

POLYMER SCIENCE AND TECHNOLOGY IN THE PAST AND THE FUTURE: HEROISM, EXPLORATION AND ENLIGHTENMENT

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Abstract The scientific and technical history of polymerization can be divided into three periods, which will be illustrated for emulsion polymerization. The first period was when emulsion polymers were originally produced, and was developed as an attempt to copy natural rubber latex. Indeed, the natural process is quite different from the synthetic process of emulsion polymerization, which in fact does not even need an emulsion to be present: the term is a misnomer! The results were functional but limited. In the second period, the first theories appeared, and a huge range of products was made for surface coatings, adhesives, commodity polymers such as SBR, neoprene, etc. The work of the outstanding pioneers was based on limited types of experimental data, and some suppositions are now seen to be incorrect. Nevertheless, many excellent products were made and have evolved to many materials currently in everyday use. The third period of emulsion polymerization is now dawning. The scientific efforts of many teams over previous decades, aided by the advent of new physical techniques for investigation, have resulted in better understanding of the fundamentals of emulsion polymerizations. Some examples from the author's group involve creating novel materials using controlled seeded emulsion polymerization from natural rubber latex and other polyenes. Latex topology and controlled free-radical chemistry can be combined to produce a) a comb polymer with hydrophobic backbone and hydrophilic "teeth", or b) with sufficient *in situ* compatibilizer between two otherwise incompatible polymers to yield a spatially uniform material down to the nanostructure level, and c) to produce controlled nanostructures.

Keywords Polymer rubber, Emulsion polymerization, Natural rubber, DMAEMA, Polybutadiene polyisoprene grafting

From a contemporary perspective, the interlinked scientific and technical history of polymerization can be divided into three periods, encompassing the first artificial polymers, the subsequent scientific and technical development which led to many of today's polymer products and the dawn of fully designed polymer products based on recent scientific developments. These are illustrated for the particular case of emulsion polymerization^[1]. Emulsion polymerization, which is a free-radical polymerization process in a disperse medium, first became a significant commercial process with products by DuPont (e.g. neoprene^[2]) and by companies making artificial rubber^[3] in the late 30's and early 40's. It has become a major process for products ranging from commodity polymers such as tyre rubber, surface coatings and adhesives, through to high-value added ones such as latexes for medical agglutination tests^[4].

THE HEROIC AGE

The first period, which might be termed the *Heroic Age*, was when emulsion polymers were originally produced. The technique was developed as an attempt to copy natural rubber latex. Now, this latex, from *Hevea brasiliensis*, is produced in the tree by a mechanism that is quite different from that in a free-radical addition polymerization in a dispersed medium. It is enzyme-mediated, and produces polyisoprene which is essentially entirely in the *cis* conformation. This *cis* conformation is one of the properties which gives natural rubber its

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special characteristics, such as a high increase in elastic constant on stretching. This, combined with its excellent film-formation properties, and hence its excellent barrier properties, gives natural rubber latex its extensive use in surgical gloves and condoms. Despite all the skills of modern synthetic polymer chemists, it has hitherto proved impossible to duplicate this all-*cis* property in an industrial plant (as distinct from the plant *Hevea brasiliensis*).

The earliest artificial latex products^[2, 5, 6] were made based on the assumption that an oil-in-water emulsion was needed to effect such a polymerization. It is now generally accepted that “emulsion polymerization” is “the process whereby monomer(s), initiator, and colloid stabilizer are mixed forming initially a nonhomogeneous system conducive to the polymerization of the monomer(s) resulting in particles of colloidal dimensions; the colloidal stabilizer may be formed *in situ* instead of (or as well as) being added separately” (this is the draft definition being developed by a nomenclature working party of the IUPAC Macromolecular Division). The term “emulsion polymerization” is in fact a misnomer, because historically it was thought that polymerization occurred in the droplets of a monomer emulsion. It is now well understood that this is generally not the case (with the exception of mini-emulsion polymerization). For example, it is possible to make a latex of the type produced by what is accepted as an emulsion polymerization without an emulsion present in the first place: e.g. polymerization of a saturated water solution of vinyl acetate produces such a latex.

Early suppositions as to the mechanism of formation of such polymers were later shown to be largely incorrect. The first commercial products were functional but limited.

THE AGE OF EXPLORATION

The second period in emulsion polymerization might be termed the *Age of Exploration*. The first theories of the process appeared in the 40's, in particular the brilliant pioneering work of Harkins^[7], Smith and Ewart^[8]. These early papers put forward the basic idea that particle formation was through a radical ion such as SO_4^- entering the monomer-rich environment of a swollen micelle. Elegant mathematical development led to simple expressions a) for the dependence of particle concentration (N_c) on the concentrations of initiator I and of surfactant S ($N_c \propto [I]^{2/5}[S]^{3/5}$), and b) for various limiting cases of the average number of free radicals per particle, $\bar{n}$. This work provided guidance for the development of a huge range of products, and indeed virtually *all* of the myriad products of emulsion polymerization we use today have evolved from the processes developed semi-empirically in the 40's and 50's. Moreover, inspection of the patent literature (e.g. [9]) shows those products such as SBR, PVA adhesives and neoprene are still made today by processes which are linearly descended from the original empirical ones. Further, such early processes often involved natural products such as rosinate as surfactant, which are inherently variable and hence may in turn produce variability in the final product. As part of product improvement, many ingredients must be added to an extant recipe, and historically these were sometimes chosen or found based on mechanistically incorrect reasons. Many common industrial “recipes” are exactly that: some ingredients were put in because they happened to be there, for example, a surfactant which was on the lab shelf at the time, and their function, if any, is now uncertain. Alas, it is a cardinal rule in current emulsion polymerization technology that one should never take an ingredient out (even if no one knows why it was put in 30 years previously), just new ones are added; this can lead to obvious problems.

As will be seen, many of the early scientific suppositions used to develop many modern products need revision. Just to give one illustration, it is thermodynamically very unfavourable for a sulfate radical ion to enter the hydrophobic interior of a monomer-swollen micelle. Modern techniques have given new insights into the complex processes involved.

These pioneering publications spawned a huge number of scientific papers. Unfortunately, some of the wisdom of the pioneers was misinterpreted. For example, Smith and Ewart pointed out that $\bar{n} = 1/2$ was a possible limiting value; this was all too often taken as meaning that this is *always* the case, and many modern textbooks still quote this totally erroneous inference. There were also innumerable experimental studies purporting to verify the 2/5 and 3/5 exponents just cited; again, it will be seen that this is also quite incorrect both experimentally and theoretically, as indeed noted years ago by Fitch^[10] and Gardon^[11].

One reason for these erroneous conclusions was that there were no accurate values available for most of the rate coefficients involved in emulsion polymerizations. For example, values quoted in the *Polymer Handbook* for the propagation rate coefficient k_p for MMA varied by orders of magnitude at ordinary temperatures^[12], and so any results could be “proved” to be consistent with any theory simply by judicious choice of the values of various rate parameters! Thus, since the value of $\bar{n}$ is inferred from the relationship between the measured rate and this quantity through k_p , one can always obtain $\bar{n} = 1/2$ from any observed rate if one chooses the “right” value of k_p . While these pioneering scientists were indeed giants, they were not omniscient, and processes were *semi-empirical*. Many suppositions used were not correct: after all, the analytical tools available then were relatively limited. Nevertheless, many excellent products were made and have evolved to many materials currently in everyday use.

THE AGE OF ENLIGHTENMENT

The third period of emulsion polymerization might be termed the *Age of Enlightenment* and is now under way. It is especially obvious in some fields such as electrically-conducting polymers, and emulsion polymerization is also moving into this era.

The scientific efforts of many teams over previous decades, aided by the advent of new physical techniques for investigation, have resulted in better understanding of the fundamentals of emulsion polymerizations. One part of this is the availability of reliable techniques for measuring rate coefficients in free-radical polymerization. The best of these new methods is pulsed-laser polymerization (PLP), first put into practice by Olaj and colleagues^[13, 14] and which has been developed as a reliable method with internal consistency tests by the combined efforts in an IUPAC Working Party^[15, 16]. There are also new techniques for measuring, for example, transfer^[17, 18] and termination^[19], which have either verified or extended earlier techniques such as the Mayo method. Indeed, it can now be said that free-radical kinetics has the same level of reliability as that attained by gas-phase kinetics 40 years ago. Thus, for example, one can now determine the value of $\bar{n}$ accurately from the measured rate in an emulsion polymerization ($\text{rate} \propto k_p N_c \bar{n}$). It is seen that $\bar{n} = 1/2$ is in fact obeyed only very rarely^[1] (a result which is completely consistent with the original Smith-Ewart paper but which still seems to confound many people).

Building on reliable values of $\bar{n}$, new techniques have been developed to obtain reliable mechanistic information on emulsion polymerization, even though these systems are extremely complex and involve many different rate processes in several different phases^[1]. For example, one important methodology is to study the growth of latex particles in a *seeded* system, in the absence of new particle formation, which thus enables the additional complexities of the latter process to be avoided. One important variant of this is to look at the kinetics of *radical loss* directly, separate from that of *radical formation*, by using γ -radiolysis initiation in the relaxation mode. This involves removing the reactor from the radiation source and watching the relaxation kinetics, which in small particles arises from exit and in large ones from intra-particle termination. These studies have been used to discover and/or verify all the basic mechanisms for particle growth. These are: the transfer-diffusion mechanism for exit^[1, 20], the Smoluchowski chain-length-dependent model for termination^[19-22], and growth to a critical degree of polymerization (*z-mer*) for entry^[1, 23]. This last mechanism obviates the apparent problem noted above with the entry of a sulfate radical ion into the hydrophobic interior of a particle in micellar nucleation: the entering species is the result of the aqueous-phase propagation of this species with monomer molecules until a sufficient degree of polymerization is attained to render the species surface-active.

Armed with this qualitative and quantitative knowledge, the complexities of particle formation can then be reliably assailed, without the obfuscation of being able to choose values of rate parameters which can “prove” any theory. For example^[24-26], for styrene and other monomers it is now possible to model quantities such as the particle size distribution, N_c and rate during particle formation without any real adjustable parameters (although some quantities have some moderate uncertainties associated with their values). The micellar nucleation mechanism is thus extended to incorporate all the models for the processes just discussed, and as well there is homogeneous nucleation which dominates in low-surfactant and surfactant-free systems. The fact that such

modelling studies give acceptable but imperfect accord with a wide range of experiments suggests that basic nucleation mechanisms are understood but also that significant details still need to be developed.

It is now possible to do what has never been done before: design an emulsion polymerization industrial process based on first-principles sound scientific knowledge, rather than evolution from a semi-empirical recipe. For example^[27-30], it is possible to create latex particles wherein the molecular architecture, on the micro- or nano-scale, appears thermodynamically unfavourable. This can be brought about by exploiting both the topology of an emulsion polymerization (*i.e.*, it takes place in a dispersed medium) combined with appropriate free-radical chemistry. Some examples include creating latexes by seeded emulsion polymerization wherein there is extensive grafting between hydrophobic and hydrophilic entities (verified both by improved colloidal stability and by solid-state NMR), or sufficient graft copolymer is created *in situ* to compatibilize two polymers with significantly different solubility parameters. In each case the new material has rather different mechanical properties from those of the parent homopolymers. The grafts are made using seeded emulsion polymerization where the seed comprises a polymer whereby appropriate initiating systems can create the right sort of graft sites: natural rubber, butadiene and chloroprene all provide suitable seeds. Indeed, one can make new products from natural rubber which retain some of the desirable properties of natural rubber but which overcome some of its disadvantages. One may say that making artificial polymer colloids, which started with attempts to imitate natural rubber, has gone a full, but widening, circle.

Intelligent, knowledge-based design is the way of the future for this important technology.

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REFERENCES

- 1 Gilbert, R.G., *Emulsion Polymerization: A Mechanistic Approach*, Academic: London, 1995
- 2 Carothers, W.H., Williams, I., Collins, A.M. and Kirby, J.E., *J. Am. Chem. Soc.*, 1931, 53: 4203
- 3 Dinsmore, R.P., 1929, U.S. Patent 1,732,795
- 4 Bangs, L.B., *Pure and Appl. Chem.*, 1996, 68: 1873
- 5 Luther, M. and Hueck, C., 1932, U.S. Patent 1,860,681
- 6 Luther, M. and Hueck, C., 1932, U.S. Patent 1,864,078
- 7 Harkins, W.D., *J. Am. Chem. Soc.*, 1947, 69: 1428
- 8 Smith, W.V. and Ewart, R.H., *J. Chem. Phys.*, 1948, 16: 592
- 9 Bare, P.O., 1947, U.S. Patent 2426854
- 10 Fitch, R.M., *Brit. Polym. J.*, 1973, 5: 467
- 11 Gardon, J.L., *J. Polym. Sci., Part A-1* 1968, 11: 643
- 12 *A Polymer Handbook*; 3rd ed., ed. by Brandrup, Immergut, E.H., Wiley Interscience, New York, 1989
- 13 Olaj, O.F., Bitai, I. and Hinkelmann, F., *Makromol. Chem.*, 1987, 188: 1689
- 14 Olaj, O.F. and Bitai, I., *Angew. Makromol. Chem.*, 1987, 155: 177
- 15 Gilbert, R.G., *Pure & Appl. Chem.*, 1996, 68: 1491
- 16 Beuermann, S. and Buback, M., *Pure and Appl. Chem.*, 1998, 70: 1415
- 17 Clay, P.A. and Gilbert, R.G., *Macromolecules*, 1995, 28: 552
- 18 Moad, G. and Moad, C.L., *Macromolecules*, 1996, 29: 7727
- 19 Clay, P.A., Christie, D.I. and Gilbert, R.G., "In *Advances in Free-Radical Polymerization*", ed. by Matyjaszewski, K. A.C.S.: Washington D.C., 1998, Vol. 685, p.104

- 20 Ugelstad, J., Mørk, P.C., Dahl, P. and Rangesen, P., *J. Polym. Sci., Part C*, 1969, 27: 49
- 21 Russell, G.T., Gilbert, R.G. and Napper, D.H., *Macromolecules*, 1992, 25: 2459
- 22 Russell, G.T., Gilbert, R. G. and Napper, D.H., *Macromolecules*, 1993, 26: 3538
- 23 Maxwell, I.A., Morrison, B.R., Napper, D. H. and Gilbert, R.G., *Macromolecules*, 1991, 24: 1629
- 24 Coen, E.M., Gilbert, R.G., Morrison, B.R., Peach, S. and Leube, H., *Polymer*, 1998, 39: 7099
- 25 Coen, E.M., PhD thesis, Sydney University, 1999
- 26 Coen, E.M., Morrison, B.R. and Peach, S., Manders, B., in preparation
- 27 Anstey, J.F., Subramaniam, N., Pham, B.T.T., Lu, X., Monteiro, M.J. and Gilbert, R.G., *Macromol. Symp.*, in press
- 28 Lamb, D., Anstey, J.F., Fellows, C.M., Monteiro, J.M. and Gilbert, R.G., in preparation
- 29 Subramaniam, N., Balic, R., Monteiro, M.J. and Gilbert, R.G., 1997, Australian Patent "Modified Rubber Polymer Latex"
- 30 Subramaniam, N., Balic, R., Taylor, J.R., Griffiths, M., Monteiro, M.J., Gilbert, R.G., Ho, C.C., Abdullah, I. and Cacioli, P.J., *Nat. Rubber Res.*, 1997, 12: 223