SYNTHESES AND SEPARATIONS USING FUNCTIONAL POLYMERS

D. C. SHERRINGTON

and

P. HODGE

SYNTHESES AND SEPARATIONS USING FUNCTIONAL POLYMERS

D. C. SHERRINGTON
Department of Pure and Applied Chemistry,
University of Strathclyde,
Glasgow, UK

and

P. HODGE
Chemistry Department
University of Lancaster
Lancaster, UK

List of Contributors

G. CHALLA   *Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

W. T. FORD   *Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA*

P. E. GARROU   *Dow Chemical Company, 5727 Westpark Drive, Charolotte, NC 28210, USA*

B. C. GATES   *Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA*

A. GUYOT   *CNRS, Laboratoire des Materiaux Organiques, BP 24-F-69390, Lyon, Vernaison, France*

P. HODGE   *Chemistry Department, University of Lancaster, Lancaster, LA1 4YA, UK*

L. JERVIS   *Department of Biology, Paisley College of Technology, High Street, Paisley, Renfrewshire, PA1 2BE, UK*

G. S. MAHLER   *University of Illinois at Urbana–Champaign, School of Chemical Sciences, 1209 W. California, Urbana, IL 61801, USA*

D. C. NECKERS   *Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, USA*

W. H. PIRKLE   *University of Illinois at Urbana–Champaign, School of Chemical Sciences, 1209, W. California, Urbana, IL 61801, USA*

D. C. SHERRINGTON   *Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow, G1 1XL, UK*

M TOMOI   *Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama 240, Japan*

v

H. J. VAN DEN BERG   *Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands,*

A. WARSHAWSKY   *Life Sciences Division, Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, USA*

H. WIDDECKE   *Technische Universität Braunschweig, D-3300 Braunschweig, West Germany*

Preface

This text has been written essentially as a sequel to our first book, *Polymer-supported Reactions in Organic Synthesis*. The topics chosen for this volume reflect the continuing growth in the use of polymer-supported species both in syntheses and in separations, a growth which shows every sign of continuing. Our original plan included Chapters on Solid Phase Synthesis and Polymer-supported Cells and Enzymes, but unfortunately these did not mature. These areas have however been well reviewed elsewhere. As before, each chapter has been produced by a leading research worker in that particular field. If the area was covered as a specific topic in the first book, then the corresponding chapter in this book, whilst giving leading references, serves only to up-date the reader from 1979. Where the area being covered is new, the author has been more comprehensive. With this in mind new research workers planning to exploit some of these advances in their own work are recommended to consult our first book before moving on to this text. On the other hand researchers who already have some general experience with polymer supports will find this text an invaluable summary of the progress made from 1979.

A number of important international symposia on Polymer-supported Reactions have been held in the 1980s, and the main papers from these have been published. These will also prove to be a valuable source of reference, and the conferences and their proceedings are listed below.

When our first book was completed there was still speculation concerning the likely use of polymer supports as an industrial technology. Today in 1988, the situation is much clearer. Polymer supports are now an important technology and they are undoubtedly here to stay. There is also no doubt that the number of industrial applications will continue to grow. Needless to say this situation is extremely rewarding for us personally, and we hope that this book will serve to stimulate further growth in the area.

We would like to thank most warmly our co-authors who have contributed to this text. Without their professional efforts our task would have been very much more difficult.

1. 1st International Symposium on Polymer-supported Reactions, Lyon, France, 1982 Proceedings, *Nouveau J. Chemie*, **6**, 12 (1982)
2. 2nd International Symposium on Polymer-supported Reactions, Lancaster, UK 1984 Proceedings, *Brit. Pol. J.*, **16**, 4 (1984)

3. 3rd International Symposium on Polymer-supported Reactions, Jerusalem, Israel, 1986 Proceedings, *Reactive Polymers*, **6**, 2–3 (1987)
4. IUPAC Microsymposium on Reactive Polymers, Prague, Czechoslovakia, 1987 Plenary Lectures, *Pure and Applied Chem. (Invited)*, **60**, 3 (1988), Lectures and Posters, *Reactive Polymers*, **8** (1988–in press)
5. 4th International Symposium on Polymer-supported Reactions, Barcelona, Spain, 1988 Proceedings, *Reactive Polymers* (to be published)

Glasgow   D. C. Sherrington
April 1988   P. Hodge

Contents

1 Synthesis and Structure of Polymer Supports

A. GUYOT

CNRS, Laboratoire des Materiaux Organiques
BP 24-F-69390, Lyon, Vernaison, France

Abbreviations

AIBN   azobisisobutyronitrile
BP   benzoyl peroxide

3-DBS	3-(1, 2-dibromoethyl)styrene
DVB	divinylbenzene
EDMA	ethyleneglycol dimethacrylate
EVB	ethylvinylbenzene
GMA	glycidyl methacrylate
SEC	size exclusion chromatography
SEM	scanning electron microscopy
TRIM	trimethylolpropane trimethacrylate
VBC	vinylbenzyl chloride
VP	vinyl-4-pyridine

1.1. INTRODUCTION

It is increasingly recognized that, when polymers are used as supports for catalysts or organic reagents, the reactivity and selectivity of the supported catalysts or reagents may be seriously changed by so-called 'polymer effects', the origins of which may be physical (viscous diffusion effects, steric effects, site-separation effects, local concentration effects, etc) or chemical (microenvironmental interactions, coordination unsaturation, etc). Some examples of these effects have been published recently.[1-4] It is then no longer possible to depict the polymer support as a simple letter P surrounded by a circle, as has so often been done before. It is also no longer possible to consider the support as a rigid and inert material like a stone cast into the liquid reaction medium. The support interacts with the surrounding medium. It may or may not swell, depending on its thermodynamic affinity with the medium and its method of synthesis. It may selectively absorb one of the reactants or products, as a result of preferential solvation. This may arise for thermodynamic reasons or because steric restriction is experienced in the micropores.

Styrene-based polymers remain by far the most widely used supports, possibly because they are commercially available, as the basis of ion exchange resins, and because they have been used by the pioneers in the field of Merrifield polypeptide synthesis. A good description of their synthesis, characteristics and functionalization is given in a previous book by the editors.[5]

The purpose of this chapter is to present a short but comprehensive review of recent work in the field and to indicate how to control the main parameters which determine the behaviour of these polymer supports—bead size and mechanical properties, distribution of crosslink density, porosity, location and accessibility of the functional groups, chemical stability of the functions.

The discussion is mostly confined to styrene-based polymers, but the basic principles are applicable to other supports, such as the acrylic ester supports which are becoming more and more popular. The review will also include other

supports which might be used because of their various anticipated properties (rigidity, thermostability, reactivity for further functionalization, etc).

Reference to inorganic supports, which because of their outstanding mechanical stability should always be considered as an alternative, will be made when necessary.

It is hoped that the reader will be alerted to the need for optimization of both the supported reagent and the reaction conditions and will form some guidelines for choosing the appropriate polymer support.

1.2. CONTROL OF BEAD SIZE AND PARTICLE SIZE DISTRIBUTION IN SUSPENSION POLYMERIZATION

There is no exact theory which can be used to predict and control the size and size distribution of the particles for the suspension polymerizations of hydrophobic monomers in water or hydrophilic monomers in hydrocarbons. Suspension polymerization is more of an art than a science. Most of the data appears in the patent literature and each school of workers uses its own methods. Typical procedures for using styrene–divinylbenzene (DVB) beads as reagent supports are given in References 5 and 6. The reader interested in the suspension polymerization process is referred to references 7 and 8.

The reasons for the lack of rationalization in suspension polymerization are essentially two-fold. Firstly, the design of the reactor and the stirrer plays a very important part in governing the shear distribution at the various locations inside the reactor. Secondly, the characteristics of the system change during the polymerization, because of the very large increase in the viscosity inside the organic phase. In a mixture of non-miscible liquids thoroughly stirred, the average size of the droplets results from a quasi-equilibrium between the thermodynamically favoured droplet coalescence and the redivision of the coalesced droplets under the shear field of stirring. Once dispersed, the system may be stabilized if the tendency to coalesce is reduced by lowering the interfacial tension (by introducing dispersing agents, stabilizers or even surfactants), diluting the system or preventing the interdiffusion of the molecules between two droplets (by using very high-molecular-weight molecules or by arranging for the glass transition of the system inside the droplets to be high).

There are various factors which determine particle size. For instance, smaller particles are obtained by increasing the water/monomer ratio or diluting the organic phase with a solvent for the polymer to be produced. Increasing the amount of crosslinker (DVB) has the opposite effect. Temperature is also an important factor. The suspension polymerization of styrene-based monomer mixtures is easier at fairly high temperatures (80 °C and above), while in the case of acrylic derivatives lower temperatures (50 °C) are preferred.[9] This is due to the range of viscosities (and glass temperature) of the corresponding polymers.

However, the two most important factors are the choice of the dispersing agent and the stirring process.

Water-soluble polymers, which may be from a natural source or synthetic, are the dispersing agents most generally used, often in conjunction with salts or polyelectrolytes. They tend to prevent the coalescence of the droplets both by increasing the viscosity of the water phase and by being adsorbed at the interface between the water and the droplets in a layer 60–2000 nm thick, depending on the suspending agent.[10] There are only a few systematic studies of the effect of the nature of the water-soluble polymer,[11] but, as stated recently by Sherrington[12] and checked in the author's laboratory,[13] larger particle sizes (250–1000 microns) are obtained by using natural gums rather than synthetic polyvinyl alcohols or polyvinylpyrrolidone (100–200 microns). Even smaller sizes (10–100 microns) are obtained if surfactants (such as sodium dodecyl sulphate) are used even in minute amounts.[14,15] Submicron sizes are obtained only when surfactants are used. These processes are often referred to as emulsion polymerizations,[16,17] but in fact are microsuspension processes, where the initiator is monomer soluble and not water soluble.

The stirring process is very important, at least during the part of the polymerization process often referred to as the 'sticky period'. Upon polymerization of the monomers, the viscosity of the organic phase inside the droplets increases. Monomer redispersion by shearing becomes more and more difficult and, up to a certain viscosity limit, the particles remain sticky and are easily coalesced upon collision. Continued coalescence may lead to the coagulation of the whole bulk of the monomer phase. On the other hand, the partially polymerized droplets also become progressively harder and harder, especially when the content of crosslinking difunctional monomer is high. Beyond a certain stage, both the redivision and the coalescence of particles becomes impossible. After this stage, the stirring process is useful only to maintain the beads in suspension. Thus, within the so-called 'sticky period', where the stirring process is very critical the particle size (and its distribution) will be fixed in the range predetermined by the choice (and the amount) of the dispersing agent. An idea of such a range is given in Figure 1.1 which shows some results obtained in the author's laboratory. The 'sticky period' is fairly short (depending on the polymerization temperature and the amount of crosslinker), so all the particles do not undergo the same shear history. The centrifugal field is variable along the diameter of the reactor, and the shear at different points is dependent on the shape of the stirring system (blade, impeller, etc). As a result the distribution of the particle sizes is rather broad. The distribution is narrower for larger reactors, therefore it is more difficult to get narrow distributions at the laboratory scale. It has been claimed[9] that the special design of a cylindrical reactor leads to a narrower distribution, but from the author's experience the effect, though true, is limited.

Particles with a narrow size distribution are easy to obtain in the submicron
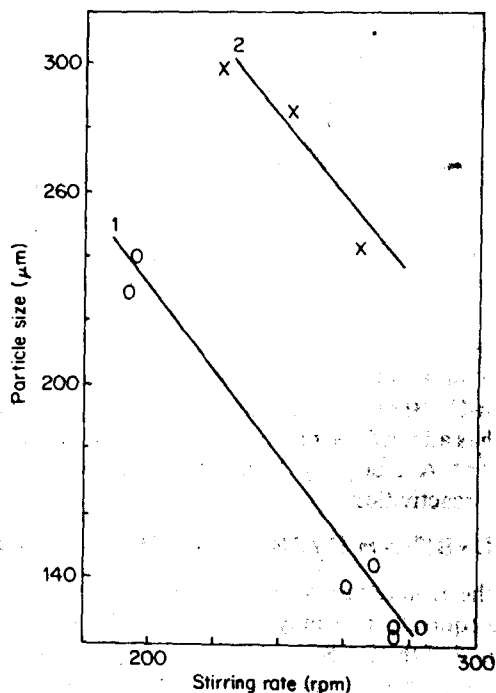
FIGURE 1.1. Stirring rate and particle size in styrene–DVB suspension polymerization at 88 °C; (1) conventional glass reactor (1 litre), (2) cylindrical reactor (0.5 litre).

range using emulsion polymerization without an emulsifier.[17] Various processes may be used to grow such monodisperse particles up to 10–50 microns. These include stepwise seeded emulsion polymerization in microgravity[18] and a thermodynamic swelling process with a monomer in the presence of an oligomer or a compound of moderately high molecular weight.[19,20] A simpler process has been recently described involving the dispersion polymerization of styrene in a non-solvating medium containing a dissolved cellulosic polymer. The particle size thus obtained, was around 10–20 microns[21] (see Chapter 11 for more details).

For the larger sizes (100–500 microns), which are preferred as supports for functional groups in organic synthesis or catalysis, the simplest way to get beads with a given particle size is to use a sieving process, as reported by Tomoi and Ford.[14] Recently a manufacturing process describing the large-scale production of monodisperse particles in this size range has been disclosed by the Dow Chemical Company. However, it seems likely that this technology will not lend itself to simple adaption for laboratory-scale work.

1.3. CHEMISTRY OF THE COPOLYMERIZATION OF STYRENE AND DIVINYLBENZENE—DISTRIBUTION OF CROSSLINK DENSITY

The chemistry of the copolymerization of styrene and DVB is a complex problem, because commercial DVB is a mixture of isomers (*para*, 33% and *meta*, 66%) of both difunctional DVB (50–60%) and monofunctional ethylvinylbenzene (EVB) (35–45%). Thus five monomers at least (there may be also minor amounts of vinylbenzene and other compounds) are involved in the copolymerization. The values of their relative reactivity ratios reported in the literature are rather varied. A critical review, which is still valid, was given in 1975 by Schwachula[22] and was based mainly on data for the binary copolymerization of styrene and *m*-divinylbenzene (*m*-DVB) or its *para* isomer (*p*-DVB). The use of gas chromato-graphic analysis has allowed the reaction of all the five monomers to be followed simultaneously.[23,24] A study by Walczynski and coworkers[25] yielded the following relative reactivities:

$$p\text{-DVB}\,(7) > m\text{-DVB}\,(4) > m\text{-EVB}\,(1.4) > p\text{-EVB}\,(1)$$
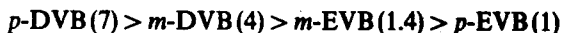
Furthermore the reactivities of both EVB isomers and of styrene may be considered to be equivalent. It may also be deduced that the reactivity of the second double bond of the DVB isomers (once the first one has been reacted, i.e. when the monomer is incorporated in the polymer) should be equal to that of styrene. On this basis, the calculated number of branch points in a copolymeriz-ation of styrene with very low amounts (0.4%) of each of the two DVB isomers was shown to be in agreement with the experimental values of the molecular weight,[26] provided that the final conversion was limited to 50%. Other results,[27] again limited to low conversion of mixture with small amounts of DVB, support this conclusion.

However, the results obtained by Kwant[26] show that, even with small amounts of crosslinker, physical effects may change the reactivity of the chemical species. As an example, the conversion curves in Figure 1.2 show a typical so-called gel or Tromsdorff effect, where the acceleration of the monomer conversion is considered to occur as a result of the decrease in the rate of the termination reaction between the growing radicals. This arises from the restriction of mobility of the polymer chains embedded in permanent entanglements.[28] Obviously such physical effects will be operative at lower conversions if the amount of DVB is high as it is in the case of materials useful as supports. Direct analysis of the residual double bonds from mono-reacted DVB may be carried out by infrared spectroscopy.[29]

Comparison of the experimental data[23] with the conversion curve for the second double bond (Figure 1.3), calculated assuming it has the same reactivity as styrene, shows a very large discrepancy. The consumption of these double bonds is much faster than calculated at the beginning of the process, but becomes limited
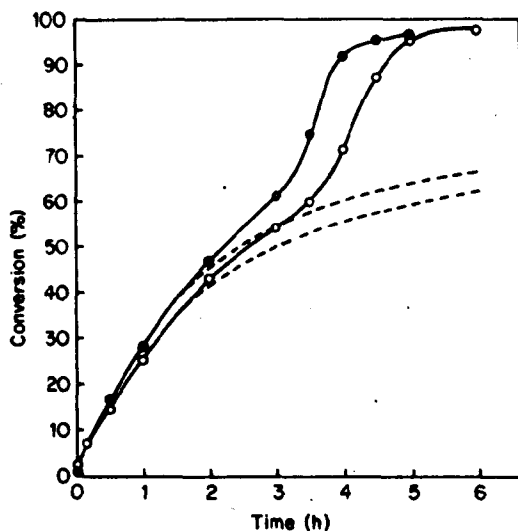
FIGURE 1.2. Time conversion plots of styrene polymerizations in aqueous suspension at 90 °C; ○:0.375 wt% benzoyl peroxide (experimental), ●:0.49 wt% benzoyl peroxide (experimental),----: calculated curves assuming that k_p^2/k_t remains constant. Reprinted by permission of John Wiley & Sons Inc from Reference 26. Copyright © 1979 John Wiley & Sons Inc.

at higher total conversion. The final amount of residual double bond is lower if more diluent is used in the recipe. At least a part of the initial discrepancy may be shown to be due to the heterogeneity of the system. Insoluble polymer is produced very early as a microgel, due to the preferential reaction of both p-DVB and m-DVB. These crosslinked microgels are then rich in second double bonds. It is shown by thermodynamics that the unconverted monomers (and also diluents) tend to be exuded from these microgels as a result of the phenomenon known as syneresis. The chemical potentials, μ_i, of such molecules, i (monomers, diluents), can be expressed as

$$\mu_i = \mu_{i0} + RT \ln \Phi_i + \left(1 - \frac{1}{x}\right)\Phi_p + \chi\Phi_p^2 + \frac{1}{\ln RET}(\Phi_p^{1/3} - \tfrac{1}{2}\Phi_p)$$

in which Φ_i and Φ_p are the volume fractions of the molecules, i, and of the polymer, respectively, x is the conversion, χ is the average interaction parameter of the polymer with the solvent medium and $\overline{\ln RET}$ is the number average length between two crosslinks. The crosslinking process, by decreasing $\overline{\ln RET}$, causes
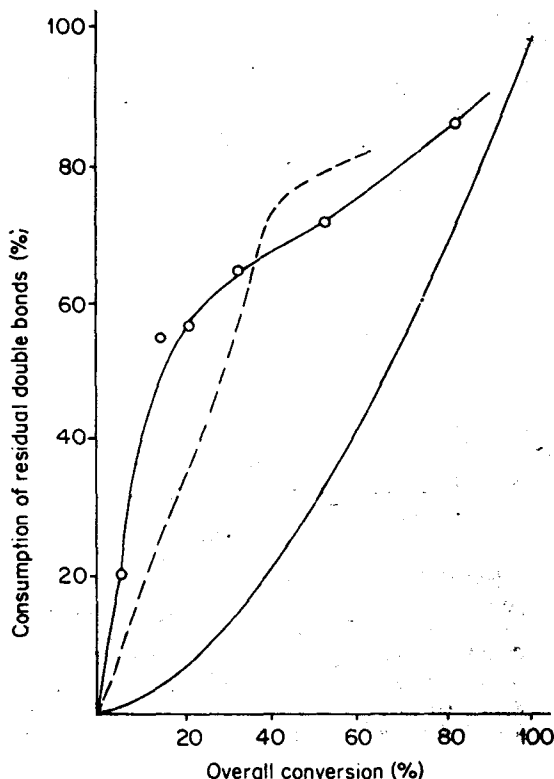
FIGURE 1.3. Calculated (——), corrected (————) and experimental (○) results for the consumption of the second double bond of DVB incorporated in the copolymer. Adapted from Reference 3.

Φ_i to decrease inside the microgels, so that the monomer is exuded from their core to their outer shells. Guillot[30] considered the microgels as a set of concentric phases in equilibrium but with varying Φ_i, Φ_p and crosslink density. He was then able to calculate Φ_i, Φ_p and $\ln \overline{RET}$ for increasing conversion from the core to the shell of the microgels. The results show that the crosslink density is very much lower at the surface of these microgels (Figure 1.4). A corrected curve for the conversion of the second double bond can be calculated (Figure 1.3) which accounts for a large part of this discrepancy. Obviously a gel effect due to the high viscosity in the core of the microgels may easily explain the residual discrepancy. At the end of the polymerization, the rate of the second double bond conversion decreases because its polymerization becomes diffusion controlled in the very highly viscous medium inside its microgels.

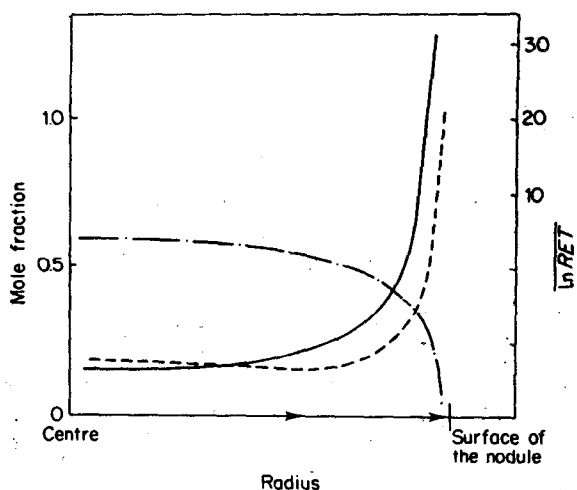Experimental evidence for the early formation of microgels and their tendency

FIGURE 1.4. Distribution of the crosslink density (ln RET) (——) and the mole fraction of the polymer, Φ_p (—·—) and of the residual double bonds (---) along the radius of a swollen nodule during the styrene–DVB copolymerization.
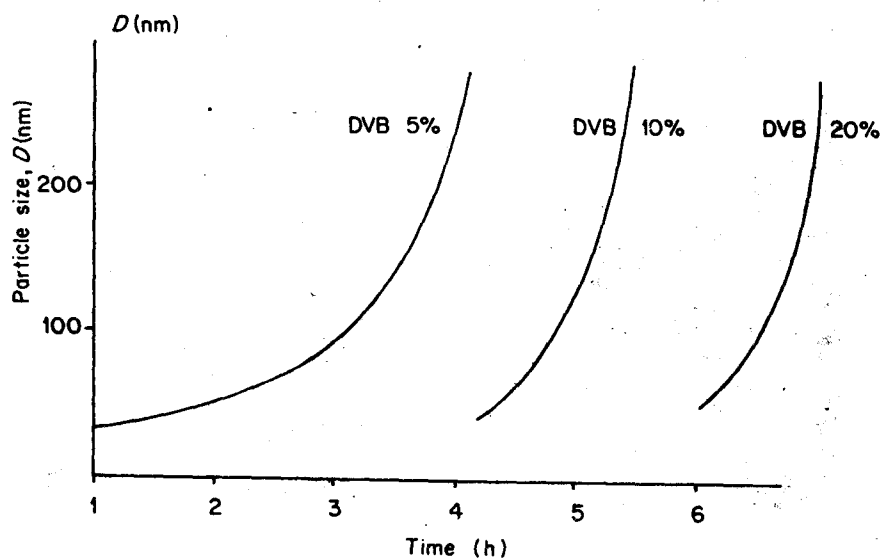

FIGURE 1.5. Particle size from quasi-elastic light scattering versus time for commercial divinylbenzene homopolymerization in toluene at different dilutions (5, 10 and 20%).

此为试读，需要完整PDF请访问：www.ertongbook.com