of applications. During this period they have also become widely used as the model system of choice in many fundamental studies of colloidal properties whether carried out in industry or academia.

The contents of this volume reflects this wide interest with chapters ranging from the preparation and properties of conducting particles, as well as composite particles and swellable particles. The ability to thoroughly characterize polymer colloids has long been a corner-stone of their use in fundamental work and new techniques such as dielectric spectroscopy and neutron scattering are becoming increasingly important. Many other materials such as proteins, polymers, polyelectrolytes and surfactants interact strongly with the surface of polymer latex particles and new work on these aspects is well covered. Finally, latices are often used because their flow properties are suitable for their use as coatings and adhesives. The rheological contributions to this volume cover many of the recent developments.

The publication of this volume coincides with the formal retirement of Professor Ron Ottewill. Ron is well known to workers in the polymer colloid field for his wide ranging and important contributions to the field over the last thirty years and we would like to take this opportunity to mark his retirement by dedicating this volume to him.

## DEDICATION



Professor R.H. Ottewill OBE FRS

During his career, there have been major advances in Colloid Science which range from new experimental techniques to theoretical understanding. During the sixties Ron helped to establish polymer latices as perhaps the best model colloidal system through his work on the stability of well characterised monodisperse latices. Subsequently he has made major contributions to the understanding of concentrated systems through his work on concentrated latices with crystalline and glassy structures. Since the seventies he has been very heavily engaged in applying neutron scattering to latex problems. In fact his contributions cover a very wide range of problems and systems so he has been a constant source of new ideas, new information and advice to most of us working in the colloid field. The diversity of his interests is extremely broad, covering areas such as surfactant behaviour, microemulsion properties, thin film and particle stability, emulsion polymerisation and colloidal crystals. Throughout his work he has always taken a problem-centred approach and brought to bear a wide range of techniques to solve each problem. With 260 papers and 8 edited books, he has provided the colloid community with a great fund of information in the general literature as well as through his efforts as a teacher.

Ron started his teaching career with a short spell at the University of London prior to going to Cambridge in 1952 to join the Department of

Colloid Science and become a Member of Fitzwilliam College. The Department was very active at that time with many major figures in the field spending time there. In 1964, after twelve years at Cambridge he brought his research group to the University of Bristol where he set up the well known one-year Masters programme which is still in place after 30 years. His research group prospered with many of his hundred plus Ph.D. students turning in theses on polymer colloid based problems. Ron became Professor of Colloid Science in 1971 and subsequently Department Head. He took the prestigious Leverhulme Chair of Physical Chemistry in 1981, a worthy successor to the line of well known incumbents since McBain in 1919. Ron has always maintained a major interest in teaching, even when he carried a high administrative load as Dean of the Science Faculty and latterly as the overall Head of School, and there are many of us who are grateful that we have had the opportunity to attend so many of his lectures.

In addition to teaching, Ron has always been a prime mover in the dissemination of information through conferences and learned societies. He is currently a Vice President and an ex-President of the Faraday Division of the Royal Society of Chemistry and has had a major involvement in the planning and running of several of the Division's Discussion meetings. Moreover he was one of the four founding members of Colloid and Interface Science Group which is now the largest subject group of that Division. During the past 25 years as committee member, secretary and finally chairman of the Group, Ron has organized a very large number of informal discussion meetings. At the beginning of the 1970s the International Polymer Colloid Group was formed with John Vanderhoff, Irvin Krieger, Bob Fitch and Ron as the founders. More recently he has helped to found the European Society, ECIS. He was Chairman of the 1987 Gordon conference on Polymer Colloids and the Director of the 1988 NATO ASI on Polymer Colloids. However Ron works hard on the dissemination of information through editorial duties on many journals. Currently he has editorial duties on *Advances in Colloid and Interface Science*, *Colloid and Polymer Science* and *Langmuir*. The *Journal of Electroanalytical Chemistry*, The *Proceedings of the Royal Society (Physical Science)* and the *Journal of Colloid and Interface Science* are previous editorial commitments.

The recognition of the many important contributions made by Ron has come from many societies and countries. In 1974 he was presented with the Surface and Colloid Medal of the Royal Society of Chemistry; in 1979 the award of the Wolfgang Ostwald medal from the Kolloid Gesellschaft in Germany; in 1981 the Collège de France in Paris, and in 1982 an award from Helsinki University in Finland and the Alexander Medal of the Royal

Australian Chemical Institute. He was elected to the Royal Society of London in 1982 and received the Liversidge Medal of the Royal Society of Chemistry in 1985. The most recent award has been the award of the first Colloid and Interface Science Group Medal to Ron at the Group's conference in Strasbourg in 1993. The greatest accolade, however, came in June 1990 when the Queen made Ronald Harry Ottewill an Officer of the Order of the British Empire, a fitting tribute to a most successful career.

*J.W. Goodwin*



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## POLYMER COLLOIDS IN NONAQUEOUS MEDIA

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### ABSTRACT

Methods for the synthesis of spherical particles with a very narrow distribution of particle sizes have been developed over the past two decades. The monodispersity of these systems together with the spherical nature of the particles has made them ideal model systems for investigations into the many phenomena associated with colloidal systems. One particular aspect of this work has been to use scattering techniques in order to probe the structure of nonaqueous dispersions. In the systems described in this article the particles were composed of a core of poly-(methymethacrylate) with a shell of poly-12-hydroxy stearic acid. In terms of particle-particle interaction it has been found that these particles behave as "nearly" hard spheres. Hence, depending on the volume fraction of the dispersions various phenomenological states are observed which are analogous to those seen in molecular systems, e.g. fluids, crystals and glasses. It is also demonstrated that using binary systems, crystals of the  $AB_2$  type can be formed.

## INTRODUCTION

Colloid science is a subject which is rich in the phenomena that are encountered in a wide range of everyday activities, in the academic laboratory, in industry, in biology and in the environment. A challenge to the academic scientist has been to understand in both chemical and physical terms both by experiment and by theory the fundamental basis of the behaviour of colloidal dispersions, from very dilute to very concentrated and even into the dried state. In order to achieve this goal experiments need to be precise and an interpretation carried out in detail so that a comparison can be made with theoretical models. In the development of theoretical models, mathematical manipulation is aided substantially by spherical symmetry of the particles and by the fact that in an ensemble of particles it can be assumed that all the spheres have the same diameter, or a very narrow distribution of particle sizes. These factors place a large premium on the chemist being able to synthesize in the laboratory spherical particles with a narrow distribution of diameters and a surface of known properties. In fact, over the last thirty years or so, considerable effort has been devoted to this subject, in particular, to the preparation of particles in which the basic material is an organic polymer; these are now frequently termed polymer colloids. In aqueous environments many different types of polymeric particles have been produced, those prepared most frequently in academe probably being polystyrene. However, the preparation of polymer colloids in nonaqueous media has not

been studied as extensively as that with water as the dispersion medium.

In a number of ways the nonaqueous environment has an advantage over the aqueous environment. These include the extensive variety of liquids available covering a wide range of properties from apolar to polar and, for example, in scattering studies the possibility to vary the refractive index of the medium, and even to match the refractive index of the dispersed particles by the use of liquid mixtures. Also, the potential energy of interaction for sterically stabilised particles in the nonaqueous environment is often very close to being that of a hard sphere. Consequently a wide range of theory developed to explain the physics of fluids becomes potentially available for transposition.

This lecture is a rather personal one and in it, I will try and review some of the work carried out in Bristol in the last two decades or so on polymer colloids in nonaqueous dispersions.

### Synthesis of Polymer Colloids in Nonaqueous Media

A critical pathway to examining the properties of colloidal dispersions at a fundamental level is the synthesis of colloidal stable, monodisperse particles of well-defined shape, at high volume fractions in a consistent and reproducible fashion. A corollary to this is to have a detailed knowledge of the particle morphology and, in particular, a knowledge of the surface and the manner in which it controls the stability of the dispersion. It is also an advantage to be able to control the mean particle diameter of the particles in order to make available a wide range of

sizes.

Historically, one of the first significant attempts to prepare sterically stabilised polymeric particles was the work of Osmond and Thompson (1). An account of this early work has been given by Barrett (2). These authors used methyl methacrylate as the monomer in a hydrocarbon solution of degraded rubber with benzoyl peroxide as the initiator; this enabled an amphipatic copolymer to be formed in situ and then grafted to the particle. Early work at Bristol (3) utilised the formation of seed particles followed by a monomer feed process to grow the particles in the presence of a polymeric stabiliser. However, in later work (4) this was superceded by a "single-shot" method which was found to be capable of producing very monodisperse systems and also of providing a wide range of particle diameters. A key ingredient in this work was the use of a stabiliser molecule in the form of a "comb", that is with a backbone composed of a copolymer of poly(methyl methacrylate) (PMMA) and poly(glycidyl methacrylate) and "teeth" of poly(12-hydroxy stearic acid) (PHS). In most preparations the "comb" backbone was subsequently covalently linked to the particle core of poly(methyl methacrylate); this prevented the possibility of desorption of the polymeric stabiliser during interaction with other particles. An illustration of this type of particle is shown schematically in Figure 1; it corresponds to a core particle of radius  $R$  with a shell of thickness,  $\delta$ . The latter is essentially the extended length of the PHS molecule, ca. 10 nm, and even though the core particle has been varied over wide limits, there has been

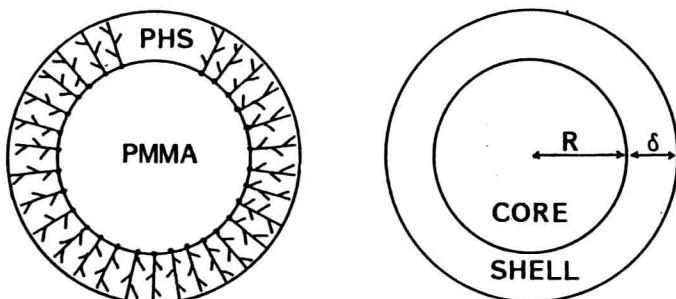


Figure 1: Schematic illustration of a PMMA core particle of radius  $R$  stabilised by a PHS shell of thickness  $\delta$

substantial agreement between various authors that the thickness of the PHS layer is essentially constant at ca.  $9 \pm 1$  nm (3-8).

The mechanism of synthesis of PMMA-PHS particles in a hydrocarbon (hexane-dodecane) - monomer environment is illustrated schematically in Figure 2. According to the procedure previously described (4) the initial monomer concentration in the liquid mixture is adjusted to be between 35 and 50% depending on the final particle size required. Initiation was achieved using azobisisobutyronitrile (ABIN) at a temperature of  $80^{\circ}\text{C}$ . As monomer is converted to polymer following initiation the polarity of the medium decreases to a point where the polymer chains essentially become insoluble; hence precipitation occurs with the consequent formation of small poly(methylmethacrylate) particles. Evidence suggests that initially these are not colloidally stable and coagulation occurs to form larger particles. However, as the polarity of the medium changes conditions also become favourable for the adsorp-

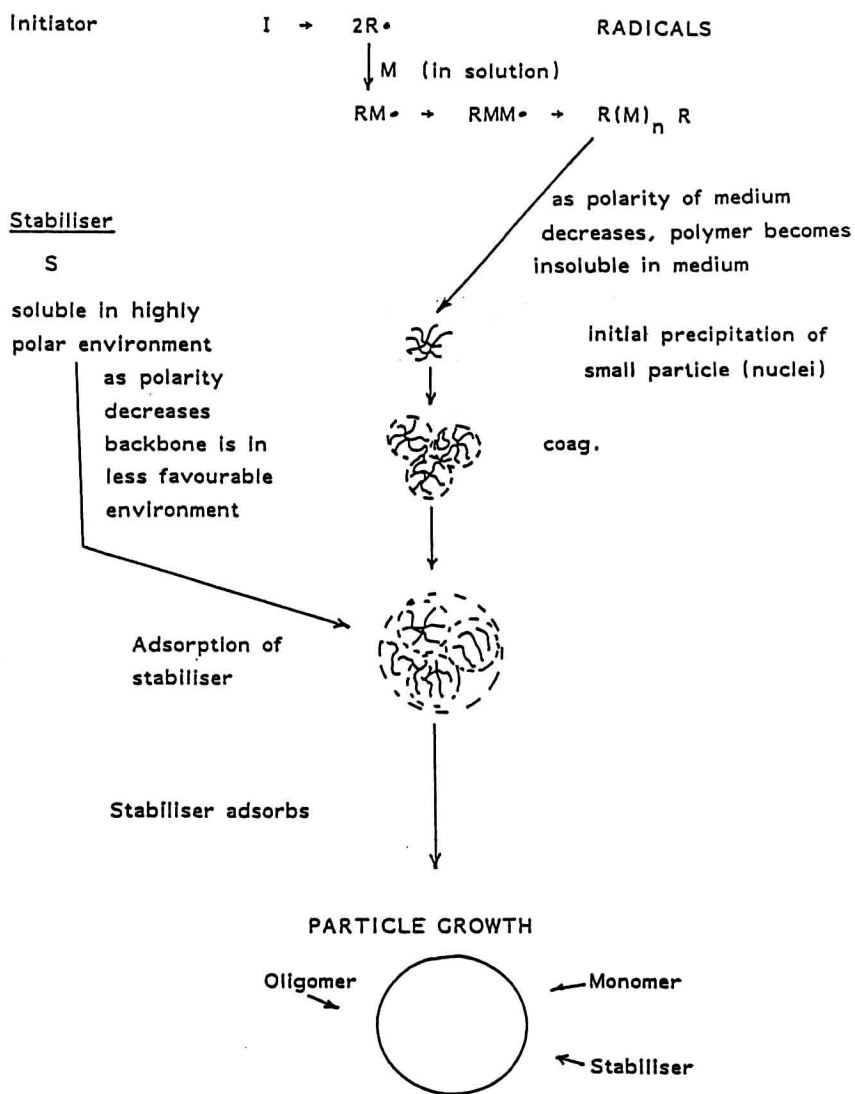


Figure 2: Mechanism of formation of PMMA-PHS particles (schematic)



tion of stabiliser molecules on to the particles; hence at this stage a stable colloidal dispersion is formed. This stage appears to control the number concentration and for the rest of the reaction, these particles continue to grow until the monomer has been consumed (2,3,4,9). The particles formed by this method generally have coefficients of variation on the mean diameter of less than 10%.

The PMMA-PHS particles form stable dispersions in aliphatic hydrocarbon media such as dodecane and in polycyclic saturated hydrocarbons such as decalin. The colloidal stabilisation of the particles is provided by the PHS chains in the outer shell of the particles. This suggests that the mechanism is steric stabilisation as indicated schematically in Figure 3. As shown later in this review and in previous investigations (3) the evidence suggests that the particles are not quite hard spheres (see Figure 3) since the shell is slightly compressible. Nevertheless, within the limits of current experimentation it appears reasonable to treat them as having a "nearly hard-sphere" behaviour.

## THE STRUCTURE OF CONCENTRATED COLLOIDAL DISPERSIONS

The preparation of monodisperse polymer colloid dispersions has led to many applications. One of the major ones in academic studies has been to use them as model systems to probe the behaviour of concentrated colloidal dispersions. An initial task in this respect is to understand the correlations which occur between particles as the system becomes more and more concentrated. In